CHEMISTRY - II
(DSCHE21)
(BSC CHEMISTRY-II)

ACHARYA NAGARJUNA UNIVERSITY

CENTRE FOR DISTANCE EDUCATION

NAGARJUNA NAGAR,

GUNTUR

ANDHRA PRADESH

CHEMISTRY

B.Sc., Second Year, Paper - II

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining a B++ (80-85) grade from the NAAC in the year 2003, the University has achieved recognition as one of the front rank universities in the country. At present Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from about 300 affiliated colleges spread over the three districts of Guntur, Krishna and Prakasam.

The University has also started the Centre for Distance Education with the aim to bring higher education within reach of all. The Centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even housewives desirous of pursuing higher studies. With the goal of bringing education to the doorstep of all such people, Acharya Nagarjuna University has started offering B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc, M.B.A. and LL.M. courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise within the stipulated time by these teachers. Constructive Ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such Ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn facilitate the country's progress. It is my fond desire that In the years to come, the Centre for Distance Education will grow from strength to strength In the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic coordinators, Editors and Lesson - writers of the Centre who have helped in these endeavours.

K. Viyyanna Rao

Prof. V. Balamohandas
Vice Chancellor,
Acharya Nagarjuna University

ACHARYA NAGARJUNA UNIVERSITY
REVISED COMMON CORE SYLLABUS FOR UG COURSES,
SYLLABUS
B.Sc., Chemistry, Paper - II Chemistry

UNIT - I (Inorganic Chemistry - II)

I. d - block elements

Chemistry of elements of First Transition Series - Electronic configuration, metallic nature, atomic and ionic radii, ionization potential - Oxidation state - relative stability of various oxidation states, ionic and covalent character, acidic and basic nature, oxidising and reducing nature of various oxidation states, redox potential - Frost and Latimer diagrams - stability, disproportionation and comproportionation of different oxidation states. Colour - d - d transition, colour and spectral behaviour of transition metal ions with respect to d^1 - d^9 configuration. Magnetic behavior - determination of magnetic moment, Gouy's balance, paramagnetism, diamagnetism. Complexation behaviour, stability of complexes - oxidation states, pi complexes, class - a, class - b and class a/b acceptors. Catalytic properties - important examples.

Chemistry of elements of Second and Third Transition series - Comparative treatment with their 3d analogues with respect to oxidation state; magnetic behavior, spectral properties. Study of Ti, Cr and Cu triads - *Titanium triad* - electronic configuration, reactivity of +III and +IV states - oxides, halides. *Chromium triad* - reactivity of +III and +VI states. *Copper triad* - reactivity of +I, +II and +III states.

II. f - block elements

Chemistry of Lanthanides - electronic structure, position in periodic table, oxidation state, Atomic and ionic radii, lanthanide contraction - cause and consequences, anamalous behaviour of post lanthanides, basicity, Complexation - type of donor ligands preferred, magnetic properties - paramagnetism. Colour and spectra - f - f transition. Occurrence and separation - ion exchange method, solvent extraction.

Chemistry of Actinides - General features - electronic configuration, oxidation state, actinide contraction, colour and complex formation. Comparison with lanthanides.

III. Metals

Theories of bonding in metals - Free electron theory - thermal and electrical conductivity of metals, drawbacks. Valence bond theory - explanation of metallic properties and its limitations. Band theory - explanation of metallic properties, conductors, semi conductors and insulators. *General methods involved in extraction of metals* - minerals and ores, ore concentration - electromagnetic separation, gravity separation - wilfley table, hydraulic classifier, leaching, froth flotation, Calcination and roasting, Acid and alkali digestion. Reduction of oxides, carbonates, halides, sulphides, sulphates - smelting, flux, auto reduction, alumino - thermic reduction, hydrometallurgy, electrolytic reduction. Purification of impure metals - liquation, fractional distillation, zone refining, oxidative processes - cupellation bassemerisation, puddling, poling, thermal decomposition, Amalgamation, Electrolysis. *Alloys* - Classification, substitutional solid solutions, interstitial solid solutions, intermetallic compounds, Hume - Rothery rules. Preparation of alloys - fusion, electro deposition, reduction and compression Uses - ferrous and non-ferrous alloys.

IV Non - aqueous solvents

Classification and characteristics of a solvent. Reactions in liquid ammonia - physical properties, auto-ionisation, examples of ammono acids and ammono bases. Reactions taking place in liquid ammonia - precipitation, neutralization, solvolysis, solvation - solutions of metals in ammonia,complex formation, redox reactions. Reactions in HF - autoionisation, reactions taking place in HF - precipitation, acid - base reactions, protonation.

UNIT - II (Organic Chemistry - II)

I. Halogen compounds :

Nomenclature and classification of alkyl (into primary, secondary, tertiary), aryl, aralkyl, allyl, vinyl, benzyl). Chemical reactivity - reduction, formation of RMgX, Nucleophylic substitution reaction - classification into S_N1 and S_N2. Mechanism of energy profile diagrams of S_N1 and S_N2 reactions. Stereochemistry of S_N2 (Walden inversion), S_N1 (Racemisation) explanation of both by taking the example of optically active alkyl halide - 2 - bromo butane. Structure and reactivity - Ease of hydrolysis - comparision of allyl, benzyl, alkyl, vinyl, and aryl halides.

II. Hydroxy compounds

Nomenclature and classification of hydroxy compounds. Preparation : from carbonyl compounds. Aryl carbinols by hydroxy methylation. Phenols - (a) by diazotisation (b) from sulfonic acid (c) from cumene (d) by hydrolysis of halobenzene. Physical properties - Hydrogen bonding (inter molecular and intramolecular) effect of hydrogen bonding on boiling point and water solubility. Chemical properties (a) acidic nature of phenols (b) Formation of alkoxide/phenoxides and their reaction with RX (c) replacement of OH by X using PCl_5, PBr_3, $SOCl_2$ and with $HX/ZnCl_2$. Esterification by (a) acid halides, anhydrides and acids (mechanism) (b) Esters of inorganic acids (c) dehydration of alcohols. Oxidation of alcohols by CrO_3, $KMnO_4$. Special reactions of Phenols - (a) Bromination, (b) Kolbe-Schmidt reaction (c) Riemer Tiemann (d) Azo coupling, identification of alcohols by oxidation - $KMnO_4$, Ceric ammonium nitrate - Lucas reagent; Phenols by reaction with $FeCl_3$, and by the solubility in NaOH, Poly hydroxyl compounds - Pinacol - Pinacolone rearrangement, Oxidative cleavage ($Pb(OAc)_4$ & (HIO_4)

III. Ethers and epoxides

Nomenclature, preparation by (a) Williamson's synthesis (b) from alkenes by the action of conc. H_2SO_4. Physical properties - Absence of Hydrogen bonding, insoluble in water, low boiling point. Chemical properties - inert nature, action of conc. H_2SO_4 and HI. Acid and base catalysed ring opening of epoxides - orientation.

IV Carbonyl compounds

Nomenclature of aliphatic and aromatic carbonyl compounds and isomerism. Synthesis of adehydes & ketones from acid chloride by using 1, 3 - dithianes, nitriles and from carboxylic acids. Special methods of preparing aromatic aldehydes and ketones by (a) Oxidation of arenes (b) Hydrolysis of benzal halides. Physical properties - absence of Hydrogen bonding. Keto-enol tautomerism, polarisability of carbonyl groups, reactivity of the carbonyl groups in aldehydes and ketones. Chemical reactivity - i. Addition of (a) $NaHSO_3$ (b) HCN (c) RMgX (d) NH_3 (e) RNH_2 (f) NH_2OH (g) $PhNHNH_2$ (h) 2, 4 DNP schiff bases, Addition of H_2O to form hydrate (unstable), comparison with chloral hydrate (stable), addition of alcohols - hemi acetal and acetal formation, Halogenation using PCl_5 with mechanism. Base catalysed reactions - with particular emphasis on Aldol, Cannizaro reaction, Perkin reaction, Benzoin condensation, haloform reaction, Knoevengeal condensation. Oxidation reactions - $KMnO_4$ oxidation and auto oxidation, reduction - catalytic hydrogenation, Clemmenson's reduction, Wolf-kishner reduction, MPV reduction, reduction with LAH, $NaBH_4$. Analysis - 2, 4 - DNP test. Tollen's test, Fehlings test, Scihff's test, haloform test (with equations). Introduction to a, b - unsaturated carbonyl compounds.

V. Carboxylic acids and derivatives

Nomenclature, classification and methods of preparation a) Hydrolysis of Nitrites, amides and esters b) carbonation of Grignald reagents b) Special methods of preparation of Aromatic Acids. Oxidation of the side chain. Hydrolysis of benzoyl chlorides, Kolbe reaction. Physical properties - hydrogen bonding, dimeric association, acidity - strength of acids with the examples of trimethyl acetic acid and trichloro acetic acid, Relative differences in the acidity of Aromatic and aliphatic acids. Chemical properties - Reactions involving H, OH and COOH groups - salt formation, anhydride formation, Acid halide formation, Esterification (mechanism) & Amide formation. Reduction of acid to the corresponding primary alcohol - via ester or acid chloride . Degradation of carboxylic acids by Huns Diecker reaction; Schmidt reaction (decarboxylation). Arndt Eistert synthesis, Halogenation by Hell - Volhard - Zelensky reaction. Carboxylic acid Derivatives - Reactions of acid halides, Acid anydrides, acid amides and ester (mechanism of ester hydrolysis by base and acid).

VI. Synthesis based on Carbanions

Acidity of α - Hydrogens, structure of carbanion. Preparation of Aceto acetic ester by Claisen condensation and synthetic application of Aceto acetic ester. [a) Acid hydrolysis and ketonic hydrolysis. Preparation of i] monocarboxylic acids ii) dicarboxylic acids (b) malonic ester - synthetic applications. Preparation of i] substituted mono carboxylic acids ii) substituted dicarboxylic acids. iii) trialkyl acetic acid.

UNIT - III (Physical Chemistry - II)

1. Phase Rule

Statement and meaning of the terms - Phase, Component and degrees of freedom, Gibb's Phase rule, phase equilibria of one component system - water system. Phase equilibria of two - component system - Solid - liquid equilibria, simple eutectic - Pb - Ag System, desilverization of lead. Solid solutions - compound with congruent melting point - (Mg - Zn) system and incongruent melting point - ($NaCl - H_2O$) system. Freezing mixtures.

II. Solutions

Liquid - liquid mixtures - ideal liquid mixtures, Raoult's and Henry's law. Non-ideal systems. Azeotropes - $HCl - H_2O$, ethanol - water systems. Fractional distillation. Partially miscible liquids - phenol - water, trimethyl amine - water, nicotine - water systems, Lower and upper consolute temperature. Effect of impurity on consolute temperature, immiscible liquids and steam distillation.

III. Electrochemistry

Electrical transport - conduction in metals and in electrolyte solutions, specific conductance and equivalent conductance, measurement of equivalent conductance, variation of specific and equivalent conductance with dilution. Migration of ions and Kholrausch's law. Arrhenius theory of electrolyte dissociation and its limitations. Weak and strong electrolytes, Ostwald's dilution law, its uses and limitations. De bye Huckel Onsagar's equation for strong electrolytes (elementary treatment only). Transport number, definition and determination by Hittorf method for attackable electrodes. Applications of conductivity measurements : Determination of degree of dissociation, determination of K_a of acids, determination of solubility product of a sprangly soluble salt, conductometric titrations. Types of reversible electrodes - gas - metal ion, metal - metal ion, metal - insoluble salt - anion and redox electrodes. Electrode reactions, Nernst equation, cell EMF and single electrode potential, standard Hydrogen electrode - reference electrodes - standard electrode potential, sign conventions, electrochemical series and its significance.

Electrolytic and Galvanic cells - reversible and irreversible cells, conventional representation of electrochemical cells. EMF of a cell and its measurement. Computation of EMF. Calculation of thermodynamic quantities of cell reactions - DG, DH and K.

UNIT - IV (General Chemistry - II)

I. Molecular Symmetry

Symmetry elements and symmetry operations in molecules. Definition of Plane of symmetry, Center of symmetry and Axis of symmetry (simple axis (C_n) and alternating axis (S_n). Examples.

II. Physical properties and molecular structure

Orientation of dipoles in an electric field, dipole moment, induced dipole moment, dipole moment and structure of molecules, magnetic properties - para magnetism, diamagnetism and ferro magnetism.

III. Molecular Spectroscopy

Electromagnetic radiation - different regions - wave length, wave number, frequency, and energy. Interaction with molecules and types of molecular spectra. Concept of potential energy curves for bonding and anti-bonding molecular orbitals. Qualitative description of s, p and n M.O., their energy levels and the respective transitions.

Ultraviolet - Visible absorption spectroscopy - presentation and analysis of spectra, types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts : Examples.

Infra red absorption spectroscopy - Energy levels of simple harmonic oscillator, molecular vibrations, Hooke's law, intensity determination force constant and qualitative relation of force constant and bond energies, effect of an harmonic motion and isotope on the spectrum. Modes of vibrations in poly atomic molecules, intensity and position of IR bands instrumentation. Characteristic absorption bands of various functional groups. Interpretation of IR spectra of simple organic molecules.

IV Stereochemistry of carbon compounds

Molecular representations : - Wedge, Fischer, Newman and Saw-horse formulae. isomerism : Definition of homomers and isomers. Classification of isomers : Constitutional and Stereoisomers -. definition and examples. Constitutional isomers : chain, functional, positional isomers and metamerism. Stereoisomers : enantiomers and diastereomers - definitions and examples. Conformational and Configurational isomerism - definition, ethane and butane.

Enantiomers : Optical activity : wave nature of light, plane polarised light, interaction with molecules, optical rotation and specific rotation. Chiral molecules : definition and criteria - absence of plane, center and Sn axis of symmetry - asymmetric and disymmetric molecules. Examples of asymmetric molecules (Glyceraldehyde, Lactic acid, Alanine) and disymmetric molecules (trans - 1, 2-dichlorocyclopropane). Chiral centers : definition - molecules with similar chiral carbons (Tataric acid) - definition of mesomers. Molecules with dissimilar chiral carbons (2, 3 - dibromopentane). Number of enantiomers and mesomers - calculation. D, L & R, S configuration for asymmetric and disymmetric molecules. Cahn - Ingold - Prelog rules. Racemic mixture, Racemisation and Resolution techniques.

Diastereomers : Definition - Geometrical isomerism with reference to alkenes - cis, trans and E, Z configuration.

V. Theory of Semi micro qualitative analysis

Principles involved - solubility product, common ion effect, classification and reactions of anions. Classification, separation and reactions of cations into groups - Group reagents.

ACHARYA NAGARJUNA UNIVERSITY

B.Sc. Degree Examination, March 2006

(Examination at the end of Second Year)

CHEMISTRY

Paper II- INORGANIC, ORGANIC AND PHYSICAL CHEMISTRY

Time : Three hours

Maximum : 100 marks

SECTION A

(4 x 15 = 60 marks)

Answer ALL questions. All questions carry equal marks.

1. a) What are Lanthanones ? Explain their oxidation states.

   b) Explain, how

      i) Atomic radii,

      ii) Ionisation energies vary with increase of atomic number in transitional elements.

   c) Explain Hume-Rothery rules with suitable examples.

   Or

   d) Describe the metallurgical reactions roasting and smelting.

   e) Explain the colour of ions of transitional metals.

   f) Compare d-block elements with f-block elements.

2. a) How the monohydric alcohols are classified ? Write any two methods of preparation of ethyl alcohol.

   b) Explain any two methods of preparation of chloroform.

   c) Explain the mechanism of

      i) Aldol condensation ii) Benzoin condensation.

   Or

   d) Explain, why

      i) Formic acid is stronger than acetic acid. ii) Propionic acid is weaker than acetic acid.

   e) Explain Perkin's reaction with mechanism.

   f) How is Benzaldehyde can be prepared from

      i) Toluene ii) Benzyl alcohol

3. a) State phase rule and apply it to salt-water system.

   b) Explain Debye-Huclde theory of strong electrolytes.

   c) What is meant by single electrode potential ? Explain stan-dard hydrogen electrode with the help of a neat diagram.

   Or

   d) Explain briefly critical solution temperature.

e) State Kohlrausch law. Explain any two applications of this law.

f) Compare Galvanic cell with electrolytic cell.

4. a) Explain bonding and antibonding molecular orbitals.

b) Write notes on :

i) Enantiomers ii) R-S configuration

c) How II and IV group cations are separated by applying common ion effect and solubility product ?

Or

d) What are conformational isomers ? Explain it by considering n-Butane.

e) Explain Walden inversion.

f) What is dipolemoment ? How it is useful to assign the molecular structures of NH_3 and BF_3 molecules.

SECTION B

(8 x 5 = 40 marks)

Answer any **EIGHT** questions.

5. Compare 1st series of transitional elements with that of 2nd and 3rd series.

6. Explain pinacole - pinacolene rearrangement.

7. Explain the mechanism of Nucleophilic addition on the carbonyl group of carbon compounds.

8. How can acetic acid be converted into

a) Ethane. b) Acetamide.

9. Explain

a) Precipitation b) Red-ox reactions that takes place in liquid ammonia.

10. Explain cupellation and polling methods of refining of metals.

11. State and explain Henry's law. What are its limitations ?

12. Calculate the e.m.f. of the cell $2I^-_{(aq)} + 2Ag^+_{(aq)}$ Ag(s) + I_2 (s). Given that the standard oxidation potential $I_2/2I^-$ is + 0.54 volts and that of Ag^+ / Ag is + 0.80 volts.

13. Explain about chiral and achiral molecules.

14. Discuss briefly the isomerism of the following pairs of compounds.

a) Acetone and Propanal b) Propanol-1 and Propanol-2.

15. Explain the following with suitable examples :

a) Triple point b) Eutectic point c) Condensed system

16. Explain the following :

a) Aldehydes give red precipitate with Fehling's solution while Ketones do not.

b) Willium son's hypothesis.

Content

TITLE PG. NO

UNIT – 1

UNIT – II

UNIT – III

UNIT – IV

UNIT – I

Lesson – I

d – Block Elements – Chemistry of Elements of First Transition Series

1.1.1

The transition elements may be defined as those which as elements or as ions have partly filled d – sub shells. Since the d – sub shell is partly filled, these elements are called as d – block elements. As their position in long form periodic table is in between s – block and p – block elements, they are called as transition elements. In d – block elements, the electrons are added to the d – orbitals of the penultimate shells (n – 1) d sub shells. The number of electrons in the outermost orbit (n) of the d – block elements remains same and hence they show similar chemical properties. But the zinc group (group 12) has completely filled (n-1) d sub shell in their elemental state as well as in the combined state and hence they are not typical transition elements. The elements of the group III A (Sc, Y, La and Ac) and IIB (Zn, Cd, Hg) are called non typical while the other transition elements are called typical transition elements. There are three series of d – block elements in the 4th, 5th and 6th periods of the periodic table in which 3d, 4d and 5d orbitals are being filled up. There is an incomplete fourth series in which 6d sub shell is being filled up.

1.1.2 Electronic configuration :

The general outer electronic configuration of a transition element is $(n-1)d^{1-10}$, ns^{1-2}. The various orbitals are filled in the increasing order of their energy (4s<3d). In the first series Cr and Cu deviate from $4s^2$ configuration which leads to 3d sub level half filled in Cr ($3d^5$) and completely filled in Cu ($3d^{10}$) due to which Cr and Cu attain extra stability.

Table 1 Electronic Configuration of Elements of the First Series

Element	Symbol	Electronic Configuration
Scandium	Sc	$1s^2, 2s^2p^6, 3s^2p^6d^1, 4s^2$
Titanium	Ti	$1s^2, 2s^2p^6, 3s^2p^6d^2, 4s^2$
Vanadium	V	$1s^2, 2s^2p^6, 3s^2p^6d^3, 4s^2$
*Chromium	Cr	$1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^1$
Manganese	Mn	$1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^2$
Iron	Fe	$1s^2, 2s^2p^6, 3s^2p^6d^6, 4s^2$
Cobalt	Co	$1s^2, 2s^2p^6, 3s^2p^6d^7, 4s^2$
Nickel	Ni	$1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^2$
*Copper	Cu	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^1$
Zinc	Zn	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2$

1.1.3 Metallic nature :

Since the number of valency electrons (ns) is very small, they are all metals. They have metallic luster ; they are good conductors of heat and electricity, they are hard, malleable and ductile and they also form alloys with other metals.

Melting and boiling points :

The melting and boiling points of transition elements are very high due to the presence of strong metallic bonding and covalent bonding by the unpaired d – electrons.

1.1.4 Atomic and ionic radii :

The atomic radii of the d – block elements of a given series generally decrease with increase in atomic number. With increase in atomic number the nuclear charge increase which tend to attract the electrons in ward resulting in decrease in atomic size. In the d – block elements, the electrons are added to an inner (n-1)d sub shell and this addition of electrons screen (Screening effect) the outer ns electrons from the nucleus. As a result the atomic radius does not alter much from Cr to Cu.

For ions of a given charge, the ionic radii decreases slowly with increase in atomic number.

Table 1.2 Atomic and Ionic Radii (A°) of the Transition Series Elements.

Radii	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic	1.62	1.47	1.34	1.27	1.26	1.26	1.25	1.24	1.28	1.33
M^{2+}	—	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.72	0.74
M^{3+}	0.81	0.76	0.74	0.69	0.66	0.64	0.63	—	—	—

1.1.5 Ionization potential :

The ionization potential of d – block elements is intermediate between s- and p – block elements. The ionization potential value increase as we move across each series from left to right. But the increase in the value is low when compared to s – and p – block elements. The reason for this – the increasing nuclear charge tends to pull the outer electron inwards with increasing force. The addition of increasing number of d – electrons provides screening effect and protects the outer s electrons from nuclear attraction. The net result is a slow increase in ionization energy. This explains that the transition elements are less electropositive than IA and II A group elements and may form ionic or covalent bonds. The tendency to form ionic bonds decreases as the atoms get larger. The atoms in lower oxidation states are ionic and are covalent in higher oxidation states.

1.1.6 Oxidation states – Relative stability of various oxidation states :

All transition elements with an exception of a few, show variable oxidation states. They show a large number of oxidation states which are related to their electronic configuration. In the first five elements the minimum oxidation state is given by the number of outer electrons in the outer s – sub shell and the other oxidation states are given by the sum outer s- and some or all d – electrons. The highest oxidation state shown by any transition metal is 8. e.g. Ruthenium and Osmium show +8 oxidation state in RuO_4 and OsO_4.

The variable oxidation states shown by the transition elements is due to the availability of both ns and (n-1)d electrons for bond formation.

Table 1.3 Relation between outer Electronic configuration and oxidation states of the Elements.of the first transition series.

Element	Outer elec. configuration		Oxidation states
Sc	$3d^1$	$4s^2$	+2, +3
Ti	$3d^2$	$4s^2$	+2, +3, +4
V	$3d^3$	$4s^2$	+2, +3, +4, +5
Cr	$3d^5$	$4s^1$	1, +2, +3, +4, +5, +6
Mn	$3d^5$	$4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6$	$4s^2$	+2, +3, +3, +5, +6
Co	$3d^7$	$4s^2$	+2, +3, +4
Ni	$3d^8$	$4s^2$	+2, +3, +4
Cu	$3d^{10}$	$4s^1$	+1, +2
Zn	$3d^{10}$	$4s^2$	+2

Relative stability of oxidation states :

Compounds are regarded as stable.

i) If they exist at room temperature.

ii) Not oxidized by the air.

iii) Not hydrolysed by water vapour and

iv) Do not disproportionate or decompse at the normal temperatures. In general the second and third row elements exhibit higher coordination numbers and their higher oxidation states are more stable than the corresponding first row elements. The relative stabilities of various oxidation states of 3d series elements can be correlated with the extra stability of $3d^0$, $3d^5$ and $3d^{10}$ configurations. Thus $Ti^{4+}(3d^0)$ is more stable than $Ti^{3+}(3d^1)$; $Mn^{2+}(3d^5)$ is more stable than $Mn^{3+}(3d^4)$ and $Fe^{3+}(3d^5)$ is more stable than $Fe^{2+}(3d^6)$.

Ionic and Covalent character :

The elements form ionic compounds in lower oxidation states and form covalent compounds in higher oxidation states. The tendency to form ionic compounds decreases as the oxidation state increases. For example Mn^{2+} forms ionic compound, MnO ; Mn^{4+} forms MnO_2 which is intermediate between ionic and covalent character. Mn^{7+} forms Mn_2O_7 which is purely covalent.

Acidic and basic nature :

The acidic nature of the oxides increases with increase in oxidation state of the elements. For example consider oxides of manganese.

$M_n^{2+}O$	$M_n^{4+}O_2$	$Mn^{+7}{}_2O_7$
basic	amphoteric	acidic

Oxidising and reducing nature :

In order to come into lower oxidation state, the transition elements exhibit strong oxidising properties in higher oxidation states.

Eg : $K_2Cr_2O_7$ (Cr in +6) and $KMnO_4$ (Mn in +7) are strong oxidising agents. Strongly oxidation states form oxides and fluorides but not iodides while strongly reducing states do not form fluorides and oxides but may form the heavier halides.

1.1.7 Redox potential diagrams :

Redox potentials are used to predict whether a particular redox reaction is thermo dynamically possible under standard conditions or not.

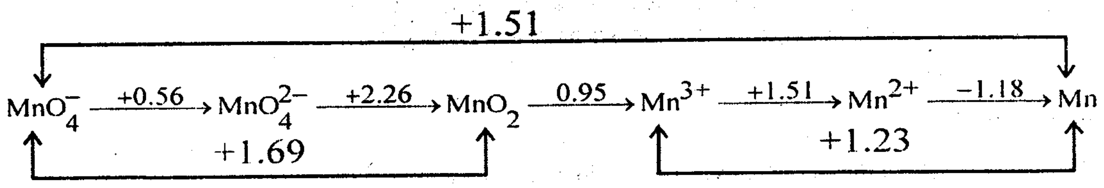
Two important redox potential diagrams are known for knowing the relative stability of different oxidation states of transition elements i.e. Frost and Latimer diagrams.

Latimer diagrams (EMF diagram) :

EMF diagram of an element is a short form in which standard reduction (or oxidation) potential values of an element in its free state or its compounds in different oxidation states are represented in a condensed form. In the EMF diagram, the species of the elements having different oxidation states are arranged from left to right in the decreasing order of the oxidation number of the element and the values of standard reduction potentials are inserted between the oxidized and reduced species. The higher oxidation state is written on the left and the lowest oxidation state on the right.

The EMF diagrams reveal the relative stability of different oxidation states of the elements.

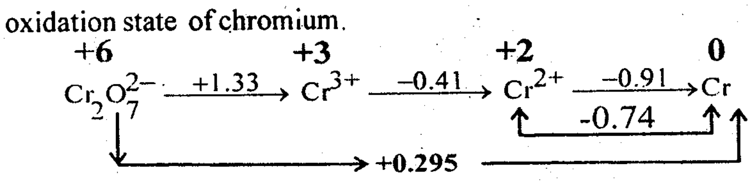
For example, the potential diagram for manganese in acidic solution (conc. Of H^+ = 1M) is given below.



From the above diagram, it is known that MnO^-_4 can be reduced to MnO_2 rather than to $M_n{}^{2-}O_4$ In other words MnO^{2-}_4 can not exist in solution during the reduction of MnO^-_4 to MnO_2 .

Example – 2

The potential diagram of chromium in acid solution.



The potential diagram of Mn and Cr in acid solution are examples of oxidation states greater than +3.

Example – 3

Potential diagram for copper in acid solution.

$$\begin{tikzcd} Cu^{2+} \arrow[r, "0.15"] \arrow[rr, leftrightarrow, bend right, "+0.34"'] & Cu^{+} \arrow[r] & Cu \end{tikzcd}$$

The higher oxidation state Cu^{2+} and the lower oxidation state Cu are connected through an intermediate oxidation state Cu^{+}.

The potential diagram of Cu in acid medium is an example of lower oxidation states.

These EMF diagrams predict about the susceptibility of any species to disproportionation.

For example. EMF diagram for $\bar{Br}$ ion in basic solution at 25°c at which OH concentration is 1M.

$$\begin{tikzcd} Br^{-} \arrow[r, "-1.07"] \arrow[rr, leftrightarrow, bend right, "-0.71"'] \arrow[rrr, leftrightarrow, bend right=50, "-0.61"'] & \frac{1}{2}Br_2(l) \arrow[r, "-0.45"] \arrow[rr, leftrightarrow, bend left, "-0.52"] & BrO^{-} \arrow[r, "-0.54"] & BrO_3^{-} \end{tikzcd}$$

a) Disproportionation of Br_2 to $Br\bar{o}$

$$\frac{1}{2}Br_2(l) + 2\bar{OH} \rightarrow BrO^{-} + \frac{1}{2}H_2O + e^{-} \qquad E^\circ = -0.45v$$

$$Br^{-} \rightarrow \frac{1}{2}Br_2(l) + e^{-} \qquad E^\circ = -1.07v$$

In the first half reaction Br_2 acts as reducing agent and in the second half reaction, it acts as oxidising agent. Disproportionation of Br_2 to $\bar{Br}$ and $Br\bar{o}$ will occur.

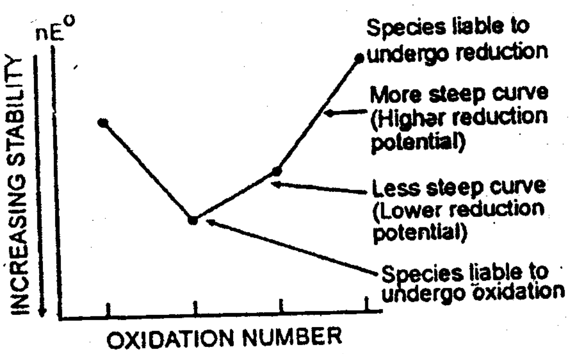
b) $BrO^{-} + 4\bar{OH} \rightarrow BrO_3^{-} + 2H_2O + 4e^{-}$ $E^\circ = -054v$

$Br^{-} + 2\bar{OH} \rightarrow BrO^{-} + H_2O + 2e^{-}$ $E^\circ = -0.71v$

For disproportionation to occur, the potential of the half reaction in which Br_2 acts as a reducing agent is higher than the potential of the half reaction in which it acts as oxidising agent.

Frost diagrams :

Frost diagrams are useful for qualitative data to understand the stability of oxidation states. The redox relationship of a metal can be studied by plotting a graph between nE° (M^{n+}/M) against the oxidation number. These plots known as Frost diagrams are drawn for elements forming oxides and Oxyanions.

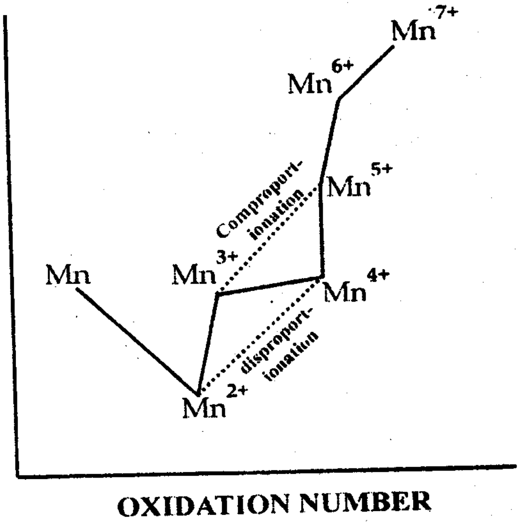


The slope of the line joining any two points is equal to the standard potential of the couple formed by the two species. If the line joining the two points is steep, the potential of the corresponding couple will be more. The oxidising agent in the couple with more positive slope is liable to undergo reduction. The reducing agent in the couple with the less positive slope is liable to undergo oxidation.

Stability :

The species lying at the bottom of the Frost diagram corresponds to the most stable oxidation state of the element.

For example, of all the oxidation states +2 state of manganese is the most stable state and so in Frost diagram Mn^{2+} lies at the bottom of the curve



OXIDATION NUMBER

Frost diagram of Mn States

1.1.8 Disproportionation and Comproportionation of different oxidation states:

Consider three consecutive oxidation states of an element and draw a line joining the first and third oxidation states. If the central ion lies above the line, it is called disproportionation or if it lies below this line, it is called Comproportionation. Consider the above diagram and if a line is drawn joining Mn^{2+} and Mn^{4+}; Mn^{3+} lies above this line. It is an example of disproportionation. Mn^{3+} is unstable with respect to the disproportionation of Mn^{2+} and Mn^{4+}. In a similar way, if a line is drawn joining Mn^{3+} and Mn^{5+}, Mn^{4+} lies below this line which is an example of Comproportionation.

1.1.9 Colour :

Most of the compounds of transition metals are coloured in the solid or in solution states. The colour of transistion metal ions is due to presence of unpaired electrons or incomplete d – orbitals. Colour of a substance arises due to the property of a substance to absorb light of certain wave length in the region of visible light (λ= 3800 – 7600A°). If a substance absorbs wave length corresponding to red light, then the transmitted light will consist of wave lengths corresponding to other colours, particularly blue colour. The transmitted light has complementary colour to that of the absorbed light. The substance will therefore appear blue. For example hydrated copper ion (II) absorbs radiations corresponding to red light and hence appear blue. Anhydrous cobalt (II) compounds also absorb red light and appear blue. The hydrated cobalt (II) compounds absorb radiations, corresponding to blue colour and hence appear red.

Table 1.5 Colours of Hydrated Ions of the First Transition Series.

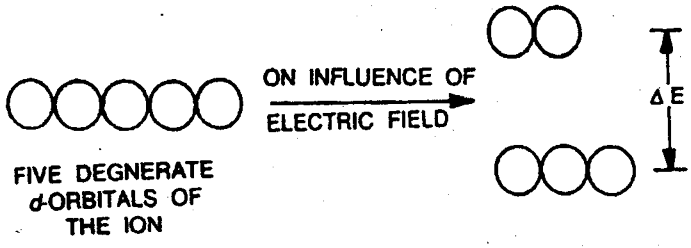
Ion	Outer electronic configuration	No. of unpaired electrons	Colour	Magnetic moment (BM)
Sc^{3+}	$3d^0$	0	colourless	0
Ti^{3+}	$3d^1$	1	purple	1.75
V^{3+}	$3d^2$	2	green	3.86
Cr^{3+}	$3d^3$	3	violet	4.80
Mn^{3+}	$3d^4$	4	violet	5.92
Fe^{3+}	$3d^5$	5	yellow	5.96
Mn^{2+}	$3d^5$	5	pink	5.0-5.5
Fe^{2+}	$3d^6$	4	green	4.4-5.2
Co^{2+}	$3d^7$	3	pink	2.9
Ni^{2+}	$3d^8$	2	green	2.9-3.4
Cu^{2+}	$3d^9$	1	blue	1.4-2.2
Cu^{+}	$3d^{10}$	0	colourless	0
Zn^{2+}	$3d^{10}$	0	colouurless	0

Transition metal ions which have completely filled d – orbitals or completely vacant d – orbitals are colourless. Eg : Sc^{3+}, Ti^{4+} ; Cu^{+} and Zn^{2+} ions do not have unpaired d – electrons and hence appear colourless.

The colour of the transition metal ion is due to promotion of one or more unpaired electrons from a lower level to a higher level within the d – sub shell. The energy required to this is in the visible light.

colour – d – d transition and spectral behaviour of transition metal ions :

In a free transition metal ion the five d – orbitals have same energy and hence are degenerate orbitals. But the groups attached to the transition metal ion exert a sort of electric field on the ion leading to the splitting of the d – orbitals into two sets namely eg set constitutes dZ^2 and $dx^2 - y^2$ orbitals and t_2g set constitutes dxy, dyz and dxz orbitals. The energy differences which is very small between the two sets is called ΔE.



Splitting of *d*-orbitals of transition metal ions.

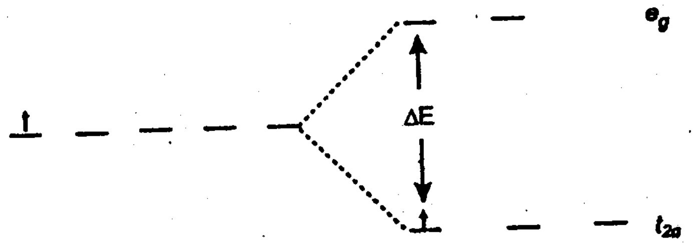
In d – d transition, the excitation of an electron from a lower level (t_2g) to a higher level (eg) takes place by absorption of visible light. The value of energy difference ΔE depends on the nature of the metal ion and nature of the groups (ligands) surrounding the metal ion. Eg – $[Ni(H_2O)_6]^{2+}$ is green and $[Ni(NH_3)_6]^{2+}$ is purple.

To get a d – d transition, there must be atleast one electron in the lower 3d-level (t_2g) and at least one vacant orbital in the upper 3d- level (eg).

Considering the above factors, we can explain the colourless nature of Sc^{3+} and Ti^{4+} (No electron in the 3d level) and Cu^{+} and Zn^{2+} (No vacancy in the 3d orbitals) ions.

Example for d configuration :

In hydrated titanium ion, $[Ti(H_2O)_6]^{3+}$ the only electron present in the lower t_2g level, on absorption of light is promoted to eg level, the ion appear purple coloured.



Splitting of 3*d* level in $[Ti(H_2O)_6]^{3+}$.

Example for d^9 configuration

Blue colour of Cu^{2+} ion in $[Cu(H_2O)_6]^{2+}$. on passing light through the solution of $[Cu(H_2O)_6]^{2+}$, the electron in t_2g level absorbs red light having energy equal to ΔE and excites to higher eg level . white light –

red light = blue colour and hence the ion appears blue in colour. So Ti^{3+} and Cu^{2+}, having d^1 and d^9 configuration d – d transition involve one electron only.

1.1.10 Magnetic behaviour :

Matter in general is associated with magnetic properties. Majority of the substances may be paramagnetic or diamagnetic.

Paramagnetism :

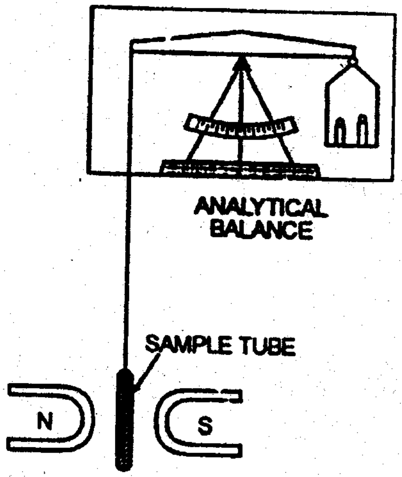
Substances, which are attracted into a magnetic field, are called paramagnetic substances. Paramagnetism is due to the presence of unpaired electrons in atoms, ions or molecules. Since most of the transition metal atoms have unpaired electrons in d – orbitals, they are paramagnetic in nature. Unpaired electrons exhibit permanent magnetic moment through spin and orbital motion.

Diamagnetism :

Substances, which are repelled by the magnetic field are called diamagnetic substances. Diamagnetic property is due to the completely filled d – orbitals. Sc^{3+}; Ti^{4+}; Zn^{2+} and Cu^{+} etc do not contain any unpaired electron and hence are diamagnetic in nature.

Determination of magnetic moment – Gouy's balance :

Compounds that show Paramagnetism when placed in a magnetic field are pulled into the field. This extent of pull by the magnetic field can be measured using Gouy magnetic balance. A sample is suspended from one arm of a balance which is partly in the electro magnetic field. In the magnetic field, the sample is either attracted or repelled by the magnetic field. The force required to maintain the position of the sample is measured by the weight that must be added or removed from the other pan of the balance to maintain equilibrium. The weight of the sample is determined with and without the magnetic field.x_M (molar magnetic susceptibility) can be obtained from the measurment of the force on the sample in a magnetic field. Each unpaired electron is regarded as a micromagnet which possess a certain value of magnetic moment.



Simplified diagram of Gouy magnetic balance.

The total magnetic moment of a cation depends upon the number of unpaired electrons. It is given by the following expression $\mu_M = \sqrt{[n(n+2)]}$ Bohr magnetons. where n is the number of unpaired electrons. The magnetic moment is expressed in Bohr magnetons.

When n = 1

$$\mu_M = \sqrt{[1\times 3]} = 1.73 \text{ B.M}$$

When n = 2

$$\mu_M = \sqrt{[2\times 4]} = 2.83 \text{ B.M}$$

and so on. The measurement of Paramagnetism gives information about the number of unpaired electrons present in a molecule.

In case of Fe, Co and Ni the unpaired electron spins are more pronounced. Hence, these elements are strongly attracted towards magnetic field these elements are called ferro magnetic substances and can be magnetized.

1.1.11 Complexation behaviour :

The transition metals have a great tendency to form complexes with several molecules or ions called ligands. The ligands which are able to donate an electron pair may be a neutral molecule like NH_3 or an ion Cl^- or CN^-. The reason for forming a number of complexes by transition metals is that they have small, highly charged ions and have vacant d – orbitals for accepting lone pair of electrons from the ligands. Complexes where the metal ion is in (+3) oxidation state are more stable than those with metal ion in (+2) oxidation state. Some metal ions i.e. first half of the transition metals form most stable complexes with ligands that contain donor atoms N, O or F. These metals are called class a acceptors. On the other hand, the metals like Ag, Au, Hg , Rh , Pd, Pt etc form their most stable complexes with the heavier elements of groups 15,16 and 17. These metals are called class - b acceptors. The second half of the transition elements of the series form complexes with both types of donors and are thus intermediate in nature. These metals are called class a/b acceptors. (type (a) metals include the smaller ions from groups 1 and 2 and the left hand side of the transition metals when they are in high oxidation state form the most stable complexes with nitrogen and oxygen donors (eg – ammonia, amines, water, alcohols etc) and also with F^- and Cl^- ions type (b) metals include ions from the right hand of the transition series and also transition metal complexes with low oxidation state. These form the most stable complexes with ligands such as I-, SCN and CN. This classification was useful in predicting the relative stabilities of complexes).

In each transition series the stability of complexes decreases with increase in atomic number.

1.1.12 Catalytic properties :

Most of the transition metals and their compounds have good catalytic properties. The transitional elements on account of their variable oxidation states are capable of forming unstable intermediate compounds. These elements can also provide a large surface area for the reactants to be adsorbed. Platinum, iron, vanadium pentoxide, nickel etc. are important examples. Platinum is used as a catalyst in the contact process, involving the formation of sulphur trioxide from SO_2 and O_2. V_2O_5 is also used in contact process. Iron is used as catalyst in the manufacture of ammonia by Haber's process, from nitrogen and hydrogen. Nickel is used as catalyst in the hydrogenation of oils.

1.1.13 Model Questions :

1) What are d – block elements ? Give their electronic configuration. How do the atomic radii of the transition elements vary with the increase in atomic number in 3d series.
2) Compounds of s- and p- block elements are generally colourless (white) but those of transition metals are generally coloured. How would you account for it ?
3) What are transition elements ? Write notes on various oxidation states of transition metals.
4) Why transition metal ions are usually coloured and paramagnetic ? Give two example of coloured ions.
5) Write notes on Frost and Latimer diagrams.
6) Discuss the catalytic properties of transition elements.
7) Write briefly on magnetic and catalytic properties of d – block elements.
8) Give the electronic configuration of Cr and Cu. Describe the common oxidation states of first transition series elements.
9) Explain the following –
    i) Cu^{2+} ions are coloured and paramagnetic while Zn^{2+} ions are colourless and diamagnetic
    ii) Transition metals are less reactive than alkali and alkaline earth metals.
    iii) Ferric salts are more stable than the corresponding ferrous salts.
10) What is meant by disproportionation and Comproportionation of oxidation states. Explain with one example each.

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UNIT – I

Lesson – II

CHEMISTRY OF ELEMENTS OF SECOND AND THIRD TRANSITION SERIES

1.2.1 Comparative treatment with their 3d analogues with respect to oxidation state, magnetic behaviour and spectral properties :

Atomic radius or size :

The size of the elements of second row series is larger than the first row series. Due to lanthanide contraction, the atomic radii of third row elements are almost equal to that of second row elements. In a group the atomic radius of transition elements increases on moving down the group. The atomic radii of second and third series are very close to each other while that of first series is very low when compared to the other two rows.

1.2.2 Oxidation states :

The higher oxidation states are more stable in case of second and third transition series. i.e. Mo (+6) W (+7), Os (+8), Ir (+8) etc. Ruthenium (Ru) of second series and osmium osmium (Os) of third series exhibit the highest oxidation state +8 thus, chromate ion (CrO_4^-) is of a strong oxidising agent but molybdate [MoO_4^-] and tungstate, [WO_4^-] are stable. The permanganate ion [MnO_4^-] is a strong oxidising agent but pertechnate [TeO_4^-] and perrhenate , [Re O_4] ions are stable. WCl_6, ReF_7, RuO_4, OsO_4 like compounds in higher oxidation states are seen in second and third series. But no compounds equal to them are observed in first series.

In the first series, +2 and +3 oxidation states are important. +4 , +5, +6 and +7 are common only in Ti, V, Cr and Mn. Hence, the elements of first series form a large number of stable complexes such as Cr Cl_6 and Co $(NH_3)_6$ etc. No equivalent complexes are given by Mo or W or Rh or Pt of the respective second and third series.

1.2.3 Magnetic behaviour :

The magnetic behaviour of the transition elements of first series can be interpreted very easily than those of second of the ligand field determines whether a low spin or a high spin complex is formed by the elements of the first transitional series. The second and third row elements tend to form low spin complexes. The elements second and third rows also show extensive temperature dependent paramagnetism.

1.2.4 Complex formation :

The first row elements form more stable complexes with N, O and F donors while those of second and third rows form stable complexes with P, S donors. The highest coordination number shown by elements of first transition series is 6 while 7 and 8 coordination numbers are seen in elements of second and third series. The first series elements form mainly tetrahedral complexes with coordination number 4 while second and third series elements form mainly square planar complexes with coordination number 4.

1.2.5 Study of titanium triad – Group IV elements electronic configuration and oxidation states :

The titanium triad consists of three elements namely Titanium, ziuconium and Hafnium. They have similar electronic configuration (n –1)d^2 ns^2. The most common and the most stable oxidation state for all the elements is +4. A large amount of energy is required to remove all the four electrons and anhydrous compounds such as $TiCl_4$ are covalent. In the oxidation state (+6), the elements have a d^0 configuration and has no unpaired electrons. Hence, their compounds are typically white or colourless and diamagnetic The oxidation state (+3) is reducing and Ti^{3+} ions are more strongly reducing than Sn^{2+}.

Table 2.1 The electronic configuration and oxidation states of Titanium Triad

Element	Electronic configuration	Oxidation States
Titanium, $_{22}Ti$	$_{18}[Ar]\ 3d^2\ 4s^2$	(—I) (0) (II) III IV
Zirconium, $_{40}Zr$	$_{36}[Kr]\ 4d^2\ 5s^2$	0 (II) (III) IV
Hafnium, $_{72}Hf$	$_{54}[Xe]\ 4f^{14}\ 5d^2\ 6s^2$	(III) IV

They are stable and exist as solids and in solution. Since the M^{3+} ions have a d^1 configuration they have one unpaired electron and are paramagnetic. With the only one d electron, there is only one d-d electronic transition and hence there is only one band in the visible spectrum and nearly all the compounds are coloured. The lower oxidation states under go disproportionation.

$$2Ti^{3+} \xrightarrow{\Delta} Ti^{2+} + Ti^{4+}$$

$$2Ti^{2+} \xrightarrow{H_2O} Ti^{0} + Ti^{4+}$$

The +2 and +3 oxidation states are not so common in the chemistry of Hafnium.

Reactivity :

The metals are unreactive at low and moderate temperatures because of the formation of a thin impermeable oxide layer. At room temperature they are unaffected by acids and alkalies. However, Titanium dissolves slowly in hot Conc. HCl giving Ti^{3+} ions and in HNO_3 giving $TiO_2(H_2O)_n$. Zirconium dissolves in hot Conc. H_2SO_4 and aquaregia. They dissolve in HF forming hexafluoro complexes.

$$Ti + 6HF \rightarrow H_2[TiF_6] + 2H_2$$

All the three metals are very reactive at higher temperatures. They form oxides, MO_2, tetrahalides, MX4, interstecial nitrides MN and interstecial carbides MC by direct combination.

Oxides and halides of (+4) oxidation state :

All the elements of titanium group form ionic oxides, MO_2 when heated above 600°c. they are soluble in water, non – volatile and are rendered refractory by strong ignition.

The basic properties of oxides increase with atomic number. TiO_2 is amphoteric and ZrO_2 and HfO_2 are basic. TiO_2 dissolves in both acids and bases forming titanates and titanyl compounds.

$$TiO_2(H_2O)_n \xrightarrow{\text{Conc. NaOH}} \underset{\text{Sodium titanate}}{Na_2TiO_3(H_2O)_n}$$

$$TiO_2(H_2O)_n \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Titanyl sulphate}}{TiO.SO_4}$$

Titranium group form halides of type MX_4. They can be prepared commercially by heating the dioxide with chlorine and carbon. The fluorides can be prepared by the reaction of $TiCl_4$ with anhydrous HF.

$$TiCl_4 + 4HF \rightarrow TiF_4 + 4HCl$$

$TiCl_4$ can be prepared by passing chlorine over a hot mixture of titanium dioxide and carbon.

$$TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$$

$TiCl_4$ is a colourless fuming liquid, covalent and diamagnetic in nature. $ZrCl_4$ is a white solid. The halides undergo hydrolysis vigorously and fumes in moist air.

$$TiCl_4 + 2H_2O \rightarrow \underset{\text{Titanium dioxide}}{TiO_2} + 4HCl$$

If water is not present in excess, it forms titanium oxochloride.

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl$$

$ZrCl_4$ on hydrolysis gives $ZroCl_2$

$$ZrCl_4 + H_2O \rightarrow ZroCl_2 + 2HCl$$

The tetrahalides act as electron pair acceptors or Lewis acids and react with a number of donors forming octahedral complexes.

$$TiF_4 \xrightarrow{\text{Conc. HF}} \underset{\text{Very stable}}{[TiF_6]^{2-}}$$

$$TiCl_4 \xrightarrow{\text{Conc. HF}} \underset{\text{Very unstable}}{[TiCl_6]^{2-}}$$

Oxides and halides of (+3) oxidation state :

All the +3 compounds have a d^1 configuration and are coloured and paramagnetic. Ti^{3+} is much more basic than Ti^{4+}. The trihalides, of titanium, TiX_3 are readily formed by reducing TiX_4 compounds.

$$Ti \xrightarrow{\text{hot HCl}} TiCl_3 \xleftarrow{650°c} TiCl_4$$

$$TiCl_3 \xrightarrow{H_2O} \underset{\text{Violet}}{[Ti(H_2O)_6]^{3+}Cl_3} + \underset{\text{Green}}{[Ti(H_2O)_5Cl]^{2+}Cl_2} \xrightarrow{\Delta} TiCl_4 + TiCl_2$$

On adding alkali to Ti^{3+} solution, precipitates Ti_2O_3 which is purple in colour. Zr^{3+} and Hf^{3+} are unstable in water and exist only as solid compounds.

$TiCl_3$ is used as a Ziegler – Natta catalyst for making polythene and other polymers.

1.2.6 Study of chromium triad :

The chromium group of transition elements consists of chromium, molybdenum and tungsten elements. They form a number of compounds on account of their several oxidation states i.e 0 to +6. The outer electronic configuration and their oxidation states are given below.

Table 2.2 The electronic configuration and oxidation states of Chromium Triad

Element	Electronic Configuration	Oxidation States
Chromium, $_{24}Cr$	$_{18}[Ar]\ 3d^5\ 4s^1$	—II —I 0 (I) II III IV (V) VI
Molybdenum, $_{42}Mo$	$_{36}[Kr]\ 4d^5\ 5s^1$	—II 0 I II III IV V VI
Tungsten, $_{74}W$	$_{54}[Xe]\ 4f^{14}\ 5d^4\ 6s^2$	—II 0 I II III IV V VI

Oxidation states :

All the three elements have oxidation states varying from 0 to 6. The most stable oxidation state for chromium is (+3) ; (+2) is reducing and (+6) state is strongly oxidising. But in case of Mo and W, the (+6) oxidation state is more stable and (+3) state is strongly reducing This shows that with increase in atomic number, the higher oxidation state becomes more stable while the lower oxidation state becomes less stable.

Reactivity :

The elements have low reactivity at ordinary temperature. Chromium becomes unreactive or passive at low temperature due to the formation of oxide layer chromium dissolves in dil HCl and H_2SO_4 giving Cr^{3+} ion. It is insoluble and become passive in HNO_3 or aquaregia. Molybdenum and tungsten do not dissolve in dil. HCl and H_2SO_4. Molybdenum reacts initially with HNO_3 at the beginning and then become passive. Chromium dissolves in dilute alkalies giving chromites. They do not react with oxygen at room temperature but on strong heating chromium forms Cr_2O_3 while molybdenum and tungsten form MO_3 type oxides. Chromium reacts with halogens to form CrX_3 halides while Mo and W form MX_6 type halides.

Due to lanthanide contraction, Mo and W shows a close similarity in size and properties.

Reactivity of (+3) oxidation state :

Cr^{3+} state is the most stable oxidation state of chromium and chromic compounds (Cr^{+3}) are ionic in nature. The Cr^{3+} ion forms a host of complex compounds.

Eg :

$[Cr(H_2O)_6]^{3+}$; $[Cr(NH_3)_6]^{3+}$ etc

In addition to the above compounds CrX_3 halides and Cr_2O_3 are known. Mo^{+3} and W^{+3} do not exist as simple ions. Mo exists in (+3) oxidation state in some of its compounds which are slowly oxidized in air and also hydrolysed in water. W^{3+} compounds are unstable.

Reactivity of (+6) oxidation state :

These metals form oxides CrO_3, MoO_3 and Wo_3 corresponding to (+6) oxidation state. All the three oxides are strongly acidic and dissolve in dilute NaOH solution forming chromate, CrO^{2-}_4 ; molybdate, MoO^{2-}_4 and tungstate, WO^{2-}_4 ; ions. Mo and W form stable halides MoF_6 and WF6 in (+6) oxidation state. The compounds of chromium, i.e CrO^{2-}_7 are strong oxidising agents. While in Mo and W has little oxidising nature.

1.2.7 Copper triad – Reactivity of +1, +2 and +3 oxidation states :

The copper triad consists of elements namely copper, silver and gold. They are also known as coinage metals since they are used in making coins. All the three elements have one electron in ns orbital and completely filled d (n-1) d sub shell. Copper and silver exhibits (+1) and (+2) oxidation states while gold exhibits (+1) and (+3) oxidation states. (+2) state is very important oxidation state in copper. (+3) state is the most stable one in gold. In aqueous solution, copper exists as Cu^{2+} ion ; in (+2) state ; silver as Ag^+ ion and gold as Au^{3+} ion.

Table 2.3 The electronic configuration and oxidation states of Copper Triad

Element	Electronic configuration	Oxidation States
Copper, Cu	$[Ar]3d^{10}\,4s^1$	I II III
Silver, Ag	$[Kr]4d^{10}\,5s^1$	I II III
Gold, Au	$[Xe]4f^{14}\,5d^{10}\,6s^1$	I (II) III

The univalent Cu^+ and Au^+ ions undergo disproportionation in their aqueous solutions.

$$2Cu^+ \rightleftharpoons Cu^{2+} + Cu$$

$$3Au^+ \rightleftharpoons Au^{3+} + 2Au$$

Copper(+1) thiocyanate, CuCNS is an example of a stable copper (I) compound which is insoluble in water. In (+1) state, most of the compounds of copper are colourless due to the presence of completely filled 3d sub shell.

Reactivity :

The coinage metals are unreactive and they have positive reduction potential values and hence lie below hydrogen in the electro chemical series. They do not react with water or liberate hydrogen with acids. The noble character of these metals increases from copper to gold. Copper reacts with concentrated HNO_3 and H_2SO_4.

$$3Cu + \underset{\text{dilute}}{8HNO_3} \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

$$Cu + \underset{\text{Concentrated}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Silver, dissolves in Conc. HNO3 and in hot Conc. H2SO4. But gold is inert to all acids excepts aquaregia. Copper reacts with oxygen but silver and gold are inert.

$$Cu + O_2 \xrightarrow{\text{red heat}} CuO \xrightarrow{\text{High temp}} Cu_2O + O_2$$

Cu and Ag react with H_2s and S but Au does not.

$$2Ag + H_2s \rightarrow Ag_2s\ H_2s$$

All the three metals react with halogens.

Reactivity of (+1) state :

(+1) oxidation state would be the most common and most stable because of the extra stability resulting from a complete d shell. Ag^+ ion is stable in both the solid state and solution but Cu^+ and Au^+ disproportionate in water.

$$2Cu^+ \rightleftharpoons Cu^{2+} + Cu$$

$$3Au^+ \rightleftharpoons Au^{3+} + 2Au$$

Cu^{+1} and Au^{+1} compounds that are stable to water are complexes. Cu_2O (basic oxide) is formed by the reduction of Cu^{2+} (Fehling solution) with sugars.

CuF is not known. other halides Cu Cl, Cu Br and CuI are formed by the reaction of Cu_2O with halogen acids.

Cyanide complexes having Cu^+, Ag^+ and Au^+ are known. For example, cuprous cyanide is precipitated by adding KCN to $CuSO_4$ solution. The precipitate dissolves in excess of KCN to form complex.

$$2Cu^{2+} + 4\bar{CN} \rightarrow 2CuCN + (CN)_2$$

$$CuCN + 3\bar{CN} \rightarrow [Cu(CN)_4]^{3-}$$

Cyanide complexes of Ag^+ and Au^+ ions are formed during the extraction of those metals.

$$4Au + 8CN + 2H_2O \rightarrow 4[Au(CN)_2]^- + 4OH^- + O_2$$

Silver forms a number of compounds in (+1) state. But most of the salts are insoluble in water, except $AgNO_3$, AgF and $AgClO_4$ which are soluble. Ag_2O is soluble, both in acids as well as in NaOH. Au^{+1} ion is less stable.

Eg : Au_2O ; $[Au(CN)_2]^-$ etc.

Reactivity of (+2) state :

The most important and stable oxidation state for copper is (+2). Its compounds are coloured and paramagnetic due to the presence of one unpaired electron. All Cu^{2+} compounds and complexes are blue or green in colour.

AgF_2 is a strong oxidising agent and a good fluorinating agent which decomposes on heating to give AgF.

Ag+2 ion forms more stable complexes.

Eg : $[Ag(Pyr)_4]^{2+}$

Reactivity of (+3) oxidation state :

(+3) state is common in case of Au and un common in Cu and Ag.

All the halides, AuX_3 are known $AuCl_3$ can be prepared by heating the elements directly or by evaporating the solution of gold in aquaregia.

$$Au + HNO_3 + HCl \rightarrow H[AuCl_4] \xrightarrow{\text{evaporation}} AuCl_3$$

Au Br_3 is prepared from elements, and AuF_3 is prepared by heating Au with Br F_3.

1.2.8 Model Questions :

1. Name the elements of the titanium triad and give their electronic configuration. How would you account for the (+3) and (+4) oxidation states of the elements.
2. Name the elements included in the chromium group of the transition elements. Give the various oxidation states exhibited by chromium. Which of these is more stable and why ?
3. Discuss in detail the various oxidation states exhibited by coinage metals. Discuss the reactivity of copper in (+1) and (+2) oxidation states..
4. Compare the elements of second and third transition series with the first transition series.

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UNIT – I

Lesson – III

F – BLOCK ELEMENTS

1.3.1

The f – block elements are also called the inner transition elements which contain incomplete d – sub shell and f – sub shell. These f – block elements contain incomplete f – orbital of the antepenultimate shell (inner to the penultimate i.e. n- 2) in addition to the incomplete d – orbital of the penultimate shell (n- 1). The f – block elements are divided into two series namely.

i) Lanthanides in which 4f sub shell is being filled up with electrons and

ii) Actinides in which 5f sub shell is filled.

i) The lanthanide series :

Lanthanum (at No or z = 57) and the next fourteen elements (Z = 58 – 71) following it are called lanthanides or lanthanones. These 15 elements closely resemble one another which can be explained on the basis of their electronic configuration. The configuration of lanthanum is [Xe] $5d^1$ $6s^2$. In the next fourteen elements, fourteen electrons are added to the empty 4f sub shell of the lanthanum configuration. In cerium, the first 4f electron is added to the lanthanum configuration while in Lutetium, the fourteenth 4f electron is added to lanthanum configuration. Since the number of electrons in the outermost shell and penultimate shell remains the same, all the fifteen elements of the lanthanides resemble one another very closely. 4f sub shell is empty in case of lanthanum while 4f sub shell is completely filled in case of lutetium, and hence strictly according to the definition, the elements from Ce to Yb only belong to the f – block elements. How ever all the elements from La to Lu have similar physical and chemical properties.

General properties of Lanthanides :

1.3.2 Electronic Configuration :

The electronic configuration of the lanthanides is not known exactly. However the more probable view is that in lanthanides, 5d orbital remains vacant and the differentiating electron enters into the 4f orbitals excepts in gadolinium (z = 64) where it enters into 5d orbital which retains the stable $4f^7$ configuration. At ytterbium ; Yb (Z = 70) since all the 4f orbitals are filled, the differentiating electron enters into 5d orbital in next element lutetium (Z = 71). The general electronic configuration of the f – block elements is, $(n-2)\,f^{1-14}$, $(n-1)\,s^2$, $(n-1)\,p^6$, $(n-1)\,d^{0-1}$, ns^2.

Table 3.1 Electronic configuration of Lanthanides

At. No.	Element	Symbol	Electronic configuration	
			One view	Second view
57	Lanthanum	La	[Xe] $4f^0 5d^1 6s^2$	[Xe] $4f^0 5d^1 6s^2$
58	Cerium	Ce	[Xe] $4f^1 5d^1 6s^2$	[Xe] $4f^1 5d^1 6s^2$ or [Xe] $4f^2$ $6s^2$
59	Praseodymium	Pr	[Xe] $4f^2 5d^1 6s^2$	[Xe] $4f^3$ $6s^2$
60	Neodymium	Nd	[Xe] $4f^3 5d^1 6s^2$	[Xe] $4f^4$ $6s^2$
61	Promethium	Pm	[Xe] $4f^4 5d^1 6s^2$	[Xe] $4f^5$ $6s^2$
62	Samarium	Sm	[Xe] $4f^5 5d^1 6s^2$	[Xe] $4f^6$ $6s^2$
63	Europium	Eu	[Xe] $4f^6 5d^1 6s^2$	[Xe] $4f^7$ $6s^2$
64	Gadolinium	Gd	[Xe] $4f^7 5d^1 6s^2$	[Xe] $4f^8$ $6s^2$
65	Terbium	Tb	[Xe] $4f^8 5d^1 6s^2$	[Xe] $4f^9$ $6s^2$
66	Dysprosium	Dy	[Xe] $4f^9 5d^1 6s^2$	[Xe] $4f^{10}$ $6s^2$
67	Holmium	Ho	[Xe] $4f^{10} 5d^1 6s^2$	[Xe] $4f^{11}$ $6s^2$
68	Erbium	Er	[Xe] $4f^{11} 5d^1 6s^2$	[Xe] $4f^{12}$ $6s^2$
69	Thulium	Tm	[Xe] $4f^{12} 5d^1 6s^2$	[Xe] $4f^{13}$ $6s^2$
70	Ytterbium	Yb	[Xe] $4f^{13} 5d^1 6s^2$	[Xe] $4f^{14}$ $6s^2$
71	Lutetium	Lu	[Xe] $4f^{14} 5d^1 6s^2$	[Xe] $4f^{14} 5d^1 6s^2$

Position in periodic table :

The lanthanide elements are placed in the sixth period of the periodic table. The 14 elements between La and HO, in which 4f orbitals are being filled are placed at the bottom of the table. These are called lanthanides because of their chemical similarity to lanthanum due to similar electronic configuration in ns and (n -1) shells. A similar set of elements in which 5f orbitals are being filled are called actinides and are placed at the bottom under the corresponding lanthanides. In order to maintain the importance of the periodic law, these two sets of elements were placed at the bottom of the periodic table.

Oxidation states :

The most common and stable oxidation state of the lanthanides is (+3) state. Lanthanum shows only (+3) oxidation state obtained by the loss of 6s electrons and the only d – electron and form La^{3+} ion. The configuration of La^{3+} ion is similar to that of xenon which is highly stable. Gadolinium (Gd) and lutetium (Lu) also form only M^{3+} ions because the removal of three electrons gives the stable $4f^7$ (half filled) and the stable 4f14 (completely filled) configurations in the two elements.

In addition to (+3) oxidation state few lanthanides also show (+2) and (+4) oxidation states. But, these (+2) and (+4) oxidation states are not common and are unstable in aqueous solution except for Ce^{+4}.salts like ceric sulphate which is used as an oxidising agent in volumetric analysis. These (+2) and (+4) oxidation states may be explained on the basis of extra stability associated with empty, half filled or completely filled 4f – sub shell.

Table 3.2 Oxidation states and Outer Electronic configuration of Lanthanides in various oxidation states.

Element	**Oxidation State**	**Outer Electronic Configuration of**			
		M	M^{2+}	M^{3+}	M^{4+}
La	+3	$5d^1 6s^2$	—	$5d^0 6s^0$	—
Ce	+3, +4	$4f^2 \ 6s^2$	—	$4f^1 6s^0$	$4f^0 6s^0$
Pr	+3, +4	$4f^3 \ 6s^2$	—	$4f^2 6s^0$	$4f^1 6s^0$
Nd	+2, +3, +4	$4f^4 \ 6s^2$	$4f^4 6s^0$	$4f^3 6s^0$	$4f^2 6s^0$
Pm	+3	$4f^5 \ 6s^2$	—	$4f^4 6s^0$	—
Sm	+2, +3	$4f^6 \ 6s^2$	$4f^6 6s^0$	$4f^5 6s^0$	—
Eu	+2, +3	$4f^7 \ 6s^2$	$4f^7 6s^0$	$4f^6 6s^0$	—
Gd	+3	$4f^7 5d^1 6s^2$	—	$4f^7 6s^0$	—
Tb	+3, +4	$4f^9 \ 6s^2$	—	$4f^8 6s^0$	$4f^7 6s^0$
Dy	+3, +4	$4f^{10} \ 6s^2$	—	$4f^9 6s^0$	$4f^8 6s^0$
Ho	+3	$4f^{11} \ 6s^2$	—	$4f^{10} 6s^0$	—
Er	+3	$4f^{12} \ 6s^2$	—	$4f^{11} 6s^0$	—
Tm	+2, +3	$4f^{13} \ 6s^2$	$4f^{13} 6s^0$	$4f^{12} 6s^0$	—
Yb	+2, +3	$4f^{14} \ 6s^2$	$4f^{14} 6s^0$	$4f^{13} 6s^0$	—
Lu	+3	$4f^{14} 5d^1 6s^2$	—	$4f^{14} 6s^0$	—

Example :

Ce^{+4}.- $4f^0$

yb^{2+}.- f^{14}

Eu^{2+}.- f^7

1.3.3 Ionic radii - lanthanide contraction :

On moving along the lanthanides, from lanthanum to lutetium, there is a decrease in the size of atom and ions, with increase in atomic number. This steady decrease in size is called lanthanide contraction.

Cause of lanthanide contraction :

As we know, in lanthanides the differentiating electron enters into 4f – sub shell. The shielding effect of 4f electrons is very small (imperfect), being even smaller than that of d – electrons in d – block elements. With increase in atomic number, there is increase in nuclear charge but no comparable increase in the shielding effect of 4f electrons occurs. This causes a condtraction in the size of 4f – sub shell and hence the atomic and ionic size decreases from La to Lu i.e. from 1.06A° (La^{3+}) to 0.85A° (Lu^{3+}). Thus lanthanum has the larger size while lutetium has the smallest size.

Though the decrease in size is continuous but not regular. This decrease is more in first six elements than in the next subsequent elements.

Consequences of lanthanide contraction :

The consequences of lanthanides contraction are as follows :

i) Occurrence of yttrium (transitions element) with heavier lanthanides. The size of yttrium is comparable to that of heavier lanthanide ions. i.e. Tb^{3+},Dy^{3+}, Ho^{3+} and Er^{3+}. Hence yttrium occurs in natural minerals along with the heavier lanthanide ions. Since the compounds of yttrium are closely related in the crystal structure and chemical properties to the compounds of heavier lanthanides, the latter are commonly known as yttrium earths.

ii) **Basicity differences :** The basic nature of the oxides and hydroxides of lanthanides decreases with increase in atomic number. Thus $La(OH)_3$ is most basic while $Lu(OH)_3$ is least basic. This can be explained on the basis of lanthanide contraction. The regular decrease in the size of lanthanide ions increases the covalent character between the lanthanide ion and hydroxide ion which in turn reduces the basic character of the lanthanide hydroxides.

iii) **Anamolous behaviour of post – lanthanides :** The elements following the lanthanides, i.e. the elements of third transitional series are called post – lanthanide elements. Lanthanide contraction affects the properties like atomic and ionic radii of post – lanthanide elements.

Atomic and ionic radii of post – lanthanides i.e. similarities in properties among the corresponding members of second and third transition series :

Generally in a sub group the atomic radii increases on moving down a group with increase in atomic number. For example, there is gradual increase in atomic radii, in III A group from Se to La. In a similar way, there must be increase from Ti to Zr (IVA) : V to Nb (VA) and so on. But actually, it is not observed in the corresponding groups. In other words, the transitional elements (III Series) following the lanthanides have the same atomic and ionic sizes as the corresponding elements present just above them, in their sub groups.

Table 3.3 Atomic (Covalent) Radii of Elements Preceding and Following Lanthanides.

21		22	23	24	25	26	27	28
Sc		Ti	V	Cr	Mn	Fe	Co	Ni
1·44		1·32	1·22	1·17	1·17	1·17	1·16	1·15
39		40	41	42	43	44	45	46
Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd
1·62		1·45	1·34	1·29	—	1·24	1·25	1·28
57	58 to 71	72	73	74	75	76	77	78
La	↑	Hf	Ta	W	Re	Os	Ir	Pt
1·69		1·44	1·34	1·30	1·28	1·26	1·26	1·29

14 Lanthanides

For example in Zr/ Hf pair, hafnium (Hf) must be bigger in size than zirconium but it is not so. The usual increase in the size of Hf has been can called due to the intervening lanthanide contraction with the result, both Zr and Hf are of the same size. Because of the similarity in size of Zr and Hf : Nb and Ta ; Mo and W etc. the two elements of each pair has same properties and occur together in nature.

1.3.4 Colour and spectra, f – f transition :

Trivalent ions of some lanthanides are coloured in the solid state as well as in aqueous solution.

Table 3.4 Colours of Lanthanide Ions

Ion	Number of 4f electrons	Colour	Ion	Number of 4f electrons	Colour
La^{3+}	0	Colourless	Lu^{3+}	14	Colourless
Ce^{3+}	1	Colourless	Yb^{3+}	13	Colourless
Pr^{3+}	2	Green	Tm^{3+}	12	Pale green
Nd^{3+}	3	Mauve	Er^{3+}	11	Pink
Pm^{3+}	4	Purple	Ho^{3+}	10	Pale yellow brown
Sm^{3+}	5	Very pale yellow	Dy^{3+}	9	Colourless
Eu^{3+}	6	Colourless	Tb^{3+}	8	Colourless
Gd^{3+}	7	Colourless			

The colour of the ions depend upon the number of f – electrons. The 4f orbitals are the main source of colour. Colour is due to light absorption from the visible region of the spectrum and hence the bands in the absorption spectra arise from the electronic transition within the 4f – level i.e f-f transition. The most important characteristic feature of the spectra of the tripositive lanthanide ions is the sharpness of the individual bands. Many of these bands are line – like which is due to the fact that the 4f orbitals are effectively shielded by $5s^2$ and $5P^6$ orbitals and hence the absorption bands arises merely from electronic transitions with in the 4f – level.

1.3.5 Magnetic properties – paramagnetism :

As we know that diamagnetism in an ion is due to the presence of paired electrons while paramagnetism arises when an atom : ion or molecule contains unpaired electrons.

La^{3+} ($4f^0$) and Lu^{3+}.($4f^{14}$) ions are diamagnetic while the rest of the trivalent lanthanide ions are paramagnetic. Since the 4f electrons are well shielded by the overlying 5s and 5p electrons, it is not possible to explain their magnetic moments in terms of the number of unpaired electrons alone. The orbital contribution which was ignored in the case of d – block elements, can not be ignored in the case of f – block elements. Hence in 4f elements magnetic moments must be calculated taking both spin and orbital contributions into account.

1.3.6 Complexation – Type of donor ligands preferred :

Though lanthanide ions have high charge (+3) ; because of their large size, they posses low charge density and hence they can not cause much polarization and consequently they do not have much tendency to form complexes. They form stable complexes with chelating oxygen ligands such as EDTA ; oxalic acid; - diketones ; Oximes etc. The tendency to form complexes and their stability increases with increase in atomic number. This property is used in the separation of lanthanides from one another. Complexes with monodentate ligands are less stable than the chelates and tend to dissociate in aqueous solution. Fluoride complexes are formed by the smaller ions. Chloride complexes are not formed in aqueous media or conc HCl. They do not form complexes with π bonding ligands.

1.3.7 Reactivity of lanthanides :

Since all the lanthanides have similar electronic configuration, they have close similarity in their chemical properties which is even more than that of transitional elements. The reasons for it is

i) the 4f electrons of lanthanides are very effectively shielded by the overlying 5s, 5p and 6s electrons and

ii) due to lanthanide contraction, there is very little difference (maximum 0.21) among the size of the trivalent lanthanide ions. Thus, lanthanides are highly electropositive and very reactive in nature.

1. They are silvery white metals, tarnish on exposure to air.
2. They dissolve readily in cold water liberating hydrogen.
3. They react with hydrogen forming non - stoichiometric hydrides eg : LnH_2 and LnH_3.
4. They react with nitrogen forming corresponding nitride, Ln N.
5. They react with acids liberating H_2.

Occurrence :

The lanthanides were originally called rare earth elements because of their occurrence in oxide mixtures. The term lanthanide is taken to include lanthanum itself which is the prototype for succeeding fourteen elements. The major source is monazite sand, the important mineral which is a lanthanide orthophosphate, containing lanthanides. Promethium occurs only in uranium ores.

1.3.8 Separation of Lanthanides :

The properties of metal ions are determined by their size and charge. Since all the lanthanides carry same charge i.e. tripositive and have almost same size, they are similar in their properties which makes the separation of lanthanides very difficult. [illegible] methods based on the slight differences in their solubility, hydration, complex formation, basic properties have been used [illegible] separation of lanthanides. The slight difference in the above properties is due to the slight difference in the size of their trivalent ions.

Ion exchange method :

This is the most useful method for separation of lanthanides. The solution containing trivalent lanthanide ions is passed through an ion exchange column containing synthetic resin with acidic functional groups like - COOH or SO_3H. The hydrogen ion of the resin are replaced by the trivalent metal ions.

$$M^{3+} + H - (Resin) \rightarrow M - (Resin)_3 + 3H^+$$

In order to recover the lanthanides ions fixed on to the resin, the column is eluted with a citric acid – ammonium citrate solution. The ions which are bound loosely to the resin are displaced by the ammonium ions first while those which are bound firmly are displaced last. The firmness with which lanthanide ions are fixed to the resin decreases from Ln^{3+} to Lu^{3+}. Thus Lu^{+3} is eluted first while La^{3+} is eluted last.

$$3NH_4^+ + M - (Resin)_3 \rightarrow 3NH_4 - Resin + M^{3+}$$

The firmness with which the lanthanide ion is attached to the ion exchange column depends on its size. Thus smaller the size, greater is its firmness. When the metal ions are eluted out of the column, form a complex with the citrate ions.

$$M^{3+} + \text{Citrate ions} \rightarrow \text{M-Citrate complex}$$

Solvent extraction method :

Solvent extraction method is based on the slight difference present in the partition coefficients of the salts of the lanthanides between water and organic solvents. For example the partition coefficient of $Gd(NO_3)_3$ between water and normal butyl alcohol is 1.06 times greater than that of Ln $(NO_3)_3$ .This means that $Gd(NO_3)_3$ can be separated from $Ln(NO_3)_3$ by repeated extraction with water from a solution of these salts in n-butyl alcohol.

1.3.9 Chemistry of actinides :

The elements from Actenium (at no :89) to Lawrencium (at.No : 103) are called actinides. The outer electronic configuration of actinium is $6d^1 7s^2$. just as in lanthanides where the antepenultimate 4f sub shell is filled successively by addition of one electron at a time, in actinides the antepenultimate 5f sub shell is filled successively by the addition of one electron at each step. Just as Lanthanum is the prototype of the lanthanides, actinium is the prototype of actinides. Lanthanides constitutes the first inner transitional series while aclinides constitutes the second inner transitional series. Since, in actinides also, the number of electrons in the outermost and penultimate shells remains same, they have close similarity in their properties.

Electronic configuration :

There is some uncertaintiy regarding the outer electronic configuration of these elements. There is a doubt, whether thorium, protactinium and uranium contain the differentiating electron in the 5f orbital or 6d orbital. It has been suggested, that in these elements, the additional electrons enter into 6d sub shell and the actual entry into 5f sub shell begins only after uranium and hence the elements following uranium in which the 5f – orbitals are definitely being filled are called uranides. The general electronic configuration of actinides is [Rn] $5f^{1-14} 6d^{0-1} 7s^2$. Accepting the view that entry of electrons in the 5f sub shell begins with thorium, the probable electronic configuration of these elements are give below.

Table 3.5 Parbable Electronic Cofiguration of Actinides

Element	Symbol	Atomic number	Electronic configurations
Actinium	Ac	89	[Rn] $6d^1 7s^2$
Thorium	Th	90	[Rn] $5f^1 6d^1 7s^2$
Protactinium	Pa	91	[Rn] $5f^2 6d^1 7s^2$
Uranium	U	92	[Rn] $5f^3 6d^1 7s^2$
Neptunium	Np	93	[Rn] $5f^4 6d^1 7s^2$
Plutonium	Pu	94	[Rn] $5f^5 6d^1 7s^2$
Americium	Am	95	[Rn] $5f^7 6d^0 7s^2$
Curium	Cm	96	[Rn] $5f^7 6d^1 7s^2$
Berkeylium	Bk	97	[Rn] $5f^8 6d^1 7s^2$
Californium	Cf	98	[Rn] $5f^{10} 6d^0 7s^2$
Einsteinium	Es	99	[Rn] $5f^{11} 6d^0 7s^2$
Fermium	Fm	100	[Rn] $5f^{12} 6d^0 7s^2$
Mendelevium	Md	101	[Rn] $5f^{12} 6d^0 7s^2$
Nobelium	No	102	[Rn] $5f^{14} 6d^0 7s^2$
Lawrencium	Lr	103	[Rn] $5f^{14} 6d^1 7s^2$

Oxidation states :

Unlike the lanthanides, actinides show a variety of oxidation states. Uranium shows oxidation states from (+3) to (+6) in a number of compounds. The most stable oxidation state in actinides is (+3). Np and Pu shows oxidation states i.e. from (+3) to (+7) Th and Pu shows (+4) oxidation state; No shows (+2) state and Pa and Np shows (+5). Curium shows only (+3) oxidation state due to stable configuration of the half filled 5f sub shell.

Table 3.6 Oxidation states of Actinides

Element	Symbol	Atomic number	Oxidation states
Actinium	Ac	89	+3
Thorium	Th	90	+4, (+3)
Protactinium	Pa	91	+5 ,(+3), (+4)
Uranium	U	92	+3, +4, +5, +6
Neptunium	Np	93	+3, +4, +5, +6
Plutonium	Pu	94	+3, +4, +5, +6
Americium	Am	95	+3, (+4), +5, +6
Curium	Cm	96	+3, (+4)
Berkeylium	Bk	97	+3, +4
Californium	Cf	98	+3
Einsteinium	Es	99	+3
Fermium	Fm	100	+3
Mendelevium	Md	101	+3
Nobelium	No	102	—
Lawrencium	Lr	103	—

Actinide contraction :

The ionic radii of actinides decreases along the series. This decrease in ionic radii, known as actinide contraction is due to the poor shielding effect of the nuclear charge by the 5f electrons.

Colour :

Most of the actinide ions are coloured and the colour is due to the presence of unpaired electrons. For example U^{4+} ions are green in colour ; U^{3+} is red and UO_2^{2+} is yellow.

Complex formation :

Actinides have a greater tendency to form complexes and the degree of complex formation decreases in the following order.

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$$

They form complexes with chelates like EDTA : oximes etc.

1.3.10 Comparison of lanthanides with Actinides :

In both the series, f – orbitals are being filled and hence they resemble each other. Due to difference in the binding energy of 4f electrons and 5f electrons, they also differ from each other.

Resemblences between lanthanides and actinides :

1. In both the series the predominant oxidation state is +3.
2. f – orbitals are being filled.
3. Both show decrease in ionic radii with increase in atomic number i.e. contraction in size.

	Lanthanides	Actinides
1.	Electrons are successively added to the 4f sub shell	Electrons are successively added to the 5f sub shell.
2.	Binding energies of 4f - orbitals are very high	Binding energies of 4f - orbitals are lower
3.	4f - electrons have greater shielding effect	5f - electrons have poor shielding effect.
4.	Except Promethium all are non - radio active	All are radio active.
5.	In lanthanides maximum oxidation state is state is +4. eg Ce+4	Actinides exhibit higher oxidation states +4 ; +5 ; +6 and +7.
6.	They do not form complexes easily	They form complexes easily.
7.	The compounds are weakly basic.	The compounds are more basic.
8.	They do not form oxocations.	They form oxocations like UO_2^{2+} ; UO+ ; NpO_2^{+} etc.
9.	Most of the trivalent ions are colourless.	Trivalent and tetravalent ions are coloured.

1.3.11 Model Questions :

1. What are f- block elements ? why are they so called ? Discuss the position of lanthanides in the periodic table.
2. Write notes on lanthanide contraction. What are its important consequences ?
3. What are inner transition elements ? Give the differences of lanthanides and actinides.
4. Give the general electronic configuration of lanthanides. Explain the oxidation states of lanthanides.
5. What are inner transition elements ? How are they classified ? Why are they placed separately at the bottom of the periodic table.
6. Why is the separation of the lanthanides so difficult ? Discuss the ion exchange method.
7. What are actinides ? Discuss the position of actinides in the periodic table. Compare and contrast lanthanides and actinides.

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UNIT- I

Lesson - IV

Metals - Theories of bonding in metals

1.4.1

Elements have been divided into metals and non- metals on the basis of the difference in their physical and chemical properties. The division, however is not sharp as there are many exceptions to most of their properties. There are some metalloids also.Metals are characterised by the following physical properties.

1. Metals have a characteristic metallic lustre. They are shiny and highly reflective.
2. They are generally hard and have high density (exception - alkali metals are soft)
3. They have high melting points and boiling points (exception) Sodium and potassium have low melting points and mercury has low boiling point.
4. They are good conductors of heat and electricity.
5. They are malleable and ductile (exceptions – Al, Bi and Sb) They can be drawn into thir sheets and wires.
6. They have high elasticity.
7. They are generally electropositive in nature.
8. They exhibit high coordination numbers of 8 or 12. Their crystal structures are always cubic close packed ;hexagonal close packed or body centred cube.
9. They form alloys.

1.4.2 Theories of bonding :

Metallic elements exhibit coordination number 8 or 12. Each atom is surrounded 8 or 12 other atoms. Therefore, the atoms in a metallic elements can not be held by covalent bonds because they do not have sufficient number of electrons in their valency shells. The atoms in a metallic element are also cannot be held by ionic bond, as the atoms in a metallic crystal are alike and hence the transfer of electron from one atom to another atom is highly unlikely. Hence atoms in a metal atom are believed to be held together by a special type of bond known as metallic bond. The nature of metallic bond is explained on the basis of theories namely free electron theory ; Valence bond theory and molecular orbital or band theory.

1. Free electron theory :

Drude and Lorentz put forward a theory known as free electron theory to explain the high electrical and thermal conductivities of metals. They suggested that on account of low ionisation energies of metals, some of the atoms lose one or more of their valency electrons and change into positive ions or cations. The electrons lost by metal atoms in this manner are not localized i.e. they are mobile and move freely through out the volume of the metal and keep the positively charged ions held together.

There fore, a metal may be regarded as an assembly of positive ions (M^+ ions) immersed in a sea of mobile electrons. The strong attractive force binds a metal ion to a number of electrons, its sphere within its sphere of influence is known as metallic bond. The movement of the electrons can be compared with the gas molecules. Hence the theory is also known as electron gas theory.

Explanation of metallic properties i.e. thermal and electrical conductivities of metals :

The high electrical conductivity of metals is due to the presence of the mobile valency electrons. They move freely in an electric field and this conduct electricity through out the metal. The high thermal conductivity of metals is also due to the presence of mobile electrons. When a metal is heated from one end ; the electrons acquire a large amount of kinetic energy and being mobile, they move fastly through the crystal and conduct heat to other parts of the metal.

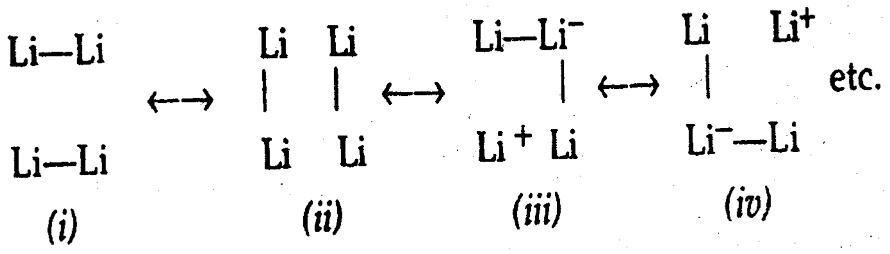
Draw backs of the theory :

Although the theory explains many of the properties of metals, no satisfactory explanation was given about semi conductance and the specific heats of metals. The theory can not explain the large variations in properties of certain metals. For example metals like sodium and potassium are so soft that they can be cut easily with a knife. Mercury melts at a very low temperature – 39°c.

2. Valence bond theory :

The valence bond theory or resonance theory was proposed by pauling. According to this theory, the bonding in metals resembles the covalent bond and exists resonance between the various bonds. In metals, each atom is surrounded by 8 or 12 other atoms. The metal does not possess sufficient number of valence electrons for the formation of covalent bonds between itself and the other atoms surrounding it.

Consider lithium as an example. Each lithium atom has one valency electron and lithium crystallizes in a body centred cubic lattice where each lithium atom is surrounded by 8 other atoms. The number of electrons required is 16 (8 x 2 = 16) for the formation of localized covalent bonds between 9 lithium atoms (i.e. Central lithium atom and the surrounding 8 lithium atoms.) Pauling explained the discrepancy on the basis that the covalent bond formed between two atoms is not localized but is highly delcoalised due to resonance. In other words the covalent bond formed between two lithium atoms resonate between various atoms in the metal crystal.



Each lithium atom consists of only one valency electron and hence it can not form covalent bond with more than one atom. So, whenever a bond formed between two atoms, it is accompanied by simultaneous shifting of the other bond formed between two other atoms. The phenomena is known as synchronized resonance. Stability increases with increase in resonanating structures. Since a number of above structures are possible it accounts for the stability of metals. Resonating structures leading to ionic forms can also be formed, when a bond between two atoms shifts to the other place, without simultaneous shifting of the bond present already in that place. Such resonance seen in ionic structures is called unsynchronised resonance. The existence of ionic forms Li+ and Li-, is possible because of the slight difference in the energy of the 2s and 2P orbitals. An electron from 2S orbital of one atom can easily get transferred to a vacant 2P orbital of another atom to form Li- ion.

Explanation of metallic properties :

Valence bond theory explains the properties of metals basing on the fact of delocalisation of electrons in metals.

Metallic lustre :

When light falls on surface of the metals, the energy is absorbed by the valency electrons and get excited into nearest higher orbital. When returned to original state, these electrons emit this absorbed energy in the form of visible light which is responsible for the metallic lustre.

Electrical conductivity :

The electrons in a metallic bond are delocalized and are free to move. The free movement of these mobile electrons is responsible for the electrical conductivity of metals.

Thermal conductivity :

The thermal conductivity in metals is due to mobile electrons. When temperature is raised these mobile electrons absorb energy at one end and pass it through out the crystal. This explains thermal conductivity of metals.

Malleability and ductility :

When hammered or some energy is applied on the surface of the metal, the atoms or cations of one layer will be slipping over atoms or cations of other layer. It is responsible for high malleability and ductility of metal. The shape is changed without breaking the crystal.

Elasticity of metals :

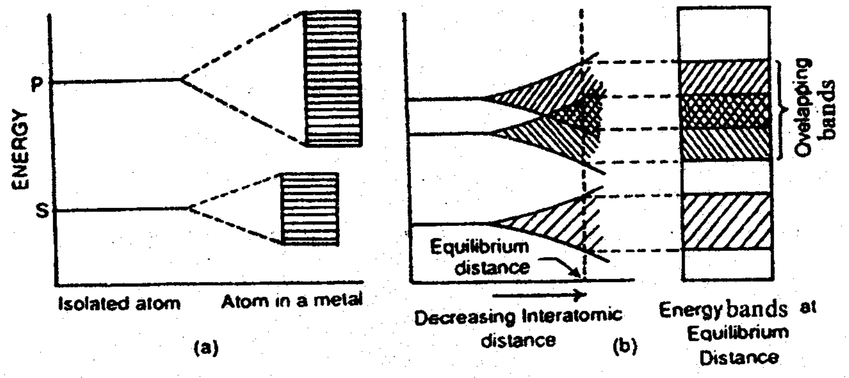
When a stress is applied, the structure will change for a moment and restore back, when stress is removed. This explains the highly elastic nature of metals.

Limitations :

Though the resonance theory provides explanation for the properties of metals, it fails to explain the same quantitatively. It also fails to explain the metallic character in molten state or in solution.

Molecular orbital theory or band theory of metals :

According to this theory, metal is a big molecule and molecular orbitals obtained by mixing of the orbitals of the individual atoms cover the entire metal. According to molecular orbital theory, combination of two atomic orbitals leads to the formation of two molecular orbitals, one molecular orbital is of lower energy and the other is of higher energy than that of the atomic orbitals. In metallic crystal lattice, the metal atoms are in a very large number and the difference in the energy between the various molecular orbitals is very small which results in the formation of closely spaced energy levels called bands. In such bands there are gaps which represent energies in which electrons cannot be present. Such gaps are called for bidden bands.



Energy levels and energy bands in isolated atoms and in metal structures

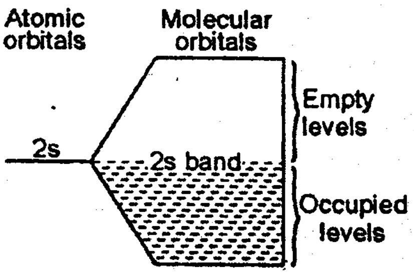
The overlapping of energy bands will also occur in some cases. The extent of overlapping depends on the inter nuclear distance. The filling up of these bands and the width of the for bidden bands explains whether the given metal is conductor, insulator or semiconductor.

Let us consider lithium as an example. Its electronic configuration is $1S^2 2S^1 2P^0$.

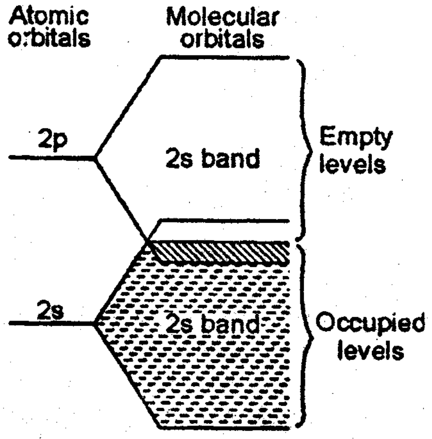
i) 1S atomic orbital is completely filled so the band formed by 1S atomic orbital is narrow and non conducting.

ii) 2S orbital is half filled. The upper half of the band is empty while the lower half is completely filled. The 2S levels are very close and hence the electron can go from lower half to upper half of the electron band even at ordinary temperature. Hence 2S band is conductive.

iii) The energy gap between 1S and 2S bands is very large so that the electrons from 1S band can not jump into 2S band. The energy gap is called for bidden zone.



(a) Metallic molecular orbitals for lithium, showing half-filled band.



(b) Metallic molecular orbitals for beryllium, showing overlapping bands.

iv) 2P atomic orbital is empty and hence 2P orbital band is also empty. The energy gap between 2S band and 2P band is not much. Hence electron from 2S band can jump into 2P band easily. The Zone is known as semi conduction band.

v) The maximum number of electrons per band can be calculated depending upon the maximum number of electrons that can be present in a particular atomic orbital.

The molecular orbitals extend in three dimensions over all the atoms in the crystal. Hence electrons have a high degree of mobility which explains the high thermal and electrical conductivity of metals.

1.4.3 Conductors, Semi conductors and insulators :

In metallic conductors, the valence band is either partly filled or it overlaps the conduction bands. So there is no significant gap between filled and unfilled molecular orbitals. perturbation can occur readily. Metals are very good conductors and the conductivity decreases with rise in temperature. When an electric field is applied to a metal, the electron present in half filled energy band jumps into higher zone of the same band and hence conduction occurs in it.

Eg : metals

In insulators i.e. non metals. the valency band is completely filled. so perturbation with in the band is not possible. In other words. the electrons present in completely filled band do not have sufficient energy to cross the for bidden zone and jump into next higher energy band. Hence. insulators do not conduct electricity.

Eg : Most of the organic (excepts graphite) In semi conductors. the energy gap between adjuscent bands is sufficiently small for thermal energy, a small number of electrons are promoted from the completely filled valency band to the empty conduction band. Now, the unpaired electron left in the valency band can conduct electricity. Since the probability of promoting electron rises with temperature. the conductivity of semiconductors increases with rise in temperature. The electrical conductivity of a semi conductors is in between conductors and insulators. Semiconductors are those solids which are perfect insulators at absolute zero but conduct electric current at room temperature.

Eg : Silicon and Germanium semiconductors are of two types namely intrinsic semiconductors and extrinsic semi conductors. Intrinsic conduction can be introduced in the crystal with out adding any external substance. Intrinsic semi conductors are poor conductors at ordinary temperature but conduction increases with rise in temperature. Due to increase in temperature. the electron cross the for bidden zone and hence conductivity increases.

Eg : Silicon and Germanium.

When a small amount of impurity is added. extrinsic semiconductors are formed due to impurity defects. Addition of group 15 and group 13 elements to the crystal lattice of group 14 elements

Eg : Silicon or germanium produces n- type and P-type semi conductors. In n – type semiconductors the element. Eg : Arsenic added as impurity contain more valency electrons than the parent element i.e. Germanium and thus the extra electron can serve to conduct electricity. Hence germanium containing traces of arsenic known as arsenic doped germanium shows high electrical conductivity.

In P – type semi conductors. the element added as impurity E.g. boron has less valency electrons than the parent element. Eg : Germanium gives rise to electron. Vacancies known as positive holes and when electric field is applied, adjuscent electrons move into the positive holes. Thus doping of germanium with small traces of boron element increases the electric conductivity of germanium. Since. current is carried by positive holes, it is known as P – type conduction. Conductivity of semiconductors increases with rise in temperature.

Semiconductors are used in transistors and in exposure metals as photo electric devices. Combination of P- and n- type semiconductors known as P-n junction known as rectifier used for converting alternating current to direct current.

1.4.4 General methods involved in extraction of metals :

Metals occur in nature in two forms namely free state and combined state. Very few metals occur in nature in native form i.e. occur in the free or elementary state.

Eg : Gold, platinum, Silver, mercury etc.

Most of the metals occur in combined state. These metals occur in nature in the form of compounds like oxides, carbonates, halides, sulphides, sulphates etc.

Examples :

Oxides – Manganese as pyrolusite (MnO_2) Aluminium as bauxite ($Al_2O_3 . 2H_2O$) and iron as magnetite (Fe_3O_4).

Carbonates – zinc as calamine ($ZnCO_3$) ;Calcium as lime stone ($CaCO_3$); Magnesium as magnesite ($MgCO_3$).

Halides – Silver as horn silver (AgCl) ; Sodium as common salt (NaCl) ; Magnesium as carnallite ($KCl. MgCl_2 : 6H_2O$)

Sulphides – Lead as galena (Pbs) ; Zinc as Zinc blende (ZnS) ; Copper as Copper pyrites ($CuFeS_2$).

Sulphates – Calcium as gypsum ($CaSO_4. 2H_2O$) ; Magnesium as Epson salt ($MgSO_4.7H_2O$) etc.

The compounds of metals occur in the earth's crust along with a rocky and other impurities are called as minerals.

A mineral from which a metal can be profitably extracted is called an ore. In general, all ores are minerals but all minerals are not ores.

1.4.5 Metallurgy :

Extraction of metals from their ores ; the process is called metallurgy. In the extraction of metals in pure form from their ores, the following steps are carried out.

i) Concentration or dressing of the ore.

ii) Treatment of the concentrated ore.

iii) Purification of metal.

Concentration of the ore :

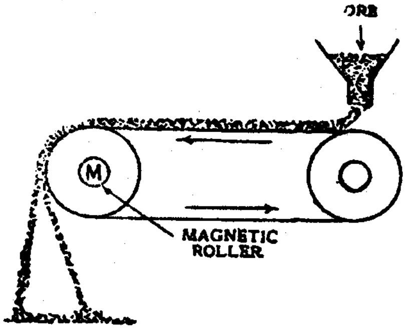
The ore or the metal in native form consists of several earthy impurities like sand, gravel etc. known as matrix or gangue. The removal of gangue from its ore is called ore dressing or concentration of the ore. The various methods used for concentration of the ore are as follows.

1) Hand Picking :

The ore can be separated from the main stock by simple hand picking and then removing the rocky material by breaking with a hammer.

2) Electromagnetic separation :

If the impurities present in the ore are magnetic in nature, they are separated by electromagnetic separation. The magnetic separator consists of a leather belt moving over two rollers, out of which one is magnetic. The powdered ore is dropped on the belt at one end and at the other end the magnetic impurity of the ore is attracted and falls nearer the magnetic roller in the form of a heap.



A Magnetic Separator

Ex : Ferromagnetic ores such as Fe_3O_4 ; tin stone an ore of tin containing wolframite $FeWO_4$ as a magnetic impurity.

3) Gravity separation :

The ore can be concentrated by considering the specific gravities of metallic ore and earthy impurities. The ore is washed with a running stream of water. The heavy ore particles settles down while the gangue is washed away. There are two methods of gravity separation.

i) Wilfley table :

The powdered ore is carried by a stream of water over wilfley table. It is a wooden table having a slanting floor on which long wooden strips called riffles are fixed. The powdered ore is washed with a stream of water on the slanting floor. The particles of the ore are obstructed by the riffles while the lighter particles of gangue are washed away.

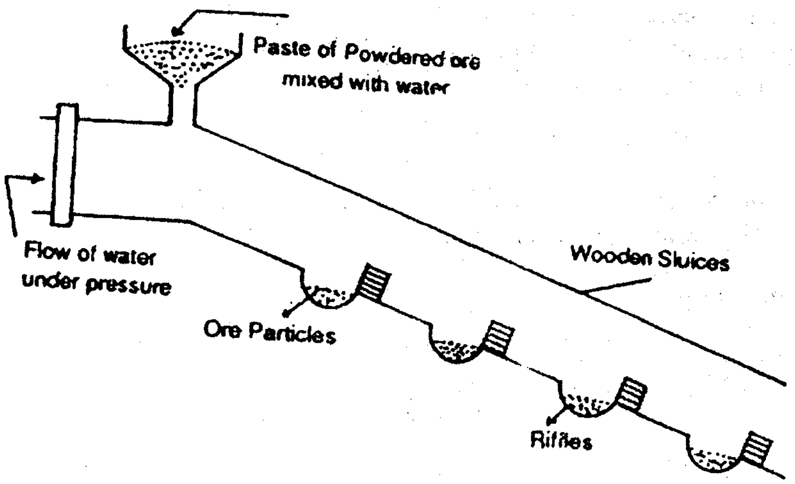


Fig :

The ore particles collected in the riffles move to one side as a result of rocking motion of the table and are collected

Ex a: oxides ore like haematite (Fe_2O_3) and tin stone (SnO_2)

ii) Hydraulic classifier method :

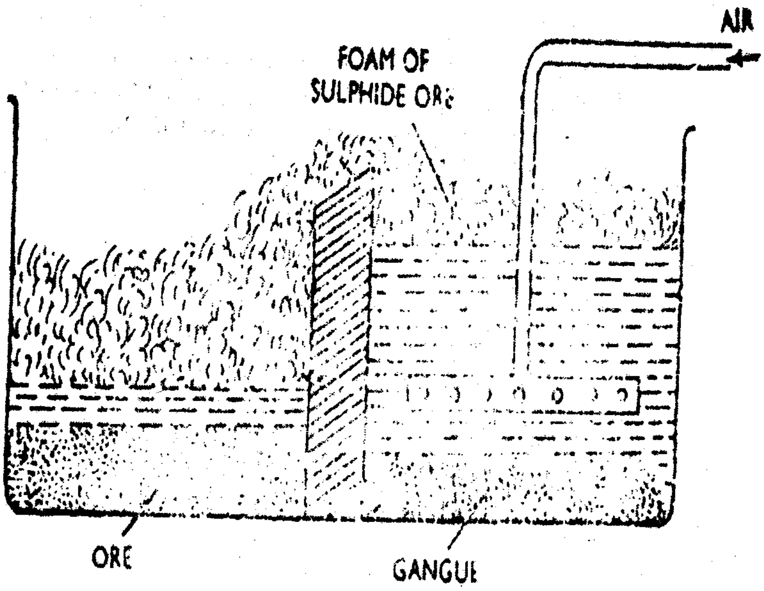
Finely powdered ore is taken in the conical reservoir called hydranlic classifier. A stream of water is allowed to flow from the bottom of the reservoir. The gangue particles are carried away by the water and the heavy ore settles at the apex of the cone.

4) Leaching method :

The powdered ore is treated with a suitable reagent which dissolves only the ore in it. Example. The ore of aluminium, bauxite contains iron oxide and silicates as impurities. Bauxite, when treated with a hot solution of NaOH at 150°c only Al_2O_3 dissolves, leaving the impurities.

5) Froth flotation process :

This method is used for the concentration of sulphide ores. The finely powdered ore is to be taken in a tank filled with water to which a small amount of pine oil or eualyplus oil is added, which acts as frothers. A small quantity of potassium ethyl X anthate coats the surface of ore particles is also added. The whole mass is agitated violently with air, when froth is formed.



Froth flotation process

The ore particles get preferentially wetted by the oil while the gangue is wetted by water. The oil rises to the top along with froth, leaving the gangue behind. The froth, overflows into another tank where the ore settles after some time.

Examples : Sulphide ores of lead, Zinc, Copper etc are concentrated by this method.

1.4.6 Treatment of the concentrated ore :

Calcination :

It is the process of heating the ore strongly in the absence of air without melting it. The organic matter, volatile impurities and moisture are expelled and thus the remaining mass becomes porous. Calcination is also used to remove water from hydrated oxide or carbon dioxide from a carbonate ore.

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
Calamine

$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$
Bauxite

$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$

Magnesite

Calcination is generally done in a reverberatory furnace.

Roasting :

It is a process of heating the ore strongly below its melting point in the presence of air in order to bring about its oxidation. Organic matter, volatile impurities. are removed. Non metallic impurities like s, As etc are oxidized and removed as oxides. The process is generally used in the case of sulphide ores and is carried out in a reverberatory furnace or in a blast furnace.

$$2Zns + 3O_2 \longrightarrow 2ZnO + 2SO_2\uparrow$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2\,CuFeS_2 + 3O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

1.4.7 Reduction of Oxide to the metal :

The calcined or roasted ore is then reduced to metal using various types of reducing agents depending upon the nature of the ore.

1) Smelting :

It is the process in which the oxides of metals like Zn, Pb, Fe etc. when mixed with carbon are reduced to metals by heating to a higher temperature in the presence of a flux. The flux reacts with the impurities (gangue) to from easily fusible slag.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Lime stone decomposes to give calcium oxide which combines with silica to form calcium silicate.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow Ca\,SiO_3$$

Smelting is generally carried out in a blast furnace or a reverberatory furnace.

Flux :

The ore even after concentration, contain some gangue (earthy matter as impurity) which is to be removed. There are certain substances which when mixed with furnace charge and heated, combine with gangue to form a fusible material insoluble in the molten metal. Such a substance is called as flux. The type of flux used depends upon the nature of the impurity to be removed.

i) **Acidic flux** : it is used when the gangue is basic i.e. impurities like CaO and other metallic oxides. Eg : Silica : borax etc.

$$\underset{\text{Gangue}}{Ca\,O} + \underset{\text{Flux}}{Si\,O_2} \longrightarrow \underset{\text{slag.}}{Ca\,SiO_3}$$

ii) **Basic flux :** Eg : lime stone, magnesite, haematite etc. These basic fluxes are used when the gangue is acidic impurities like silica and silicates.

$$SiO_2 + MgCO_3 \rightarrow MgSiO_3$$

Gangue Flux slag.

Auto - reduction or self reduction :

In some cases, no reducing agent is required. The sulphides of less active metals like Hg ; Cu and Pb are unstable to heat. A part of the sulphide ore is converted to the oxide which then reacts with the remaining part to give the metal and SO_2.

Eg : Copper

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

In Some cases the ore is converted into metallic state during roasting.

Eg : Mercury

$$HgS + O_2 \rightarrow Hg + SO_2$$

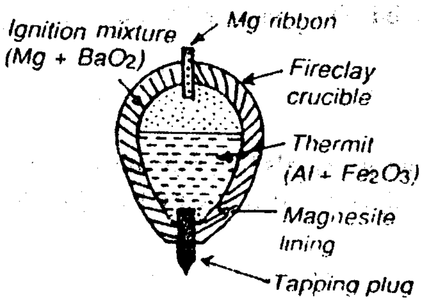
Aluminothermic reduction:

Glodschmidts aluminothermic process:

Oxides of metals like chromium, manganese, iron which cannot be easily reduced with carbon are **reduced with aluminium** powder which acts as reducing agent. The charge consists of a mixture of the **metallic oxide,** and aluminium powder known as thermite is taken in a steel crucible and covered with an **ignition mixture** of magnesium powder and barium peroxide. The charge is ignited by a magnesium **ribbon. The reaction** is highly exothermic and the heat produced is sufficient to melt the metal. The **process is used** in thermite welding.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + Heat$$

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr + Heat$$



Goldsmidt's Process

Hydro metallurgy or Precipitation :

This method is based on the fact that more electropositive metal displaces the less electro positive metal from its salt solution. The ore is dissolved in a suitable solvent and then the metal is precipitated by adding a more electropositive metal. Thus argentite Ag_2S. silver ore is dissolved in sodium cyanide to give a complex salt from which silver is obtained by adding zinc.

$$Ag_2S + 4\,NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

Sodium argento cyanide

$$2Na[Ag(CN)_2] + Zn \rightleftharpoons 2Ag + Na_2[Zn(CN)_4]$$

Electrolytic reduction :

Highly electropositive metals like Na. K. Ca. Al etc are extracted by electrolysis of their oxides, hydroxides or chlorides in fused state.

Eg : Aluminium is obtained by the electrolysis of alumina mixed with cryolite.

$$2\,Al_2O_3 \rightarrow 4Al + 3O_2$$

Reducation of halides : $TiCl_4 + 2Mg \xrightarrow{750^\circ} Ti + 2MgCl_2$

H_2; co, water gas (H_2 + Co) etc are also used as reducing agents and extract metals from their oxides.

Examples : $Fe_2O_3 + 3\,Co \xrightarrow{400^\circ c} 2Fe + 3\,Co_2$

$WO_3 + 3H_2 \xrightarrow{850^\circ c} W + 3\,H_2o$

$Ni\,O + H_2 \rightarrow Ni + H_2o$

$Ni\,O + Co \rightarrow Ni + CO_2$

1.4.8 Refining or purification of impure metals :

i) Liquation :

This method is used for easily fusible metals like tin and lead. The impure metal is placed on the sloping hearth of a reverberatory furnace and heated. The metal melts and flows down leaving the infusible impurities called dross.

Distillation :

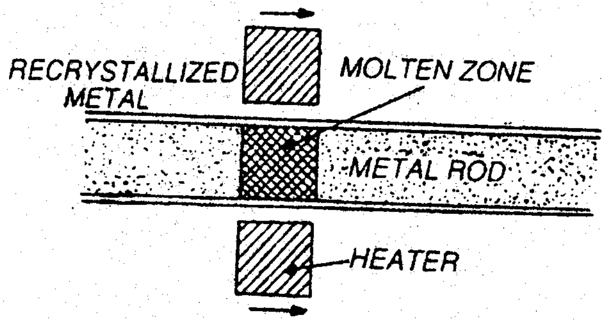
This method is used for the refining of volatile metals like zinc, mercury etc. The impure metal is heated in a retort and the vapours of metal are collected and condensed separately. Thus the non volatile impurities are left behind in the retort.

Zone refining :

The method is based on the fact, that when a molten solution of impure metal is solidified, the pure metal crystallizes leaving behind the impurities in the melt. Zone refining process is used to get metals of high purity.

A circular heater is fitted around a rod of impure metal and slowly moved along the rod. At the heated zone, the rod melts. As the heater moves along, pure metal crystallizes out of the rod melt while the impurities are carried away in the molten zone to one end of the rod.

Ex : Ge, Si and Ga used as semiconductors are refined by this method.



Zone Refining

Oxidative processes :

Oxidation process is used for refining when the impurities present have a great affinity for oxygen and are oxidized more readily than the metal. The oxides which are formed, removed from the surface by skimming. Sometimes the oxide of the metal itself is added which supplies oxygen to the impurities. Thus copper oxide is added to impure molten copper which supplies oxygen for the oxidation of the impurities.

Cupellation :

The impurity of lead in silver is removed by heating it in a cupel, a boat shaped crucible made of bone ash under a blast of air. Lead is oxidized to litharge, PbO and is carried away by air, leaving pure silver behind.

Bessemerisation :

i) Molten matte ($Cu_2S + FeS$) is transferred to a bessemmer converter which is a pear – shaped furnace and provided with a basic lining of lime or magnesia. It is mounted on trunnions and can be tilted in any position. It is fitted with tuyers through which sand and hot air is blown.

$$3FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

The molten metal is poured off. The copper produced is of 98% pure and is known as blister copper.

ii) Molten cast iron from blast furnace is taken in a bessemmer converter and the impurities are oxidized by a blast of air.

Puddling :

Steel was made by puddling which involved mixing molten pig iron with haematite, Fe_3O_4 and burning of all the carbon and other impurities to give wrought iron which is soft and malleable. Now wrought iron can be converted into steel by adding the required amount of carbon or other metals to give the type of steel required.

Poling :

The impure molten metal is stirred with green wood poles. The impurities come to the surface and get oxidised. Hydrocarbons from wood reduce the oxide of the metal to metallic state.

Eg : Copper and tin are purified by this method.

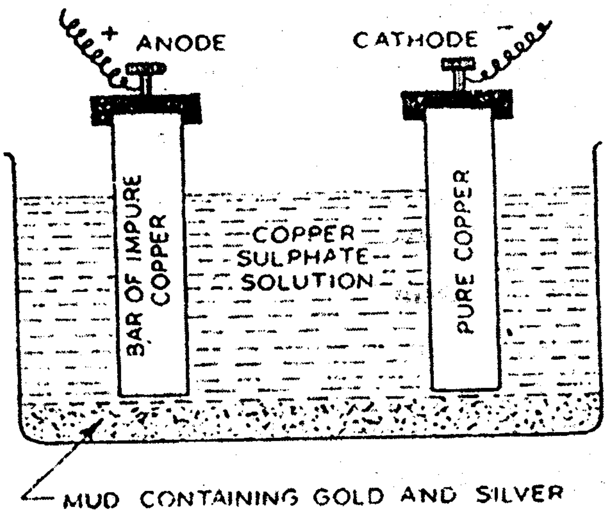
$$3Cu_2O + CH_4 \rightarrow 6Cu + CO + 2H_2O$$

Amalgamation:

This process is used for the extraction of noble metals like gold and silver from the native ores. The finely crushed ore is treated with mercury which takes up the metal forming an amalgam. The metal is then recovered by distilling the amalgam.

Electrolysis :

Here, the impure metal in the form of blocks is made the anode and a thin plate of pure metal acts as the cathode. The electrolyte is a solution of a soluble salt of the metal. On passing current, the pure metal passes from the anode to the cathode through the electrolyte and gets deposited while the impurities settle near the anode as anode mud. This method is used for the refining of copper, silver, gold, lead etc.



Electrolytic Refining

1.4.9 Alloys :

An alloy is a homogeneous mixture of two or more metals. Alloys can be prepared by mixing a metal with a non metal also. So an alloy can be defined as a metallic intimately mixed solid mixture of two or more different elements, atleast one of which is a metal. Alloys are homogenous in molten state but in solid state they may be either homogeneous or heterogenous. Chemically alloys may be mixtures or solid solutions of constituents in one another. When one of the metals is mercury, the alloy is called an amalgam.

Eg : Copper amalgam is an alloy of copper and mercury. Sodium amalgam is an alloy of sodium and mercury. In alloys, the chemical properties of the component elements are retained and only certain physical properties are improved, alloys are usually harder and less malleable and ductile than their constituents, have lower melting point and resists corrosion and is stable to acids.

1.4.10 Purpose of making alloys :

The purpose of making alloys is to develop some new property not possessed by the components individually.

i) To increase the hardness of the metal. Pure metals are generally soft while the alloys are harder. E.g : Copper increases the hardness of silver in coins. Gold is mixed with copper in making ornaments. 0.5% Arsenic is added to lead to make very strong lead bullets.

ii) To lower the melting point. In general, the alloy possess lower melting point than the original metals. For example : the wood's metal is an alloy of bismuth, lead; cadmium and tin has a melting point of only 71°c which is much lower than the melting point of any of the metals present in the alloy.

iii) To increase the tensile strength. Alloys, have greater tensile strength than the metals present in it. For example, addition of 1% carbon increases the tensile strength of pure iron by 10 times.

iv) To get good casting. Expansion of metal on solidification is the most important requirement for its use as casting material. For example, Type metal (alloy of lead and antimony) ; bronze (alloy of copper and tin) have good casting properties.

v) To modify colour. Aluminium bronze which has 90% copper and 10% aluminium has a golden colour.

vi) To resist corrosion. Pure metals are reactive and hence easily corroded by atmospheric gases, moisture etc. But alloys are more resistant to corrosion. For example stainless steel is more resistant to corrosion while iron is corroded easily even by moisture.

1.4.11 Substitutional solid solutions :

Substitutional solid solutions are those in which some of the atoms of a metal M are replaced by the atoms of another metal M^1 to form an alloy of type MM^1. In other words, when two metals are completely miscible with each other, they can form a continuous range of solid solutions.

Ex : Cu/ Au ; Cu/ Ni ; K/Rb ; K/Cs etc.

These are of two types namely random and ordered super lattice or Substitutional solid solution. For example, in the case of alloy of copper and gold, at temperatures above 450°c the alloy exists as a random or disordered structure but on slow cooling it leads to the formation the more ordered super lattice structure. Hume – rothery has shown the following three rules for the formation of ordered Substitutional alloys i.e.

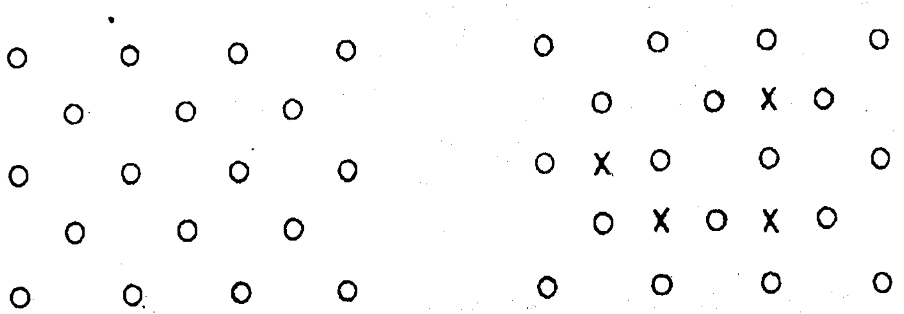
i) The two metals should be similar in size i.e. their metallic radii should not differ by more than 14 – 15%

ii) Both the metals must have the same crystal structure.

iii) The chemical properties of the two metals must be similar. Their number of valency electrons should be same.

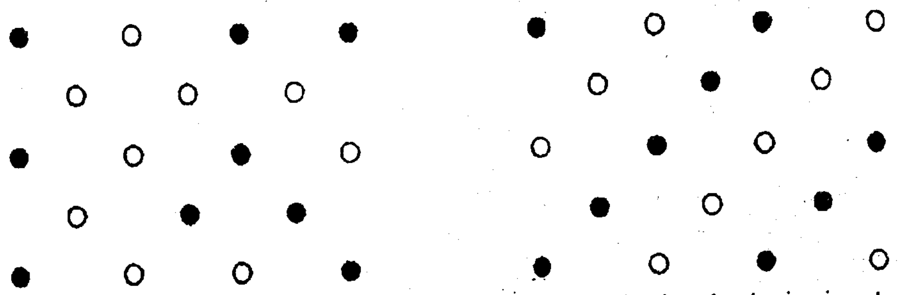
Ex : Copper and gold alloy :

Here, the metallic radii of Cu and Au differ by only 12.5% ; both have cubic close packed structures and also have similar properties since they belong to the same group in the periodic table.



(a) pure metal lattice

(b) interstitial alloy (X atoms occupy interstitial positions)



(c) random substitutional alloy

(d) superlattice (ordered substitutional alloy)

Fig : Metal and alloy structures

If only one or two rules are satisfied, then random Substitutional solid solutions will only form at the two extremes of composition.

Eg : Alloy of sodium and potassium. The two metals. Na and K are structurally and chemically similar but they differ in their metallic radii by 23.7% and hence. It is an example for random Substitutional solid solutions.

1.4.12 Interstecial alloys :

Many metals have a close packed lattice structure with many tetra hedral and octahedral holes or interstices. When a lighter non metallic element is added to a metal. The non metallic atoms can be accommodated in these holes or interstecial positions without changing the structure of the metal. Transition metals with non metallic elements like hydrogen, boron, carbon, and nitrogen will form interstecial alloys. For formation of interstecial alloy, the radius ratio of the smaller atom to larger atom should be in the range of 0.414 – o.732. The chemical composition of these interstecial alloys may vary over a wide range depending on how many holes are occupied. Thus hydrides; borides, carbides and nitrides of the transition elements are examples of interstecial alloys. Interstecial borides, carbides and nitrides are extremely hard, chemically inert and have high melting points. Interstecial carbides of iron are of great importance in the various forms of steel.

1.4.13 Intermetallic compounds :

When two metals form a continuous range of solid solutions one or more intermediate phases having different structure from that of metals may be formed. These phases which have different structure when compared to the original metals are known as intermetallic compounds. These are not true compounds and have variable composition. In an intermetallic compound, the two elements combine in stoichiometric proportions and they have different number of valency electrons.

Eg : Cu5 Sn : Cu_{31} : Sn_8 ; Fe_3 C etc.

The intermetallic compounds possess many of the characteristic properties of metals. The atom of one metal replaces those of another in the crystal lattice. The intermetallic compounds are usually formed between atoms of elements that possess low electron affinities.

The inter metallic compounds of Cu and Zn have three phases with different composition and structure Phase

CuZn - 45.5%Zn - β
Cu_5Zn_8 - 60.65%Zn - γ
$CuZn_3$ - 82.88%Zn - ϵ

β - Phase has body centred cubic structure : γ - phase has cubuic structure and ϵ - phase has hexagonal close packed structure.

Hume - Rothery Rules :

Each phase can be represented by a typical composition or ideal formula even though it exists over a wide range of composition. Hume – Rothery studied the compositions of the phases formed and found that the β – phase always occurs in alloys when the ratio of the sum of the valency electrons to the number of atoms is 3:2. So, according to Hume – Rothery, the ratio of the total number of valency electrons to the number of atoms is constant. Thus, the ratio 3:2 indicates β – Phase 21 :13 γ - Phase and 7:4 ϵ – Phase

Table 4.1

Examples	Valence electrons	No. of atoms	Ratio	
CuZn	$1+2=3$	2	3 : 2	β-structure
Cu_5Sn	$5+4=9$	6	3 : 2	
AgZn	$1+2=3$	2	3 : 2	
Cu_3Al	$3+3=6$	4	3 : 2	
AuCd	$1+2=3$	2	3 : 2	
$CoZn_3$	$0+6=6$	4	3 : 2	
Cu_5Zn_8	$5+16=21$	13	21 : 13	γ-structure
Cu_9Al_4	$9+12=21$	13	21 : 13	
$Cu_{31}Sn_8$	$31+32=63$	39	21 : 13	
Au_5Cd_8	$5+16=21$	13	21 : 13	
Co_5Cd_{21}	$0+42=42$	26	21 : 13	
$CuZn_3$	$1+6=7$	4	7 : 4	ε-structure
$AgCd_3$	$1+6=7$	4	7 : 4	
Au_3Sn	$3+4=7$	4	7 : 4	
Cu_3Sn	$3+4=7$	4	7 : 4	
$AuCd_3$	$1+6=7$	4	7 : 4	
$FeZn_7$	$0+14=14$	8	7 : 4	

The explanation of why similar binary metallic phases are formed at similar valency electron to atom ratios is not fully understood.

1.4.14 Preparation of alloys :

1) Fusion method :

By melting together the metals in big fire clay crucible. The molten mass is thoroughly stirred with a graphite rod in order to bring uniform mixing. The surface of the molten mass is covered with a layer of powdered carbon to avoid oxidation of the component metals. The molten mass is cooled slowly to get solid alloy. Brass and bronze alloys are prepared by this method.

2) Electro deposition :

The method involves the simultaneous deposition of different metals from their salt solution mixture.(acts as electrolyte) by passing electricity.

Eg : Brass is obtained by the electrolysis of a mixed solution of copper and zinc cyanides dissolved in sodium cyanide.

Reduction :

In this method, there is the reduction of oxide of one of the constituent metals by the other metal of the alloy. For example aluminium bronze is obtained by reducing alumina in the presence of copper in electric furnace.

Compression method :

In this method, metals are taken in proportions and are then compressed together under pressure.

Ex : wood's metal, soldier (tin and lead)

By Chemical method :

Ferrochrome, an alloy of iron and chromium is obtained by heating FeO Cr_2O_3 with powdered aluminium or carbon.

$$3\,(FeO.Cr_2O_3) + 8Al \longrightarrow \underset{\text{Ferrochrome}}{3Fe + 6Cr} + 4Al_2O_3$$

$$FeO.Cr_2O_3 + 4C \longrightarrow \underset{\text{Ferrochrome}}{Fe + 2Cr} + 4CO$$

1.4.15 Uses – Ferrous and non- ferrous alloys :

To study the applications; alloys are classified according to their components into two types namely ferrous and non – ferrous alloys.

Ferrous alloys :

Ferrous alloys contain iron as the major constituent. They are often known as steels.

The main purpose of adding carbon, manganese, copper, vanadium, cobalt, silicon etc in traces to iron, in making ferrous alloys is to improve tenacity, ductility, hardness, corrosion, resistance acid and chemical resistance etc.

In addition to iron and carbon steels always posses another element basing on which, steels are classified into vanadium steels having vanadium, chromium steels containing chromium etc.

Vanadium steels are used in high pressure boilers, locomotive parts, gears etc. chromium steels are used in ball bearings, surgical instruments etc. Manganese steels are used for railway points and across – over and for helmets.

Cobalt steels are used in high speed tool steels.

Nickel steels are used for gears, transmission parts etc.

Tungsten and molybolenum steels are used in the manufacture of high - speed cutting or drilling tools.

Non - ferrous alloys :

These alloys do not contain iron as one of the constituents. These alloys usually contain aluminium, copper, zinc, tin and nickel. Some important alloys are given below.

Non – ferrous alloys usually contain aluminium : copper : zinc ; tin and nickel. Some important alloys are given below.

	Alloy	Composition	Uses
1.	Duralumin	95% Al; 4% cu; 0.5% Mn and 0.5 % Mg	Used in making aeroplane bodies, automobile parts etc
2.	Y-alloy	4% Cu; 1.5% Mg; 2% Ni; 0.5% Si; 0.5% Mn: 0.5% Fe and the remaining is Al.	Pistons; Cylinder heads etc
3.	Magnalumin	70% Al and 30% Mg	cheap balance
4.	Election	9 to 11 % Mn and the remaining is Mg	For Constructionof oil tankers, petrol bunkers etc
5.	Bronze or Franch golet	90% Cu: 10% Zinc	Costure fewellery
6.	Dutch metal	80% Cu. 20% Zn	Musical instruments, battery caps etc.
7.	German Silver	50% Cu, 20% Zn, 30%Ni	Utensils, Ornaments, Coins etc
8.	Gun metal	88% Cu; 10% Sn; 2% Zn	Guns

1.4.16 Model Questions :

1. Mention the various theories of bonding in metals and explain the free electron theory.
2. On the basis of valency bond theory how would you explain the following properties of metals ?
   a) metallic lustre
   b) Electrical conductivity
   c) Thermal conductivity and
   d) Malleability and ductility.

3) What are semi conductors ? What is meant by n – type and p –type semi conduction ? What is the effect of temperature on semi conduction ?

4) Explain the difference between conductors, insulators and semiconductors. Give examples.

5) What is meant by the term metallurgy ? Describe the various methods used for concentration of the ore.

6) Describe the various methods employed in the refining of metals.

7) Explain the following terms with suitable examples.
   a) Calcination
   b) Roasting
   c) Smelting

8) Describe the following processes –
   a) Electromagnetic separation
   b) Froth floatation process
   c) Liquation

9) Differentiate between
   a) gangue and flux
   b) calcination and roasting
   c) alloy and amalgam.

10) What are alloys ? How are they classified ? What are their advantages ?

11) Write notes on Substitutional solid solution and interstitial solid solutions.

12) What are intermetallic compounds. Give examples.

13) What are alloys ? How are they prepared ?

14) Explain Hume – Rothery rule with suitable examples.

15) What are Hume – Rothery rules ? Discuss the importance of Hume – Rothery rules in explaining the composition of $CuZn$; Cu_5Zn_8 and $CuZn_3$ alloys.

16) Discuss the difference between ferrous and non ferrous alloys. Give two examples each, with composition.

17) What are ferrous and non ferrous alloys ? Give the composition of german silver ; gun metal ; bronze and electron .

18) Define the term flux. How are they classified ? Give examples.

19) Define the terms gangue ; flux and slag. Give examples.

20) Write notes on
   a) Auto reduction
   b) Cupellation
   c) Tamman rules.

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UNIT-I

Lesson-V

NON-AQUEOUS SOLVENTS

1.5.1 Water was regarded as a universal solvent for ionic reactions. Considering the following factors –

i) Its plentiful occurrence in nature.

ii) Its ability to dissolve a large number of inorganic and organic compounds.

iii) Its non – Poisonous nature and its wide range of physical and chemical characteristics. Inspite of its many desirable properties there are instances where a non aqueous medium can serve certain needs that an aqueous one can not. Although work on solvent other than water started in 1892, it was Cady in 1897 and Franklin and Kraus in 1899 discovered ammonia as the first non aqueous solvent having similarity in reactions with water. Walden in 1899 used sulphur dioxide as the non aqueous solvent. The differences between water and other solvents are in general, only differences in degree and they can usually be correlated with solvent parameters such as dielectric constant, coordinating ability of the solvent, melting and boiling points.

1.5.2 Classification of solvents :

Classification of solvents are frequently based on acid – base properties. One of the simplest classification of solvents is in terms of polarity. Solvents can be classified into different classes. It is generally found, that the manner of classification will depend on the particular solvent properties of interest.

a) Protonic and non protonic solvents :

Solvents which contain hydrogen and releases a solvated proton on auto ionisation or self ionisation are known as protonic solvents.

Eg : H_2O ; NH_3 ; HF ; HCN and low molecular weight alcohols. The solvents which do not release hydrogen are called non protonic or aprotic solvents

Eg : CCl_4 ; C_6H_6 ; SO_2 etc.

b) Acidic (Protogenic) ; basic, amphiprotic and aprotic solvents :

Solvents which have a strong tendency to donate protons are known as acidic solvents.

Eg : H_2SO_4 ; HF; glacial acetic acid etc.

Solvents which have a strong affinity for protons are known as basic solvents.

Eg : liquid ammonia ; Pyridine ; ethylene diammine etc.

Solvents which can act either as acids or bases are known as amphoteric solvents

Eg : H_2O and low molecular weight alcohols.

Solvents which are inert to proton transfer i.e. have no tendency to lose or gain protons.

Eg : CCl_4 ; C_6H_6 etc.

C) Ionising and non – ionising solvents :

Solvents which undergo antoionisation are known as ionizing solvents. They posses high dielectric constant.

Eg : H_2O ; NH_3 ; HF ; SO_2 etc.

Solvents which have low dielectric constant and do not undergo auto ionisation are known as non ionizing solvents.

Eg : CCl_4 ; C_6H_6 etc.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + \bar{O}H$$

1.5.3 Reactions in liquid ammonia :

Liquid ammonia has been studied more extensively than any other non aqueous solvents. It is a g solvent for many types of organic and inorganic synthesis. Its physical properties resemble those of w. except in having a low dielectric constant (22) which results in its decreased ability to dissolve ionic compo like carbonates, sulphates etc. but ammonia may be a better solvent than water towards non polar molec The physical properties of liquid ammonia are a follows –

Boiling point	-33°c
Freezing point	-78°c
Dielectric Constant	22
Dipolemoment	1.47D
Viscocity	0.00265 dyne-sec/cm^2
Ionic product	1.9×10^{-33} (- 50°c)

Just like pure water, pure liquid ammonia is also a poor conductor of electricity.

1.5.4 Auto - ionisation or self ionisation :

Liquid ammonia undergoes auto ionisation in a similar way like that of water.

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + N\bar{H}_2$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Substances that produce NH_4^+ ions in liquid ammonia are acids and substances that produce $N\bar{H}_2$ ions are called as bases. Thus in liquid ammonia, NH_4^+ ion behaves as an acid eg : NH_4Cl. And metallic amides eg : KNH_2; imides and nitrides behave as bases.

1.5.5 Solubility of substances in liquid ammonia :

Salts containing highly polarisable anions are more soluble. Covalent organic compounds are more soluble in liquid ammonia than in water. Ammonia has the ability to dissolve free metals which are strong reducing agents without any chemical reaction. For eg- liquid ammonia dissolves the alkali metals to give blue solutions which are characterised by its colour, density, conductivity and Para magnetism. The blue colour of the alkali metals in liquid ammonia is due to the presence of free electrons. In dilute solution, alkali metals dissociate to form alkali metal cations and solvated electrons.

$$M \xrightarrow{\text{liquid ammonia}} M^+ + [e\,(NH_3)\,x\,]^-$$

This dissociation into cation and anion accounts for the electrical conductivity. Alkaline earth metals i.e. calcium, strontium and barium, aluminum, zinc, lanthanum, cerium etc are also soluble in liquid ammonia. The solutions of metals in liquid ammonia are very good reducing agents because of the presence of free electrons. When alkali metal solution in liquid ammonia is evaporated, the free metal is recovered.

The solubilities of inorganic salts in liquid ammonia are different from their solubilities in water. In organic compounds containing anions i.e. iodide, nitrate, perchloride cyanide and thiocyanate are soluble in liquid ammonia.

1.5.6 Precipitation reactions :

Several precipitation reactions which take place in aqueous solutions also occur in ammonia solutions.

Eg : Ammonium sulphide dissolved in liquid ammonia when added to the nitrate solution of metals like Cu ; Cd ; Bi ; Co ; Zn etc precipitates the metallic sulphides.

$$(NH_4)_2S + Cu\,(NO_3)_2 \rightarrow 2NH_4NO_3 + Cu_2\,S\downarrow$$

Most of the chlorides are insoluble in liquid ammonia and can be precipitated out.

$$Ba\,(NO_3)_2 + 2\,AgCl \rightarrow 2AgNO_3 + BaCl_2\downarrow$$

$$AgCl + KNO_3 \rightarrow KCl\downarrow + AgNO_3$$

1.5.7 Acid – base reactions or neutralization reactions :

The process of neutralisation in liquid ammonia involves the combination of NH_4^+ and $N\bar{H}_2$ to form unionised ammonia.

$$NH_4Cl + KNH_2 \rightarrow KCl + 2NH_3$$

$$NH_4Cl \rightarrow NH_4^+ + \bar{Cl}$$

$$KNH_2 \rightarrow K^+ + N\bar{H}_2$$

$$NH_4^+ + N\bar{H}_2 \rightarrow 2NH_3 \text{ (Neutralisation)}$$

NH_4Cl known as an ammono acid is a strong acid and KNH_2 known as ammono base in liquid ammonia solution. Thus ammono acid is a substance which produces NH_4^+ ions in liquid ammonia and an ammono base is a substance which produces $N\bar{H}_2$ ions in liquid ammonia solution.

1.5.8 Solvolysis or ammonolysis reactions :

Ammonolysis is similar to hydrolysis reaction. Metal hydrides : oxides : inorganic and organic halides are ammonolysed.

$$MH + NH_3 \rightarrow \underset{\text{metal amide}}{MNH_2} + H_2$$

$$M_2O + 2NH_3 \rightarrow 2MNH_2 + H_2O$$

$$BCl_3 + 6NH_3 \rightarrow B(NH_2)_3 + 3\ NH_4X$$

$$Cl_2 + 2NH_3 \rightarrow NH_2Cl + NH_4^+ + \bar{Cl}$$

$$RX + NH_3 \rightarrow RNH_2 + NH_4X$$

$$RX + RNH_2 \rightarrow R_2NH + NH_4X$$

$$RX + R_2NH \rightarrow R_3N + NH_4X$$

1.5.9 Ammoniation or solvation reactions :

The attachment of solvent molecules to a soluble substance is called ammoniation or solvation.

$$BF_3 + NH_3 \rightarrow BF_3.NH_3$$

$$Si\ F_4 + 2NH_3 \rightarrow Si\ F_4 . 2NH_3$$

1.5.10 Complex formation :

Certain complex formation reactions take place in liquid ammonia which are similar to those occurring in water.

Example – Formation of potassium argento cyanide when excess of potassium cyanide is added to silver nitrate solution in liquid ammonia.

$$AgNO_3 + KCN \rightarrow AgCN\downarrow + KNO_3$$

$$AgCN + KCN \rightarrow K[Ag(CN)_2]$$

$$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^-$$

Ammonozincates formed by the addtion of excess of potassium amide to zinc nitrate.

$$Zn(NO_3)_2 + 2KNH_2 \rightarrow Zn(NH_2)_2\downarrow + 2KNO_3$$

$$Zn(NH_2)_2 + 2KNH_2 \rightarrow K_2[Zn(NH_2)_4]$$

1.5.11 Reactions in hydrogen fluoride :

Anhydrons hydrogen fluoride is an strong acidic solvent. has low conductance a high dielectric constant (84) ; a high dipolemoment (1.9D) and a strong tendency to under go association.

Solubility of substances in liquid HF :

It dissolves HNO_3 ; H_2O ; KF, Several organic compounds. All these substances accept proton from HF and hence act as bases.

$$H_2O + HF \rightleftharpoons H_3O^+ + F^-$$

$$HNO_3 + HF \rightleftharpoons H_2NO_3^+ + F^-$$

$$(C_2H_5)_2O + HF \rightleftharpoons (C_2H_5)_2O^+H + F^-$$

$$CH_3COOH + HF \rightleftharpoons CH_3COO^+H_2 + F^-$$

Certain metallic salts i.e. perchlorates, iodates ; periodates etc dissolve and undergo dissociation.

$$KClO_4 \rightleftharpoons K^+ + ClO_4^-$$

Some non metallic fluorides dissolve in HF to give acid solutions.

$$BF_3 + HF \rightleftharpoons BF_4^- + H^+$$

$$AsF_5 + HF \rightleftharpoons AsF_6^- + H^+$$

Alkalimetal chlorides ; bromides ; cyanides etc dissolve in HF to give free acids.

$$NaCl + HF \rightarrow Na^+ + F^- + HCl\uparrow$$

1.5.12 Auto ionisation of HF :

HF undergoes auto ionisation to give fluoronium ion and fluoride ion.

$$HF + HF \rightarrow H_2F^+ + F^-$$

Any substance that gives H_2F ions in HF will act as an acid while those giving F^- ions will act as base.

Acids like HNO_3 ; H_2SO_4 behave like bases in HF.

$$\underset{\text{base}}{HNO_3} + HF_{(liq)} \rightarrow H_2NO_3^+ + F^-$$

$HClO_4$, the strongest acid in aqueous solution behaves as an amphoteric substance in liquid HF.

$$HClO_4 + HF \rightarrow H_2ClO_4^- + F^-$$

$$HClO_4 + HF \rightarrow ClO_4^- + H_2F^+$$

Certain electron deficient fluorides behave as acids in liquid HF.

$$BF_3 + 2HF \rightleftharpoons H_2F^+ + BF_4^-$$

1.5.13 Precipitation Reactions :

A number of compounds have been precipitated in presence of liquid HF.

$$AgF + HCl \rightleftharpoons AgCl\downarrow + HF$$

$$AgF + HBr \rightleftharpoons AgBr\downarrow + HF$$

$$2AgF + Na_2SO_4 \rightleftharpoons Ag_2SO_4\downarrow + 2NaF$$

Protonation reactions :

Nitric acid and nitrates dissolve in HF.

$$HNO_3 + HF \rightleftharpoons H_2NO_3^+ + F^-$$

$$NaNO_3 + 4HF \rightleftharpoons Na^+ + H_2NO_3^+ + HF_2^-$$

Oxides and hydroxides react with liquid HF.

$$H_2O + 2HF \rightleftharpoons H_3O^+ + HF_2^-$$

1.5.14 Model Questions :

1. Define solvent. Give the characteristics of a solvent. How do you classify the solvents. Explain with examples.
2. What is meant by auto ionisation ? Explain ammono acids and ammono bases with examples.
3. Discuss the precipitation and neutralisation reactions taking place in liquid ammonia.
4. What is meant by the terms Solvolysis and Solvation ? Give examples.
5. Discuss the solutions of metals in ammonia and complex formation reaction.
6. Explain the auto – ionisation reaction taking place in HF. Discuss precipitation reactions in HF.

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UNIT – II ORGANIC CHEMISTRY

Lesson – I

HALOGEN COMPOUNDS

2.1.1 Nomenclature and classification of alkyl (Primary, Secondary, Tertiary), aryl, aralkyl, allyl, vinyl, benzyl. Chemical reactivity – reduction, formation of RMgX, Nucleophilic substitution reaction – Classification into SN^1 and SN^2, mechanism of energy profile diagrams of SN^1 and SN^2 reactions, Stereochemistry of SN^2 (Walden inversion), SN^1 (recemisation) explanation of both by taking examples of optically active halide-2-bromobutane. Structure and reactivity – ease of hydrolysis – Comparison of allyl, benzyl, alkyl, vinyl and aryl halides.

2.1.2 Classification :

The compounds in which hydrogen atoms of hydrocarbons are replaced by halogen atoms are called halogen compounds.

Halogen compounds are classified as mono, di, tri or tetra depending up on the number of hydrogen atoms replaced by halogen atoms.

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Mono halogen derivative	dihalogen derivative	trihalogen derivative	tetrahalogen derivative

2.1.2.1 Alkyl halides :

Compounds of alkanes are known as alkylhalides.

$$\underset{\text{Alkane}}{R-H} \xrightarrow{X_2} \underset{\text{Alkylhalide}}{R-X} + HX$$

These are further classified as primary, secondary and tertiary alkyl halides based on the nature of carbon atom containing halogen atom.

P - halides :

In primary halides the halogen atom is attached to the primary carbon atom.

Ex: CH_3Cl Methyl chloride CH_3CH_2Cl Ethyl chloride

S- halides :

In Secondary halides the halogen atom is attached to the secondary carbon atom.

Ex : $(CH_3)_2CHCl$
Isopropyl chloride

T – halides :

In tertiary halides the halogen atom is attached to the tertiary carbon atom.

Ex : $(CH_3)_3CCl$
T –butyl chloride

2.1.2.2

Alkenyl halides :

Halogen compounds of alkenes are known as alkenyl halides.

$$\underset{\text{Alkane}}{CH_2 = CH_2} \xrightarrow{X_2} \underset{\text{Alkenylhalide}}{CH_2 = CH X + HX}$$

Vinyl halides :

In vinyl halides halogen atom and double bond are on the same carbon.

$CH_2 = CH - Cl$
Vinyl chloride

Allyl halides :

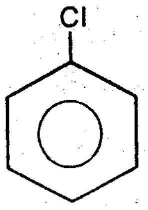
In allyl halides halogen atom and double bond are on the adjacent carbons.

$CH_2 = CH - CH_2 - Br$
Allyl Bromide

2.1.2.3

Aryl halides :

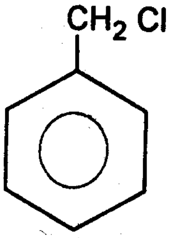
In aryl halides the halogen atom is directly attached to the aromatic ring.



Chlorobenzene

Aralkyl halides :

In aralkyl halides the halogens atom is attached to the carbon atom of the side chain containing aryl group.



Benzyl Chloride

2.1.3 Nomenclature :

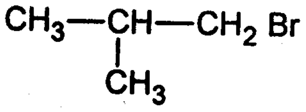
2.1.3.1 Common names :

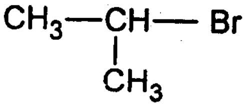
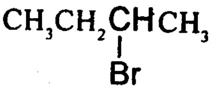
The individual members are named by joining the name of the alkyl group with that of the halogen as halide.

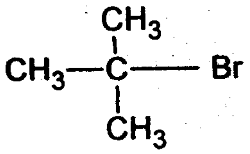
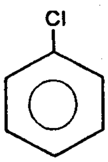
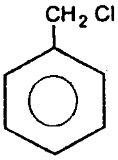
CH_3Cl	CH_3CH_2Br
Methyl chloride	Ethyl bromide

2.1.3.2 IUPAC names :

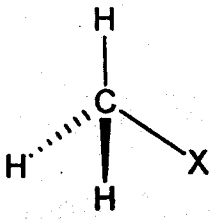
According to this system alkyl halide is regarded as a haloderivative of alkane. The name of halogen is prefixed to the name of the alkane. In higher members the carbon atom carrying halogen gets the least number.

CH_3Cl	CH_3CH_2Br	 $CH_3{-}\underset{\displaystyle CH_3}{\underset{\mid}{C}H}{-}CH_2Br$
Chloromethane	Bromo ethane	1-bromo - 2- methyl propane

S.NO	Structural formula	Commonname	IUPAC name
1.	CH_3Cl	Methyl chloride	Chloromethane
2.	CH_3CH_2Br	Ethyl chloride	Bromo ethane
3.	$CH_3CH_2CH_2Br$	n- Propyl bromide	1- bromopropane
4.	 $CH_3{-}\underset{\displaystyle CH_3}{\underset{\mid}{C}H}{-}Br$	IsoPropylbromide	2- bromopropane
5.	$CH_3CH_2CH_2CH_2Br$	n- butyl bromide	1-bromobutane
6.	 $CH_3CH_2\underset{\displaystyle Br}{\underset{\mid}{C}H}CH_3$	Sec -butyl bromide	2-bromobutane

7.	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$	Ter -butyl bromide	2-bromo-2-Methyl propane
8.	$CH_2=CH-Cl$	Vinyl chloride	Chloroethene
9.	$CH_2=CH-CH_2-Cl$	Allyl chloride	3- Chloro - prop -1- ene
10.		Chlorobenzene	Chlorobenzene
11.		Phenylmethyl chloride	Benzyl Chloride

2.1.4 Chemical reactivity :



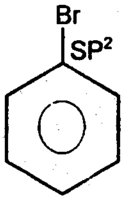
In C-X bond, X is more electronegative than carbon. So, the C-X bond is polar and haloalkanes are active.

$$\overset{\delta+}{C}-\overset{\delta-}{X}$$

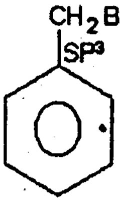
Positive charge on the carbon atom can be easily attacked by a nucleophile and leads to nucleophilic substitution reactions. The positive charge on the carbon atom leads to elimination reactions also.

The halogen atom linked to SP^2 hybridised carbon atom is inert to nucleophilic substitution reactions like hydloysis with aqueous KOH. The halogen atom linked to SP^3 hybridised carbon atom is reactive to nucleophilic substitution reactions. Thus alkylhalides easily undergo nucleophilic substitution reactions than arylhalides.

SP^3	SP^2	SP^3
CH_3-CH_2-Br	$CH_2=CH\ Br$	$CH_2=CH-CH_2\ Br$
Alkyl Bromide	Vinyl Bromide	Allyl Bromide
reactive	inert	reactive



Arylbromide
inert



Aralkylbromide
reactive

2.1.5 Reduction :

Alkyl halides on reduction form alkanes where as aryl halides form arenes.

$$R-X + 2H \rightarrow \underset{\text{alkane}}{RH} + HX$$

$$Ar-X + 2H \rightarrow \underset{\text{arene}}{ArH} + HX$$

a) with hydrogen in the presence of Ni or Pd

$$C_2H_5Br + H_2 \xrightarrow{Ni} C_2H_6 + HBr$$

b) with zinc and dil.HCl

$$Zn + 2HCl \rightarrow ZnCl_2 + 2H$$

$$C_2H_5Br + 2H \rightarrow C_2H_6 + HBr$$

c) with zn – cu couple and Ethanol.

$$Zn + C_2H_5OH \xrightarrow{Cu} (C_2H_5O)_2\ Zn + 2H$$

$$C_2H_5Br + 2H \rightarrow C_2H_6 + HBr$$

2.1.6 Formation of Grignad reagents :

Alkyl halides react with magnesium in dry ether forming alkyl magnesium halides known as Grignard reagents (R MgX).

$$R-X + Mg \xrightarrow{\text{dry ether}} RMgX$$

$$C_2H_5Br + Mg \xrightarrow{\text{dry ether}} C_2H_5\ Mg\ Br$$

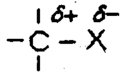
2.1.7 Nucleophilic substitution reactions :

Substitution reactions which involue the attack of nucleophiles are called nucleophilic substitution reactions.

$$C_2H_5Cl + KOH(aq) \rightarrow C_2H_5OH + KCl$$

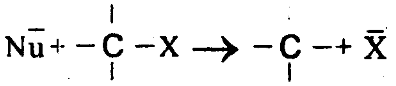
Explanation :

In alkyl halides, the halogen atom attached to the carbon atom is more electronegative. So, carbon atom gets partially positive charge and halogen atom gets partially negative charge.



$$-\overset{\delta+}{C}-\overset{\delta-}{X}$$

The positive charge on the carbon atom is a good site for attack by nucleophiles.



$$\bar{Nu} + -C-X \rightarrow -C- + \bar{X}$$

Where $\bar{Nu} = \bar{O}H, \bar{N}H_2, \bar{O}C_2H_5, \bar{C}N, CH_3CO\bar{O}, \bar{S}H$ etc.

Classification :

There are two types of nucleophilic substitution reactions –

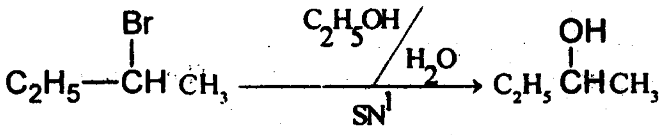
1. Unimolecular nucleophilic substitution reactions (SN^1 reactions)
2. Bimolecular nucleophilic substitution reactions (SN^2 reactions).

2.1.7.1 SN^1 reactions :

Nucleophilic substitution reactions in which rate of the reaction depends only on the concentration of the reactant are called Unimolecular nucleophilic substitution reactions.

Rate α [reactant]

Ex : Hydrolysis of 2 – bromobutane with ethanol and water undergoes SN^1 reaction.

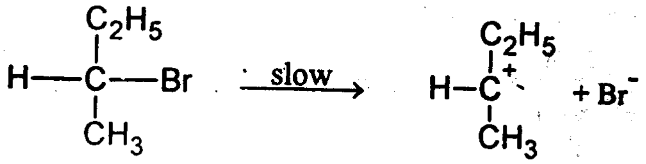


$$C_2H_5-\overset{Br}{CH}CH_3 \xrightarrow[SN^1]{C_2H_5OH / H_2O} C_2H_5\overset{OH}{CH}CH_3$$

2- butanol

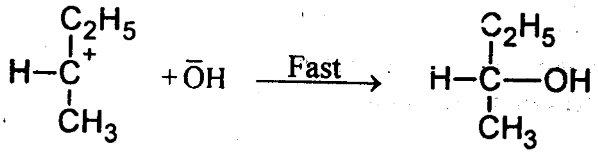
Mechanism : It takes place in two steps

1st stage : In the first stage carbocation is formed slowly.



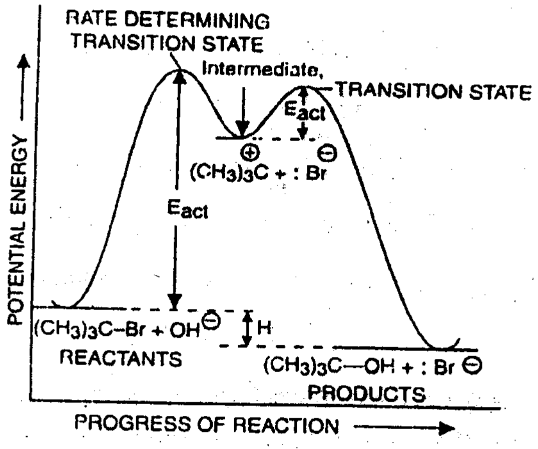
$$H-\underset{CH_3}{\overset{C_2H_5}{C}}-Br \xrightarrow{slow} H-\underset{CH_3}{\overset{C_2H_5}{C^+}} + Br^-$$

2nd stage : In the 2nd stage carbocation undergoes fast and non – rate determining nucleophilic attack forming the product.



$$H-\underset{CH_3}{\overset{C_2H_5}{C^+}} + \bar{O}H \xrightarrow{Fast} H-\underset{CH_3}{\overset{C_2H_5}{C}}-OH$$

Energy profile diagram of SN¹ reactions :



Transition states in SN¹ reaction.

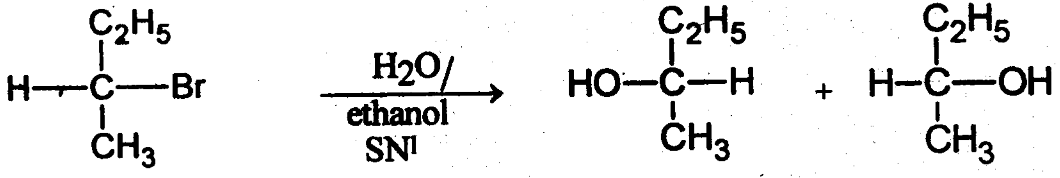
The energy level diagram has two transition states with carbocation as intermediate. In the first step ionisation of alkyl halide results in the formation of carbocation. It is highly endothermic. It has high activation energy. So, the first step in SN¹ reactions becomes slow and is the rate determining step.

In the second step nucleophile attacks the carbocation. It is highly exothermic. It has low activation energy. So, second step in SN¹ reactions becomes fast and is non – rate determining. Thus concentration of the nucleophile does not effect the rate of SN¹ reactions.

Stereo chemistry :

In the intermediate stage of SN¹ reactions carbocation is formed. The structure of carbocation is planar and positively charged carbon is SP² hybridised. The nucleophile can attack from either side. Hence in SN¹ reactions optically active halide should yield a recemic mixture. But complete recemic mixture is not formed because the attack of nucleophile is fast and occurs on ion pair. Hence back side attack is preferred and more inverted product is formed.

Ex : Hydrolysis of optically active pure (-) -2- bromobutance gives 83% (+) and 17% (-) -2-butanol.



(-) -2- bromobutane

(+) -2- bromobutanol
83%

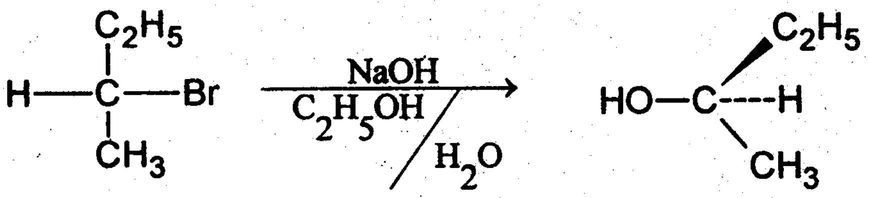
(-)-2- bromobutanol
17%

2.1.7.2 SN² reactions :

Nucleophilic substitution reactions in which rate of the reaction depends on the concentration of both the reactant and the reagent are called bimolecular nucleophilic reactions.

Rate α[reactant] [reagent]

Ex : Hydrolysis of -2- bromobutane in the presence of NaOH undergoes SN² reactions.

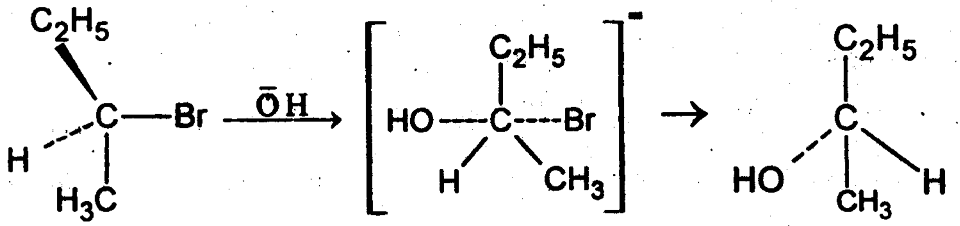


-2- bromobutane

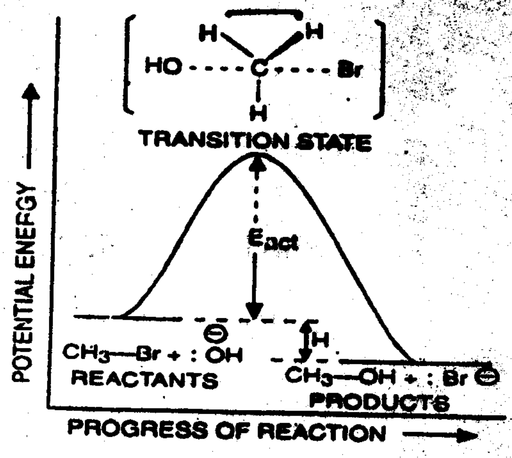
2- butanol

Mechanism :

In SN² reactions the attacking nucleophile forms bond simultaneously as the bond of the leaving group breaks away.



Energy profile diagram of SN^2 reactions :



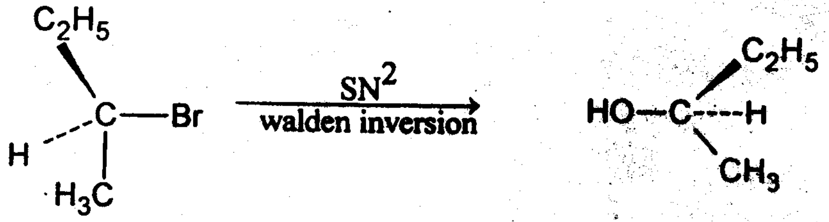
Potential energy profile for an SN^2 reaction.

The energy level diagram has a single transition state with central carbon atom SP^2 hybridised. It shows that no intermediate is formed. The transition state represents a highest energy state in which carbon atom is linked to five atoms. The reaction is exothermic. The conversion of transition state into product involves rehybridisation of carbon from SP^2 to SP^3 and configuration of the product is inverted.

Stereochemistry :

In the intermediate stage of SN^2 reactions both the attacking group and the leaving group are bonded in opposite directions. So, complete inversion of the molecule takes place. It is called Walden Inversion.

Ex : (-) – 2- bromobutane on hydrolysis under SN^2 conditions gives (+) -2- bromobutane.



2.1.7.3 Difference between SN^1 and SN^2 reactions :

S.NO	SN^1 reaction	SN^2 reaction
1.	It follows first order kineties	It follows second order kineties
2.	The product is formed with partial recemisation	The product is formed with complete inversion
3.	SN^1 reactions mainly occur in tertiary halides.	SN^2 reaction mainly occur in primary halides.
4.	Polar solvents favour SN^1 reactions	Non - Polar solvents favour SN^2 reactions

5.	Mild nucleophiles favour SN^1 reactions	Strong nucleophiles favour SN^2 reactions.
6.	Low concentration of the nucleophile favours SN^1 reactions	High concentration of the nucleophile favours SN^2 reactions
7.	Rearrangement is possible	Rearrangement is not possible.
8.	Reaction rate is influenced by electronic factors.	Reaction rate is influenced by Steric factors.

2.1.8 Hydrolysis – comparison of alkyl, vinyl, allyl , aryl and aralkyl halides :

$CH_3CH_2Cl + NaOH \longrightarrow CH_3CH_2OH + NaCl$

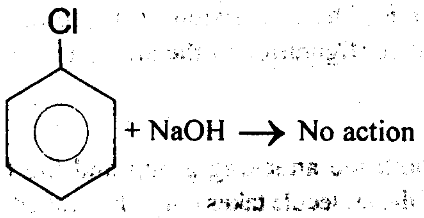
Alkyl Chloride

$CH_2 = CHCl + NaOH \longrightarrow$ No action

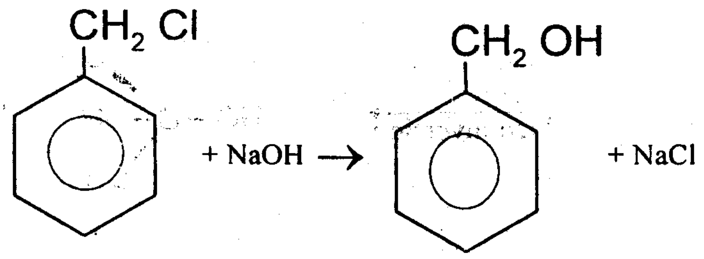
Vinyl Chloride

$CH_2 = CHCH_2Br + NaOH \longrightarrow CH_2 = CH - CH_2OH + NaBr$

Allyl bromide



Alkyl Chloride



Alkyl Chloride

2.1.8.1 Alkyl halides :

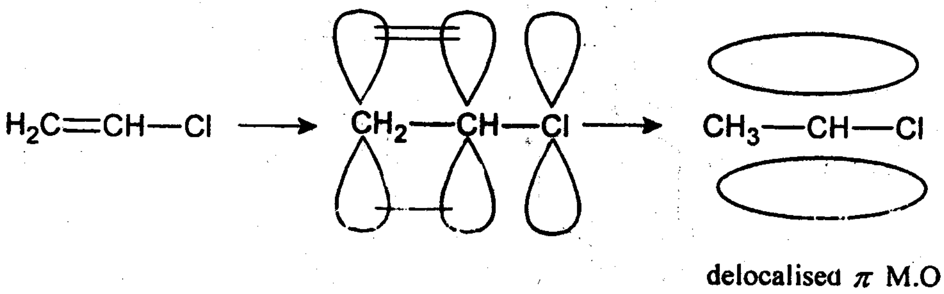
In alkyl halides C – X bond is highly polarised covalent bond and carbon atom is SP^3 hybridised.

$$\overset{\delta+}{C}\text{——}\overset{\delta-}{X}$$

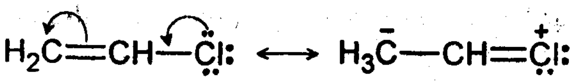
So, alkyl halides are very reactive and easily undergo hydrolysis.

2.1.8.2 Vinyl halides :

Compared to alkyl halide, the halogen atom in vinyl halide is inert. In vinyl halide C – X bond is formed by the SP^2 hybridised carbon and also **delocalized π molecular** orbital is formed.



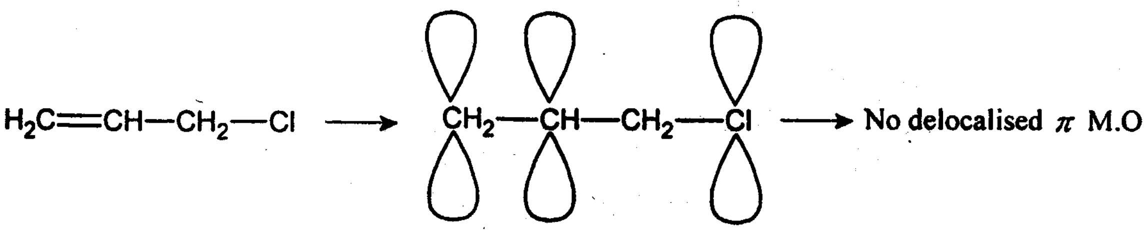
Also vinyl chloride has the following resonance structures.



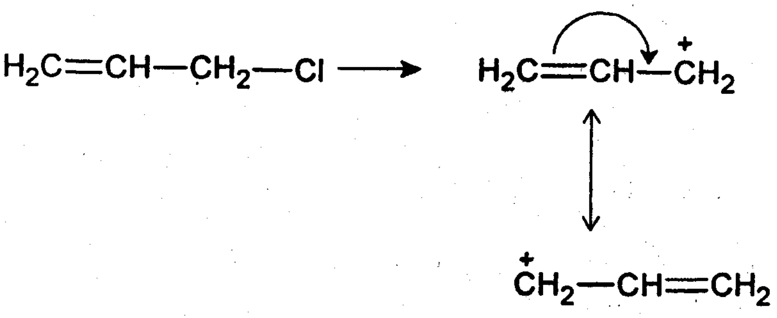
$$H_2C{=}CH{-}\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow H_3\bar{C}{-}CH{=}\overset{+}{\underset{\cdot\cdot}{Cl}}:$$

Allyl halides :

In allyl halides, C -- X bond is formed by the SP^3 hybridised carbon atom. The delocalized π molecular orbital can not be formed.



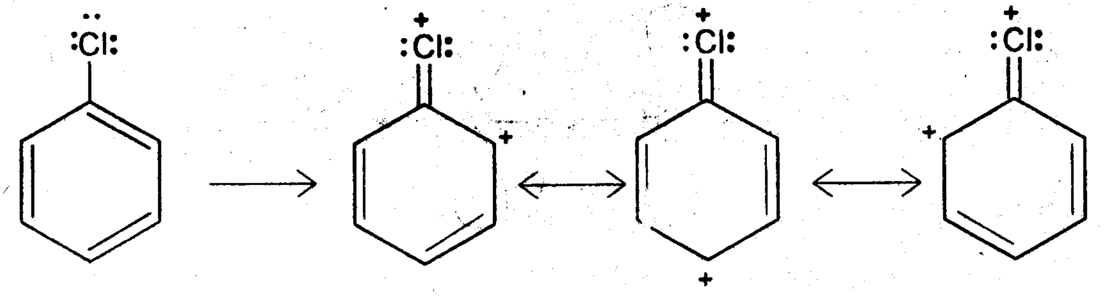
The reactivity of halogen atom is due to its ionisation forming allyl carbonium ion. The allyl carbonium ion is stabilised by resonance.



$$H_2C{=}CH{-}CH_2{-}Cl \longrightarrow H_2C{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2$$

2.1.8.4Aryl halides :

In aryl halides C – X bond is formed by SP^2 hybridised carbon atom. The halogen atom is inert. The low reactivity of halogen atom in aryl halide is due to resonance.

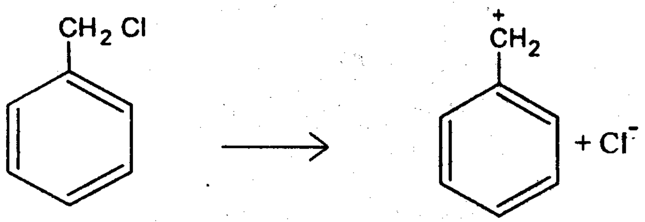


Resonance in chlorobenzene

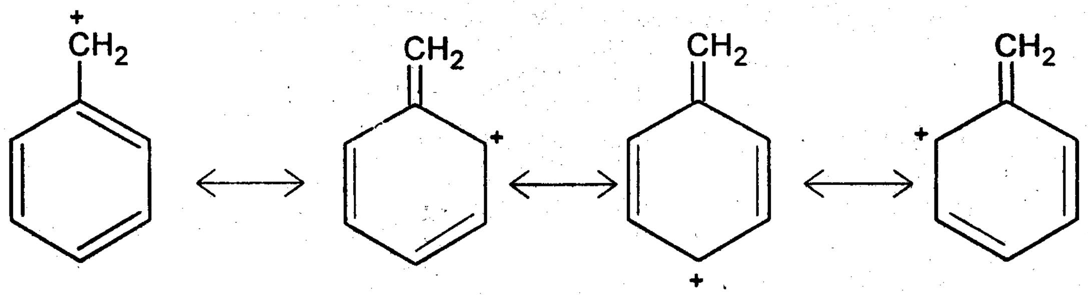
However aryl halides can be made to undergo hydrolysis under drastic conditions.

2.1.8.5 Aralkyl halides :

In aralkyl halides. C – X bond is formed by the SP^3 hybridised carbon atom. Aralkyl halides behave like alkyl halides. Aralkyl halides having halogen atom on the α- carbon of the side chain are more reactive than alkyl halides. It is duet to the formation of resonance stabilised carbonium ion which is not possible in alkyl halides.

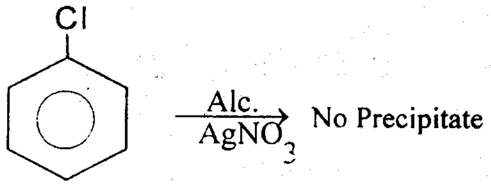


Benzyl Chloride

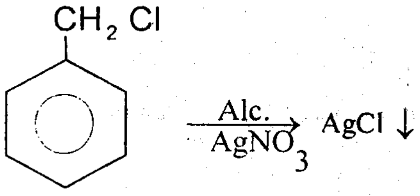


2.1.9. Distinction between aryl halide and aralkyl halide :

Arylhalide is inactive where as aralkyl halide is active. Aralkyl halide gives white precipitate with AgCl but not aryl halide.



Chlorobenzene
inert



benzyl chloride
active

White precipitate

Similarly alkyl halide and allyl halide gave white precipitate with AgCl but not vinyl halide.

Alkyl halides, aralkyl halides, allyl halides easily undergo hydrolysis with aqueous NaOH but not vinyl and aryl halides.

2.1.10. Model Questions :

1. Alkyl halides are detected by precipitation as silver halides with silver nitrate solution but not aryl and vinyl halides. Explain.
2. Give the mechanism of SN1 and SN2 reactions.
3. Write difference between SN1 and SN2 reactions.
4. Explain energy profile diagrams and stereochemistry of SN1 and SN2 reactions.
5. How are alkyl halides classified?
6. Compare the reactivity of allyl. benzyl, alkyl and vinyl halides.
7. How are Grignard reagents prepared from alkyl halides?
8. Explain Walden inversion with example
9. How can you account for the activity or inactivity of halogen atom in
   a. Allyl chloride and ii) Vinyl chloride.
10. Explain why allylcholride undergoes substilution easily but not vinyl chloride.

Dr. S. Siva RamBabu, M.sc., Ph.D.

UNIT - II

Lesson - II

HYDROXY COMPOUNDS

2.2.0 :

Nomenclature and classification of hydroxy compounds. Preparation : From carbonyl compounds Aryl carbinols by hydroxymethylation.

Phenols –

a) By diazotization
b) From sulfonic acid
c) From Cumene
d) By hydrolysis of halobenzene.

Physical Properties – Hydrogen bonding (intermolecular and intramolecular), effect of hydrogen bonding on boiling point and water solubility.

Chemical properties –

a) Acidic nature of phenols
b) Formation of alkoxides / phenoxides and their reaction with R X
c) Replacement of OH by X using PCl_5, PBr_3, $SOCl_2$ and with HX / Zn Cl_2.

a) Esterification by – acid halides, anhydrides and acids (mechanism)
b) Esters of inorganic acids
c) Dehydration of alcohols.

Oxidation of alcohols by CrO_3, $KMnO_4$. Special reactions of phenols

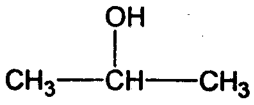
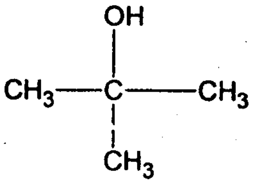
a) Bromination
b) Kolb – Schmidt reaction
c) Reimer – tiemann reaction
d) Azo coupling

Identification of alcohols by oxidation – $KMnO_4$, Ceric ammonium nitrate, lucas reagent. Phenols by reaction with $FeCl_3$ and by solubility in NaOH. Polyhydroxy compounds, pinacol – pinacalone rearrangement, oxidative cleavage (Pb(OAC)$_4$ and HIO_4).

2.2.1 Nomenclature :

Alcohols are the hydroxy derivatives of alkanes. In IUPAC system alcohols are named as alkanols. The names of various alcohols are obtained by replacing the suffix 'e' of the corresponding alkane by 'ol'.

Ex :

Compound	IUPAC Name	Common name
$CH_3\ OH$	Methanol	Methyl alcohol
CH_3CH_2OH	Ethanol	Ethyl alcohol
 $CH_3-\overset{\overset{OH}{\vert}}{C}H-CH_3$	Propanol - 2	Isopropyl alcohol
 $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{OH}{\vert}}{C}}-CH_3$	2 - Methyl Propanol -2	T- butyl alcohol

2.2.2 Classification :

Monohydric alcohols :

These alcohols contain only one hydroxyl group.

Ex : $CH_3\ OH$ Methyl alcohol
CH_3CH_2OH Ethyl alcohol

Dihydric alcohols :

These alcohols contain two hydroxyl groups.

Ex : $\begin{array}{l} CH_2OH \\ \vert \\ CH_2OH \end{array}$ Ethylene glycol

Trihydric alcohols :

These alcohols contain three hydroxyl groups.

Ex : $\begin{array}{l} CH_2OH \\ \vert \\ CHOH \\ \vert \\ CH_2OH \end{array}$ glycol

Polyhydric alcohols :

These alcohols contain more than three hydroxyl groups.

Ex : Mannitol. $CH_2OH\ (\ CHOH)_4\ CH_2OH$

2.2.2.1. Classification of Monohydric alcohols :

Primary, Secondary and Tertiary alcohols :

When the hydroxyl group is attached to primary (1°) carbon, the alcohol is known as P–alcohol.

Ex : CH_3OH Methyl alcohol

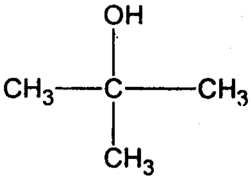
CH_3CH_2OH Ethyl alcohol

When the hydroxyl group is attached to Secondary (2°) carbon, the alcohol is known as S– alcohol.

Ex : $CH_3 CHOH CH_3$ Isopropyl alcohol

When the hydroxyl group is attached to Tertiary (3°) carbon, the alcohol is known as T– alcohol.

Ex :



$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

T- butyl alcohol.

2.2.3 Preparation of Alcohols :

From carbonyl compounds :

Aldehydes on reduction gave primary alcohols where as ketones gave secondary alcohols.

2.2.3.1. Bouveault - blanc reduction :

Carbonyl compounds on reduction with sodium and ethanol gave alcohols.

$$CH_3OH \xrightarrow{Na/C_2H_5OH} CH_3CH_2OH$$

Acetaldehyde Ethylalcohol

$$CH_3COCH_3 \xrightarrow{Na/C_2H_5OH} CH_3CHOHCH_3$$

Acetone Isopropyl alcohol

2.2.3.2 Reduction with metal hydrides :

Carbonyl compounds on reduction with lithium aluminium hydride or sodium hydride gave alcohols.

$$CH_3CHO \xrightarrow{NaBH_4} CH_3CH_2OH$$

$$CH_3COCH_3 \xrightarrow{LiAlH_4} CH_3CHOHCH_3$$

2.2.3.3 Catalytic hydrogenation :

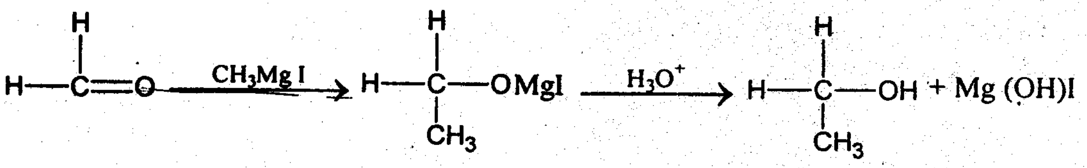
Carbonyl compounds on reduction with hydrogen in the presence of suitable catalyst gave alcohols.

$$CH_3CHO+H_2 \xrightarrow[heat]{PtO_2} CH_3CH_2OH$$

$$CH_3COCH_3+H_2 \xrightarrow[heat]{PtO_2} CH_3CHOHCH_3$$

2.2.3.4 By the action of Grignard reagents :

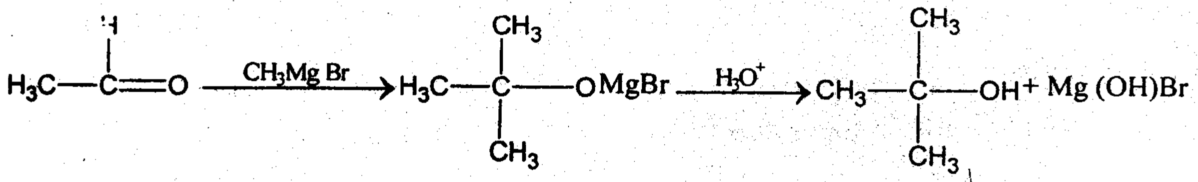
a) Primary alcohols : Formaldehyde reacts with Grignard reagent forming P- alcohol.



$$H-\overset{H}{C}=O \xrightarrow{CH_3MgI} H-\overset{H}{\underset{CH_3}{C}}-OMgI \xrightarrow{H_3O^+} H-\overset{H}{\underset{CH_3}{C}}-OH + Mg(OH)I$$

Ethyl alcohol

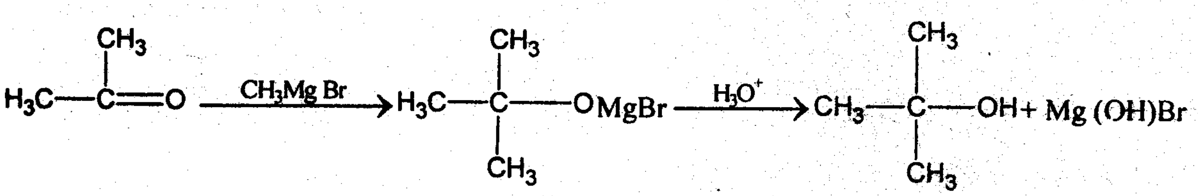
b) Secondary alcohols : Aldehydes other than formaldehyde react with Grignard reagent forming S- alcohol



$$H_3C-\overset{H}{C}=O \xrightarrow{CH_3MgBr} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Mg(OH)Br$$

Isopropyl alcohol

c) Tertiary alcohols : Ketones react with Grignard reagent forming T - alcohols.

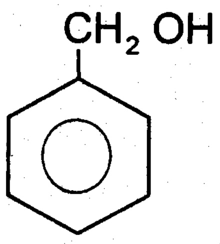


$$H_3C-\overset{CH_3}{C}=O \xrightarrow{CH_3MgBr} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Mg(OH)Br$$

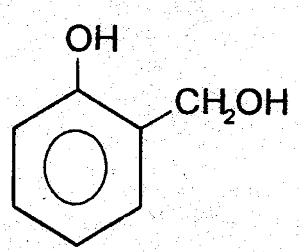
T- butyl alcohol

2.2.4. Aryl Carbinols :

Aryl carbinols are aromatic alcohols. Aromatic alcohols are the aryl derivatives of aliphatic alcohols.



Phenyl carbinol
(benzyl alcohol)

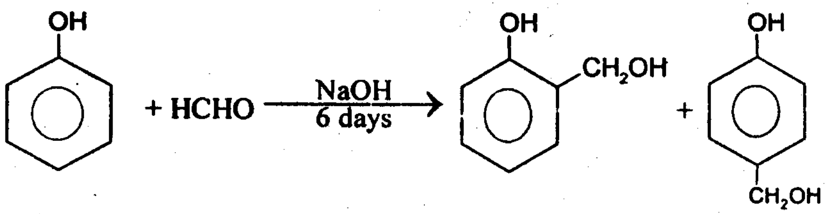


Saligenin
(Salicyl alcohol (or) O- hydroxy benzyl alcohol)

Preparation :

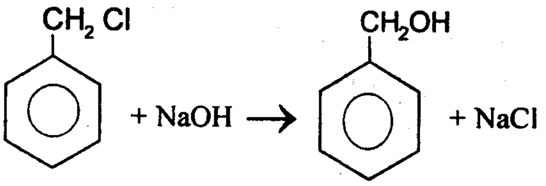
2.2.4.1.Lederer - Manasse reaction : (hydroxy methylation)

Phenol on condensation with formaldehyde in the presence of dilute acid or alkali form O- hydroxy and P- hydroxy phenyl carbinols.



2.2.4.2. Hydrolysis :

Benzyl chloride on hydrolysis with aqueous sodium hydroxide forms phenyl carbinol.

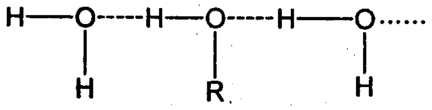


2.2.5. Physical Properties :

2.2.5.1. Hydrogen bonding :

Solubility :

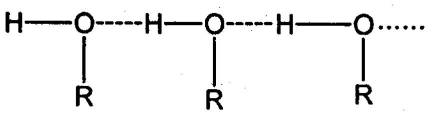
Alcohols are readily soluble in water. It is due to the formation of hydrogen bonds between alcohol and water molecules.



$$H-\underset{H}{\underset{|}{O}}\cdots\cdots H-\underset{R}{\underset{|}{O}}\cdots\cdots H-\underset{H}{\underset{|}{O}}\cdots\cdots$$

Boiling Points :

Boiling points of alcohols are much higher than those of the corresponding alkanes because alcohols undergo molecular association due to hydrogen bonding.



$$H-\underset{R}{\underset{|}{O}}\cdots\cdots H-\underset{R}{\underset{|}{O}}\cdots\cdots H-\underset{R}{\underset{|}{O}}\cdots\cdots$$

Hydrogen bonding occurs due to the polarity of - OH group which is due to high electronegativity of the oxygen atom.

$$R-\overset{\delta^-}{O}-\overset{\delta^+}{H}$$

2.2.5.2. Nature :

Alchols are neutral because alkoxide ion has no resonance stabilisation. They are less acidic than water.

$$R\text{-}OH \rightleftharpoons \underset{\text{no resnance}}{RO^- + H^+}$$

2.2.6. Chemical Properties :

2.2.6.1. Formation of alkoxides :

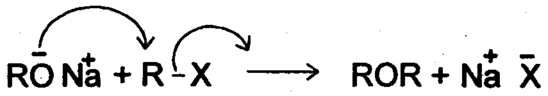
Alcohols react with Na, K, Ca, Mg forming alkoxides.

$$2ROH + 2\,Na \rightarrow \underset{\text{Sodium alkoxide}}{2RONa} + H_2$$

Alchols do not form alkoxides with NaOH because alcohols are less acidic than water.

2.2.6.2. Reaction of alkoxides with RX : (williamson synthesis)

Alkoxides react with alkyl halides forming ethers.



Alkoxide ion is better nucleophile than alcohol.

2.2.6.3. Replacement of OH by - X :

a) Action with PCl_5 :

Alcohols react with PCl_5 forming alkyl chlorides.

$$ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$$

b) Action with PBr_3 :

Alcohols react with PBr_3 forming alkyl bromides.

$$3ROH + 3PBr_3 \rightarrow 3RBr + H_3\,PO_3$$

c) Action with thionyl chloride ($SOCl_2$):

Alcohols react with $SOCl_2$ forming alkyl chlorides.

$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

d) Action with halogen acids :

Alcohols react with HCl in the presence of anhydrous $ZnCl_2$ forming alkyl chloride.

$$ROH + HCl \xrightarrow[\text{anhydrous}]{ZnCl_2} RCl + H_2O$$

2.2.6.4. Esterification :

Alcohols react with carboxylic acids, acid halides and acid anhydrides forming esters.

$R\text{-}OH + R^{I}COOH \rightarrow RCOOR^{I} + H_2O$
Carboxylic acid Ester

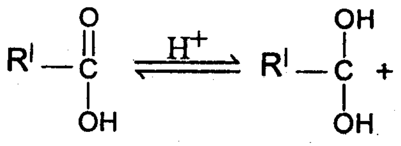
$R\text{-}OH + R^{I}COCl \rightarrow RCOOR^{I} + HCl$
acid chloride

$R\text{-}OH + (R^{I}CO)_2O \rightarrow RCOOR^{I} + R^{I}COOH$
acid anhydride

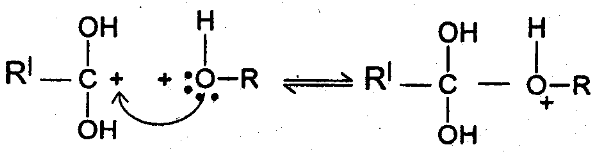
In all these reactions hydrogen of - OH group is replaced by an acyl group (- COR^{I})

Mechanism :

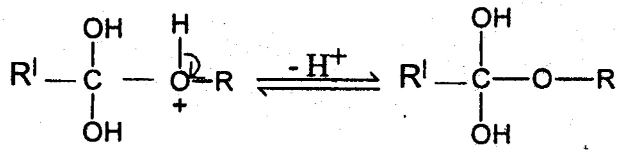
i) **Protonation of carboxylic acid :**



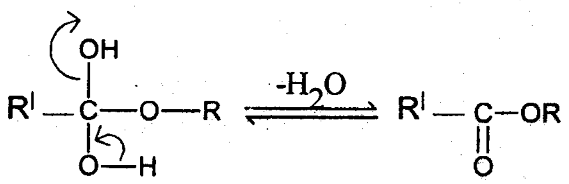
ii) **Nucleophilic attack of ROH :**



iii) **Elimination of Proton :**



iv) **Elimination of water molecule :**



2.2.6.5. Esters of inorganic acids :

Alcohols react with mineral acids forming esters.

$$ROH + HONO_2 \rightarrow RONO_2 + H_2O$$

$$ROH + HOSO_3H \rightarrow ROSO_3H + H_2O$$

The ease of replacement of - OH follows the order ter > sec > primary.

2.2.6.6. Dehydration of alcohols :

Dehydration of all alcohols leads to olefins. Dehydration is done with

i) By heating alcohol with Conc. H_2SO_4 at 200°c - 250°c.

ii) By heating alcohol with phosphoric acid at 200°c - 250°c.

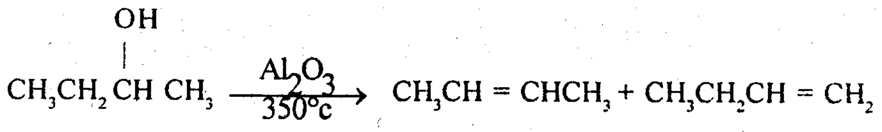
iii) By passing vapour of alcohol over alumina at 350°c - 400°c.

a) Primary alcohols :

$$CH_3CH_2OH \xrightarrow[200^\circ c]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethylene

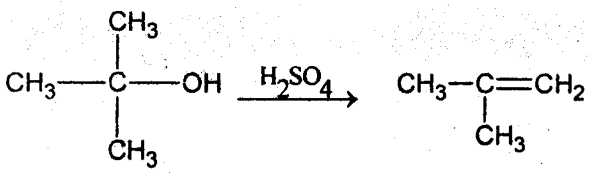
b) Secondary alcohols :



$$\overset{OH}{\underset{|}{}}\;CH_3CH_2\overset{OH}{CH}CH_3 \xrightarrow[350^\circ c]{Al_2O_3} CH_3CH = CHCH_3 + CH_3CH_2CH = CH_2$$

2- butanol Butene-1 (major) Butene-2

c) Tertiary alcohols :



t - butanol 2- methyl - 1- propene

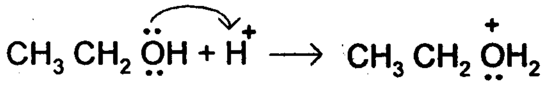
The order of ease of dehydration is

Tertiary > Secondary > Primary.

This is inaccordance with the stability of carbonium ions.

Mechanism :

i) **Protonation of the alcohol :**

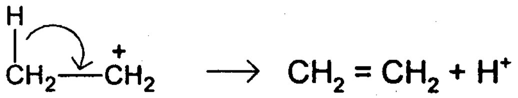


$$CH_3\,CH_2\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}H + \overset{+}{H} \longrightarrow CH_3\,CH_2\,\underset{\cdot\cdot}{\overset{+}{O}}H_2$$

ii) **Elimination of H_2O forming carboniumion :**

$$CH_3\,CH_2\,\underset{\cdot\cdot}{\overset{+}{O}}H_2 \longrightarrow CH_3\,\overset{+}{C}H_2 + H_2O$$

iii) **Elimination of proton forming alkene :**



$$\overset{\displaystyle H}{\overset{|}{C}H_2}-\overset{+}{C}H_2 \longrightarrow CH_2 = CH_2 + H^+$$

Ethylene

2.2.6.7. Oxidation with alcohols :

Oxidation with CrO_3 :

a) Primary alcohols are oxidised to aldehydes and then to carboxylic acids containing same number of carbon atoms.

$$RCH_2OH \xrightarrow{CrO_3,\,H^+} RCHO \xrightarrow{CrO_3,\,H^+} RCOOH$$

b) Secondary alcohols are oxidised to ketones containing same number of carbon atoms.

$$CH_3CHOHCH_3 \xrightarrow{CrO_3,\,H^+} CH_3COCH_3$$

c) **Collin's reagent :** It is chromium trioxide pyridine complex ($CrO_3 . 2Py$). It is used in non-aqueous solvents to check the oxidation of aldehydes to acids.

$$RCH_2OH \xrightarrow[CH_2Cl_2]{(CrO_3.2py)} RCHO$$

d) **Sarett's reagent :** It is chromic anhydride pyridine complex.

i) It checks the oxidation of aldehydes to acids.

ii) It oxidises - OH group selectively in the presence of C = C.

$$RCH_2OH \xrightarrow[\text{reagent}]{\text{Sarett's}} RCHO$$

2.2.7. Identification of alcohols : (distinguishing primary, secondary and tertiary alcohols)

2.2.7.1. Oxidation with KMnO4 :

Primary Alcohols :

Primary alcohols are oxidised first to aldehydes and then to carboxylic acids, both having same number of carbon atoms as the parent alcohol.

$$CH_3CH_2OH \xrightarrow[KMnO_4]{Akaline} CH_3CHO \xrightarrow[KMnO_4]{Akaline} CH_3COOH$$

Ethyl alcohol no.of carbon atoms = 2	Acetaldehyde no.of carbon atoms = 2	Acetic acid no.of carbon atoms = 2

Secondary Alcohols :

Secondary alcohols are oxidised first to ketones having same number of carbon atoms as in alcohol. Then ketones are oxidised under drastic conditions forming carboxylic acids containing less number of carbon atoms.

$$CH_3CHOHCH_3 \xrightarrow[KMnO_4]{Akaline} CH_3COCH_3 \xrightarrow[KMnO_4]{Acidified} CH_3COOH + HCOOH.$$

Isopropyl alcohol no.of atoms = 3	Acetone no.of atoms = 3	Acetic acid no.of atoms = 2

Tertiary Alcohols :

Tertiary alcohols are oxidised under drastic conditions first to ketones and then to acids both having less number of carbon atoms.

$$(CH_3)_3C-OH \xrightarrow[KMnO_4]{Acidified} (CH_3)_2CO \xrightarrow[KMnO_4]{Acidified} CH_3COOH + HCOOH$$

Isoprcpyl alcohol no.of carbon atoms = 3	Acetone no.of carbon atoms = 3	Acetic acid no.of carbon atoms = 2	Acetic acid no.of carbon atoms = 2

$$(CH_3)_3C-OH \Big\downarrow \text{alkaline } KMnO_4$$

no action.

2.2.7.2. Lucas reagent test :

Cocentrated hydrochloric acid in the presence of an hydrous Zinc chloride is called Lucas reagent. Alcohols react with Lucas reagent to form alkyl halides. The order of reactivity is ter> Sec.> ~~Pri~~..

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

The three types of alcohols undergo this reaction with different rates. At room temperature

i) If cloudiness appears immediately, the alcohol is tertiary.

ii) If cloudiness appears with in 5 minutes, the alcohol is secondary.

iii) If no cloudiness is formed, the alcohol is primary, because primary alcohols do not react with Lucas reagent at room temperature.

2.2.7.3. Ceric ammonium nitrate test :

It is a qualitative test for alcohols. 4 -5 drops of the compound to be identified are added to an aqueous ceric ammonium nitrate solution. Formation of red colour indicates the presence of alcohol.

Alcohols replace nitrate ions in complex cerate anions there by causing change in colour.

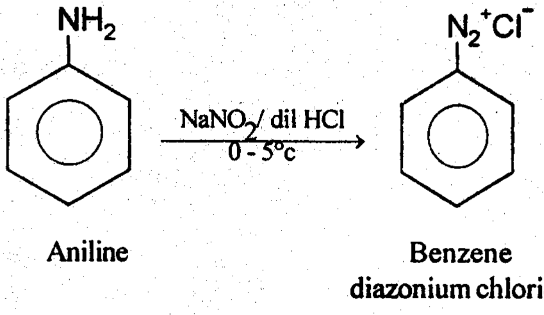
$$\underset{\text{Yellow}}{(NH_4)_2\,Ce(NO_3)_6} + ROH \rightarrow \underset{\text{Red}}{[(NH_4)_2\,Ce\,(NO_3)_5\,(OR)]} + HNO_3$$

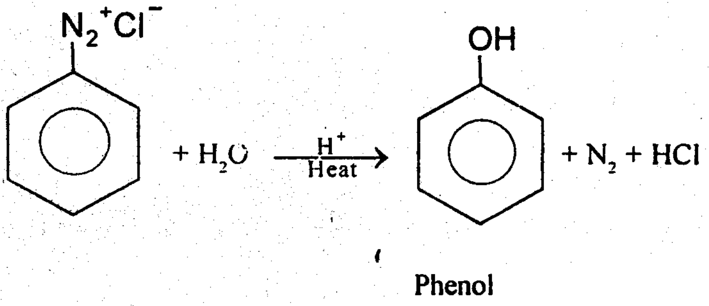
Aliphatic bases interfere with this test by forming precipitates.

2.2.8. Preparation of Phenols :

2.2.8.1. Diazotisation :

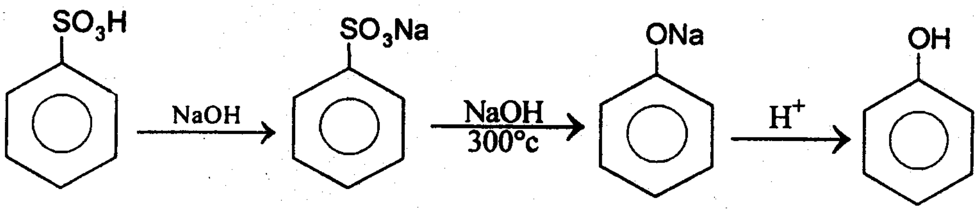
Amines react with $NaNO_2$ and dil.HCl at 0-5°c forming diazonium salts. It is called diazotisation. Diazonium salts on hydrolysis with dil H_2SO_4 form Phenols.





2.2.8.2. From Sulphonic acid :

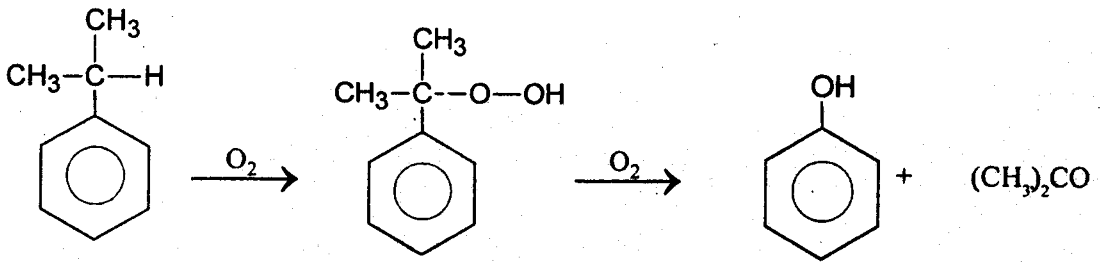
Sodium salts of aromatic sulphonic acids on fusion with NaOH at 300°c form sodium phenoxide. The sodium phenoxide on acidification gives Phenol.



Benzene sulphonic acid Sod.sulphonate Sod. Phenoxide Phenol

2.2.8.3. From Cumene :

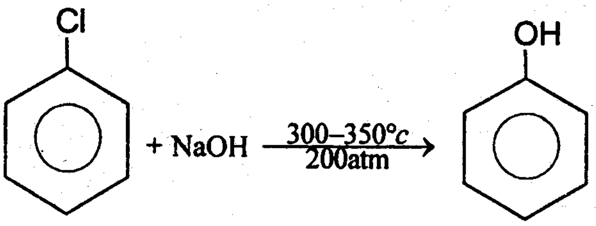
Cumene on oxidation with oxygen forms cumene hydroperoxide which on decomposition with acid forms phenol.



Isopropyl benzene (Cumene) Phenol Acetone

2.2.8.4. Hydrolysis of halobenzene : (Dow's process)

Chlorobenzene on heating with 10% NaOH at 300°c temperature and 200 atmospheres pressure form phenol. 10% diphenyl ether is added to inhibit side reaction.

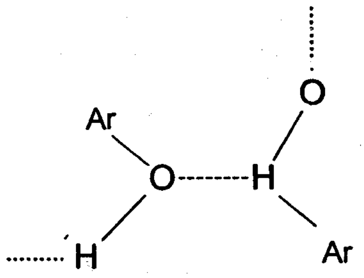


Chlorobenzene Phenol

2.2.9. Physical Properties : (Intermolecular and Intramolecular hydrogen bonding)

Intermolecular hydrogen bonding : (Boiling Points) :

Phenols undergo intermolecular hydrogen bonding. So, they have high boiling points than the corresponding hydrocarbons, aryl halides and alcohols.

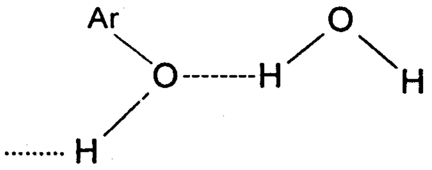


Inter molecular hydrogen bonding in phenols.

Also O-H bond is more polar in phenols than in alcohols. Consequently intermolecular hydrogen bonding in phenols is stronger than in alcohols.

Solubility :

Phenols and polyhydric phenols are soluble in water due to strong hydrogen bonding between phenols and water molecules.

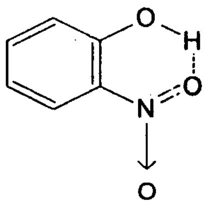


Hydrogen bonding between phenol and water molecules

Intramolecular hydrogen bonding : (chelation)

Phenols containing - NO_2 or - COOH groups in orthoposition to the - OH group form intramolecular hydrogen bonds. So, they have lower boiling points and less solubility in water corresponding to the meta or para isomer.

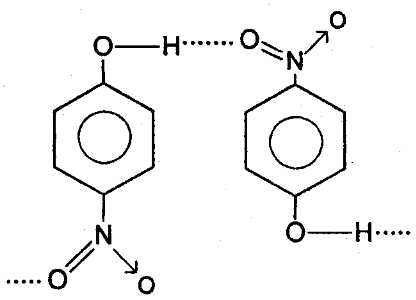
Ex : Orthonitrophenol and paranitrophenol.



O- Nitrophenol

Intramolecular hydrogen bonding takes place.

Intermolecular hydrogen bonding is not possible



P- Nitrophenol

Intra molecular hydrogen bonding is not possible.

Inter molecular hydrogen bonding takes place.

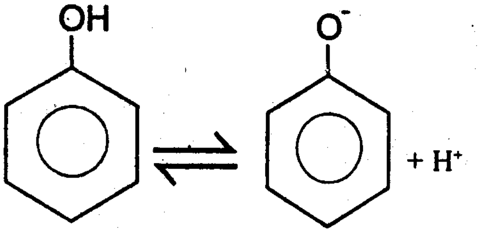
Due to intramolecular hydrogen bonding ortho isomers can neither undergo molecular association nor form hydrogen bonds with water molecules. So, ortho isomer has low b.p. and less solubility in water. Meta and para isomers undergo molecular association or form hydrogen bonds with water. So, meta and para isomers have high b.p. and more solubility in water.

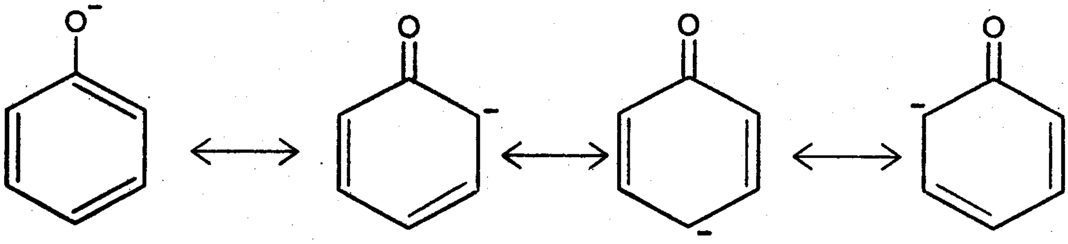
2.2.10. Chemical properties :

2.2.10.1. Acidic nature :

Phenols are stronger acids than alcohols but weaker than carboxylic acid.

Acidic nature of phenols is due to resonance stabilisation of phenoxide ion. No charge seperation is noticed in the resonance forms of phenoxide ion.

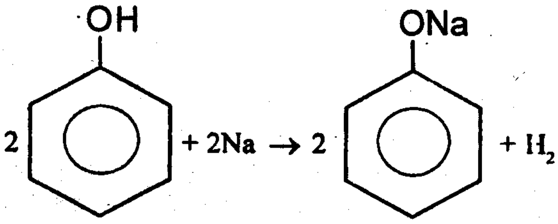




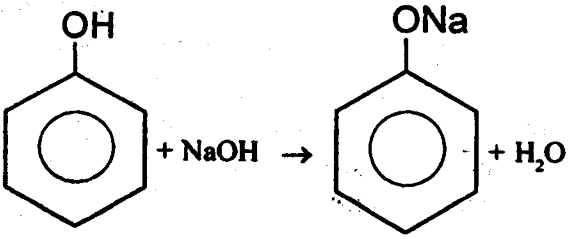
Resonance of phenoxide ion

Formation of phenoxides :

Phenols react with alkalimetals and their hydroxides forming phenoxides or phenates.



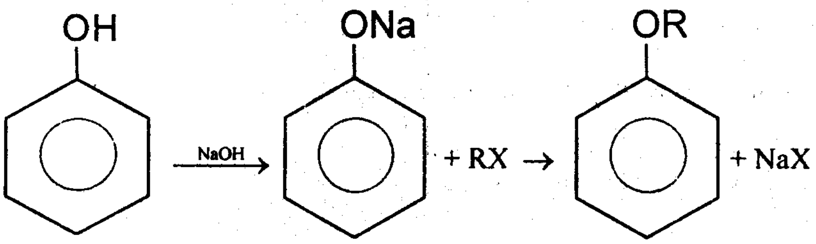
Sodium Phenoxide



Phenols do not react with carbonates (difference from carboxylic acids) Phenols form phenoxides with NaOH because they are more acidic than water.

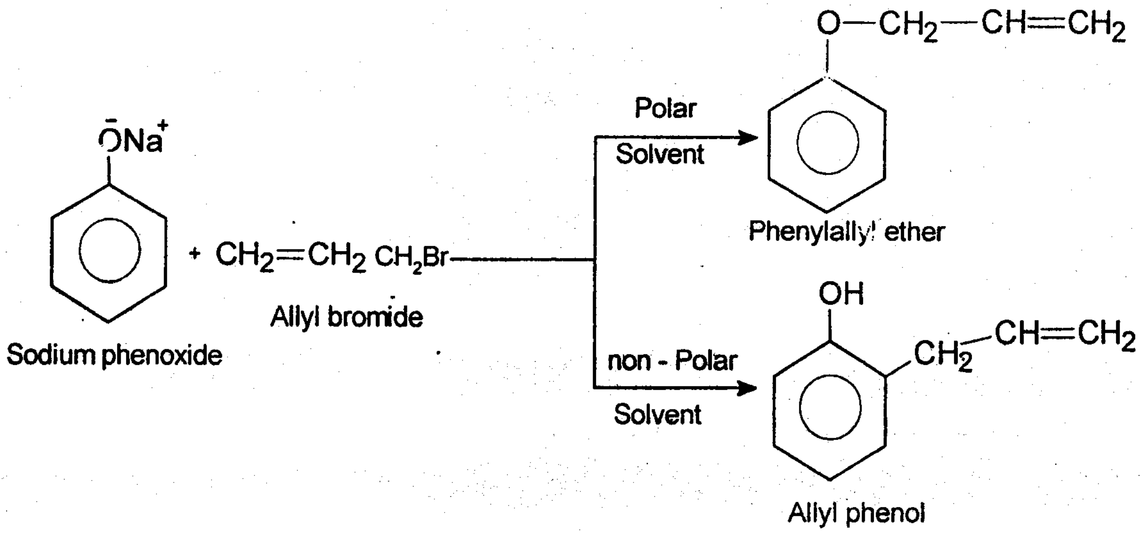
2.2.10.2 Reaction of Phenoxide with RX :

Phenols react with alkylhalide forming phenolic ethers (williamson synthesis).



Phenolic ether

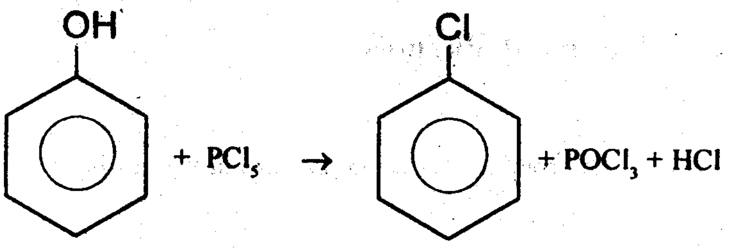
The reaction of phenoxide ion with RX depends on the nature of the solvent used.



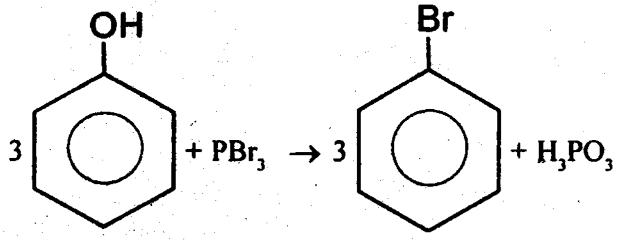
In the presence of polar solvent ethers are formed while in the presence of non - polar solvent negative charge on the phenoxide ion delocalise into the ring. Hence alkylation takes place in the ring.

2.2.10.3. Replacement of - OH by - X :

Unlike alcohols, it is difficult to replace - OH group of phenols by halogen. Halogen acids do not react with phenols. Phosphorus trihalides give phosphorus esters. How ever, Phenols react with PCl_5 or PBr_3 or $SOCl_2$ forming arylhalides.

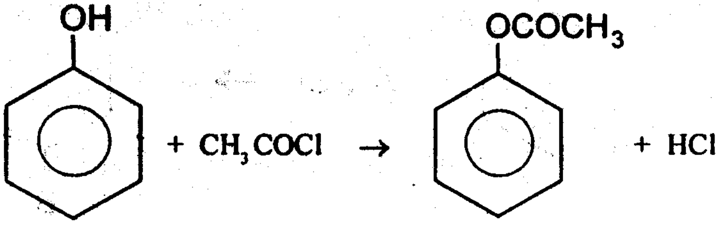


Chloro benzene

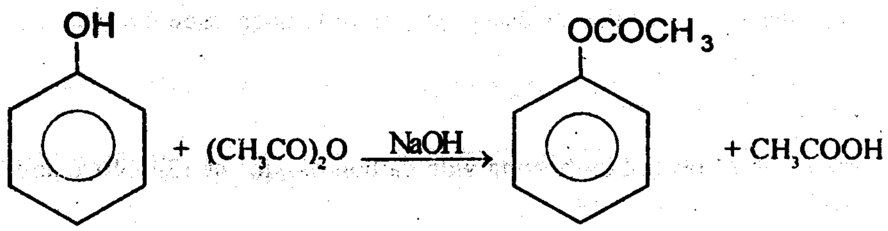


2.2.10.4. Esterification :

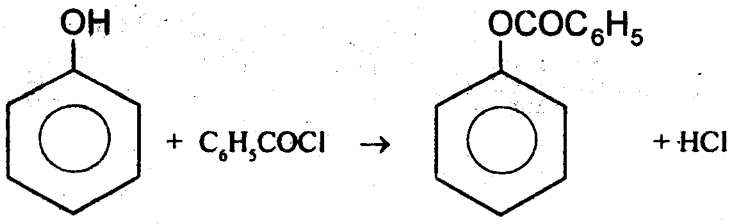
Phenols react with acid chlorides or acid anhydrides to form esters.



Acetyl chloride Phenylacetate



Aceticanhydride



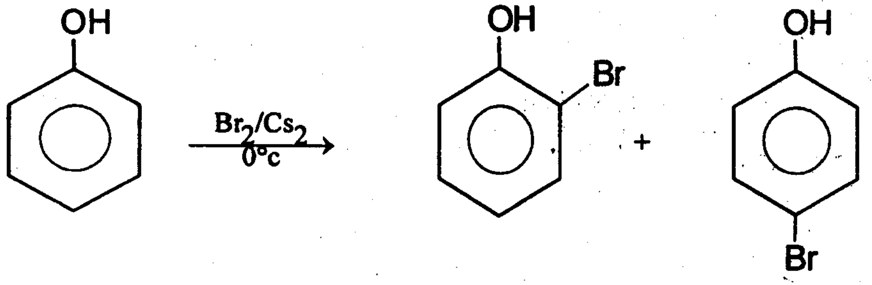
benzoyl chloride

The reaction with benzoyl chloride is known as schotten - Baumann reaction.

2.2.11. Special reactions of Phenols :

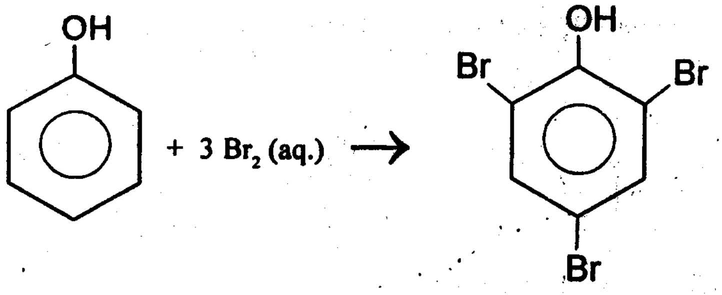
2.2.11.1. Bromination :

a) Phenol reacts with bromine at low temperature in the presence of non - polar solvent forming monobromophenol.



Phenol O- bromophenol P - Bromophenol

b) Phenol reacts with aqueous solution of bromine forming a white precipitate of tribromophenol.

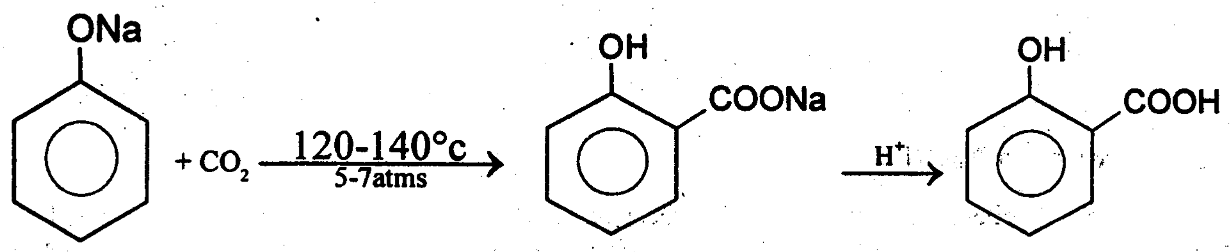


Tri bromophenol

Here water facilitates the ionisation of phenol to phenoxide ion which is more reactive towards electrophilic substitution.

2.2.11.2. Kolb - schmidt reaction :

Sodium salt of phenol on heating with carbon dioxide at 120-140°c under pressure forms ortho hydhoxybenzoic acid (Salicylic acid).

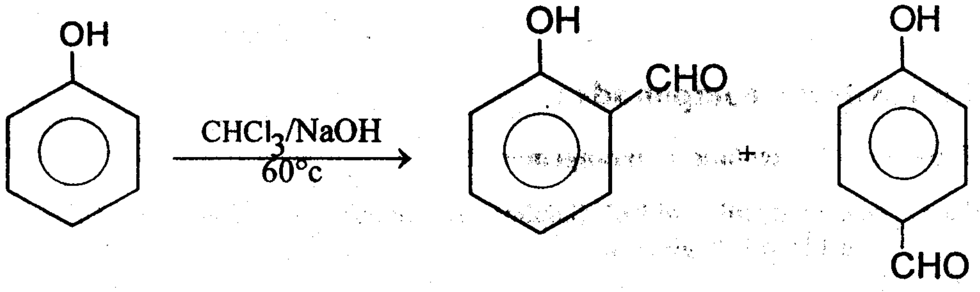


Sodium phenoxide Salicylic acid

A small amount of P- hydroxy benzoic acid is also formed. If potassium salt is used P - isomer is the main product.

2.2.11.3. Reimer - Tiemann reaction :

Phenol when treated with chloroform and sodium hydroxide, an aldehyde group is introduced into the benzene ring.



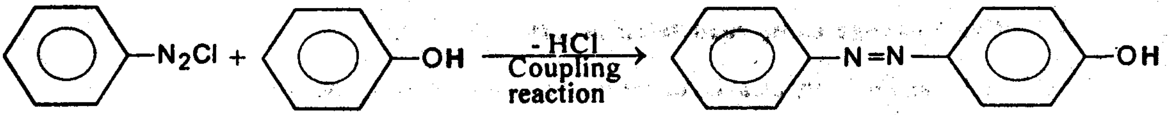
Phenol

O- hydroxybenzaldehyde
(Salicyl aldehyde)

P - hydroxybenzaldehyde

2.2.11.4. Azo Coupling :

Phenol undergoes coupling reaction with benzene diazonium chloride forming an orange azodye.



Benzene diazonium

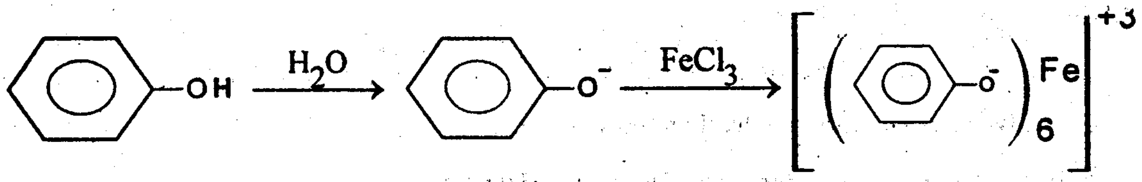
Phenol

P - hydroxyazo benzene (orange dye)

2.2.12. Identification of Phenols :

2.2.12.1. Reaction with Ferric chloride :

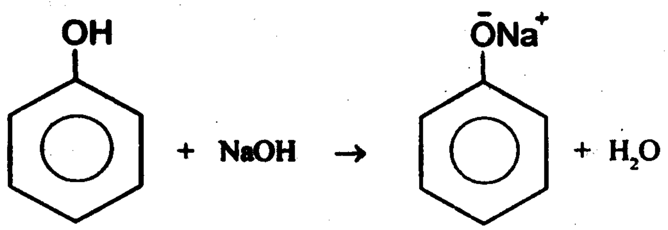
Phenols form coloured complexes with ferric chloride in aqueous solution.



Hex coordinated
Complex (violet)

2.2.12.2. Solubility in NaOH :

Most of the phenols are stronger acids than water. They are weakly acidic when compared to carboxylic acids. A compound which is not soluble in aqueous $NaHCO_3$ but soluble in aqueous NaOH is likely to be phenol.

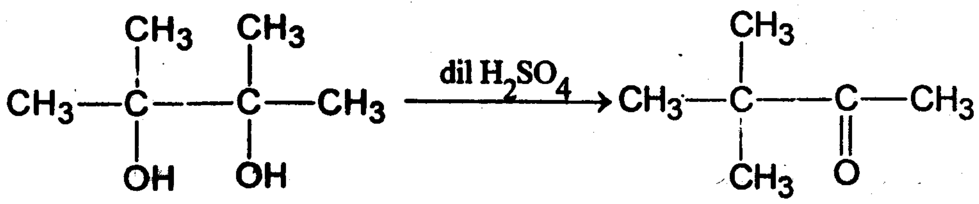


Sodium Phenoxide

2.2.13. Polyhydroxy compounds :

2.2.13.1. Pinacole - Pinacolone rearrangement :

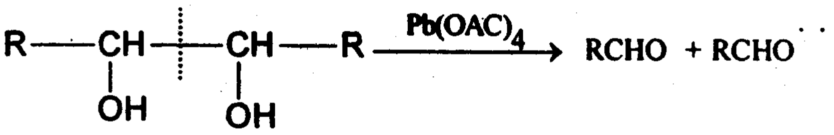
When pinacole is distilled with 6N Sulphuric acid or refluxed with 50% phosphoric acid, pinacolone is formed. It is applicable to 1,2 - glycols.



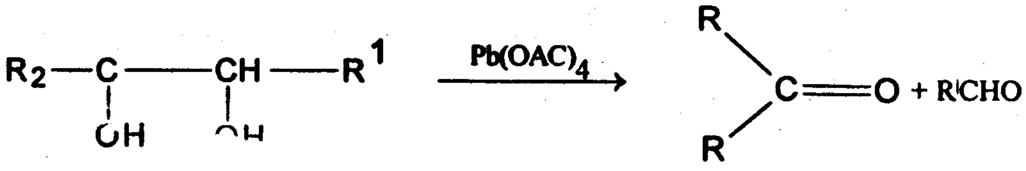
$$CH_3-C(CH_3)(OH)-C(CH_3)(OH)-CH_3 \xrightarrow{\text{dil } H_2SO_4} CH_3-C(CH_3)_2-C(=O)-CH_3$$

2.2.13.2. Oxidative cleavage using lead tetra acetate [Pb (OAC)$_4$] :

1,2 - Glycols can be easily cleaved under mild conditions using lead tetra acetate.



$$R-CH(OH)-CH(OH)-R \xrightarrow{Pb(OAC)_4} RCHO + RCHO$$



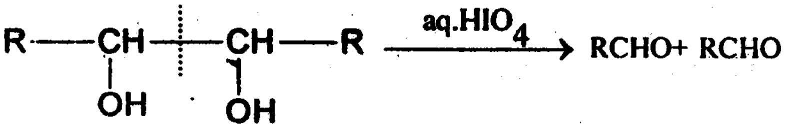
$$R_2-C(OH)-CH(OH)-R^1 \xrightarrow{Pb(OAC)_4} R_2C=O + R^1CHO$$

Cis – glycols react more rapidly than trans - glycols.

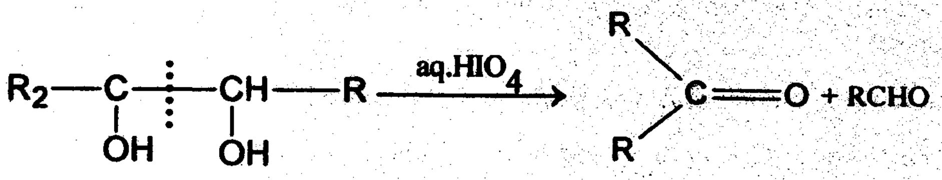
2.2.13.3. Oxidative cleavage using periodic acid (HIO$_4$) :

Vicinal diols and vicinal triols can be selectively cleaved using periodic acid.

i) Oxidation of Vicinal - diols to carbonyl compounds.



$$R-CH(OH)-CH(OH)-R \xrightarrow{aq.HIO_4} RCHO + RCHO$$



ii) Oxidation of Vicinal - triols.

$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R^1 \xrightarrow{aq.HIO_4} RCHO + HCOOH + R^1CHO$$

For Glycols, number of C- C bonds cleaved is equal to the number of periodic acid molecules consumed.

2.2.14. Model Questions. :

1. What are alcohols? How are they classified?
2. How do you distinguish primary, secondary and tertiary alcohols?
3. What is an aryl carbinol ? Give an example with preparation?
4. Explain
   a. Kolbe's reaction
   b. Riemer – Tiemann reaction
   c. Pinacol – pinacolone rearrangement
5. a) Explain the methods of preparation of phenol
   b) Phenol behaves as a weak acid but alcohol does not. Why?
6. Write preparation of alcohols from carbonyl compounds
7. How do you convert phenol to salicylaldehyde.
8. What is lucas reagent ? what for it is used ? explain with suitable example.
9. Give the mechanism of esterification of alcohol.
10. Discuss the general method of preparing ethyl alcohol. Explain how it reacts with
    i) RMgx
    ii) PCl_5
11. How P- hydroxy azobenzene is prepared from phenol.

12. What kind of difference is noticed in the oxidation products of primary, secondary and tertiary alcohols.
13. How can you distinguish intermolecular and intramolecular hydrogen bond with two examples ?
14. Phenol has higher boiling point and is more soluble in water than toluene. Explain.
15. Phenols are more acidic than alcohols but less acidic than carboxylic acids. Explain.

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UNIT -II

Lesson –III

ETHERS AND EPOXIDES

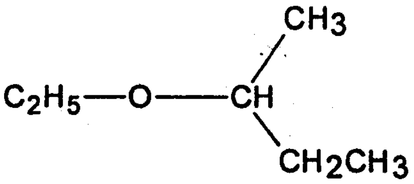
2.3.0 Nomenclature : Preparation by (a) Williamsons synthesis (b) From alkenes by the action of Conc. H_2SO_4. Physical properties - Absence of Hydrogen boding, insolubility in water, low boiling point. Chemical properties – inert nature, action of Conc. H_2SO_4 and HI. Acid and base catalysed ring opening of epoxides – orientation.

2.3.1 Nomenclature :

In IUPAC System, ethers are named as alkoxyalkanes. The larger alkyl group is considered to be the parent alkane.

$CH3 – O – CH_2CH_3$

Methoxy ethane



2 – ethoxybutane.

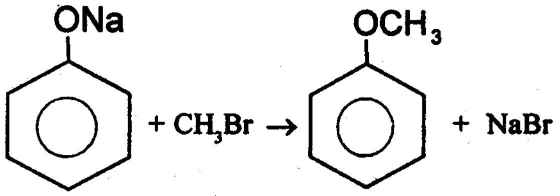
2.3.2 Preparation :

a) Williamson synthesis :

Alkyl halides on heating with sodium or potassium alkoxides or phenoxides form ethers.

$$RONa + R^IX \rightarrow ROR^I + NaX$$

$$C_2H_5ONa + CH_3Br \rightarrow CH_3 – O – C_2H_5 + NaBr$$



Sodium Phenoxide Methyl Phenylether.

This method is also useful for preparation of mixed ethers.

Tertiary alkyl halides undero elimination forming alkenes. So, for preparing unsymmetrical ethers tertiary alkoxide and P – alcohol are used.

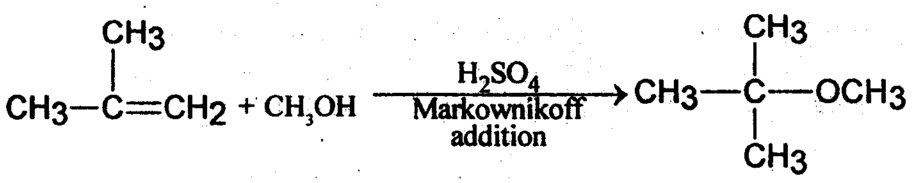
$$(CH_3)_3CONa + CH_3\,CH_2\,Br \rightarrow (CH_3)_3\,C – O – CH_2CH_3 + NaBr$$

Sod. ter butoxide

Here $(CH_3)_3$ CBr and CH_3CH_2O Na gives only alkene.

b) From alkenes :

Alkenes on addition with alcohols in the presence of Conc. H_2SO_4 form ethers.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_3OH \xrightarrow[\text{Markownikoff addition}]{H_2SO_4} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OCH_3$$

With simpler molecules.

$$CH_2 = CH_2 \xrightarrow{H_2SO_4} CH_3CH_2OSO_3H$$

$$CH_3CH_2OSO_3H + CH_3OH \rightarrow CH_3CH_2OCH_3 + HOSO_3H$$

2.3.3 Physical Properties :

a) Absence of hydrogen bonding : (low boiling point)

There is absence of – OH group in ethers. They can not form associated molecules due to the absence of hydrogen bonding. Hence their boiling points are much lower than the corresponding alcohols and nearer to those of respective hydrocarbons.

b) Solubility in water :

The hydroxyl group of water can form hydrogen bond with the oxygen atom of ether. So, They are sparingly soluble in water.

2.3.4. Chemical properties :

2.3.4.1. Inert nature :

a) Ethereal oxygen (C – O – C) :

In ethers, ethereal oxygen (C – O – C) is linked between two carbon atoms. It is comparatively inert . So, ethers are comparatively unreactive. They are as inert as alkanes. The ether linkage is quite stable. Ethers are inert to bases, cold or dilute acids, reducing agents and oxidising agents like aqueous $KMnO_4$.

b) Carbon – oxygen bond : (C-O)

In ethers, carbon – oxygen bond is fairly stable. But it is not stable as carbon – carbon (C- C) linkage. It undergoes cleavage in the presence of a number of reagents.

2.3.4.2. Action of Conc. H_2SO_4 :

a) Ethers form Oxonium salts with Conc. H_2SO_4.

$$(CH_5)_2\,O + H_2SO_4 \rightarrow [(C_2H_5)_2\,OH] + H_2SO_4$$

Ether Oxinium salt

b) Ethers on heating with Conc. H_2SO_4 form alkyl hydrogen sulphates.

$$C_2H_5 - O - C_2H_5 + H_2SO_4 \xrightarrow{Conc.} C_2H_5OH + C_2H_5\,H_2SO_4$$

$$C_2H_5\;OH + H_2SO_4 \rightarrow C_2H_5H_2SO_4 + H_2O$$

2.3.4.3. Action with Hydrogen Iodide :

a) In Cold :

Ethers react with HI forming the corresponding alkyl iodide and alcohol.

$$C_2H_5 - O - C_2H_5 + HI \xrightarrow{Cold} C_2H_5OH + C_2H_5I.$$

In the case of mixed ethers the iodine atom is always attached to smaller alkyl group due to less steric hinderance. It follows SN^2 mechanism.

$$CH_3 - O - C_2H_5 + 2HI \rightarrow CH_3I + C_2H_5OH$$

Propyl isopropyl ether, propyl tertiary butyl ethers are exceptions. They follow SN^1 mechanism.

$$CH_3CH_2CH_2 - O - CH(CH_3)_2 + HI \rightarrow CH_3CH_2CH_2OH + (CH_3)_2CHI$$

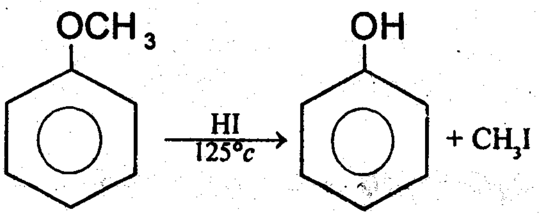
b) In hot :

Ethers on heating with HI form two molecules of alkyl iodide.

$$C_2H_5 - O - C_2H_5 + 2HI \xrightarrow{heat} 2C_2H_5I + H_2O$$

The reaction of ethers with HI forms basis of Ziesel method for the detection and estimation of alkoxy group in a compound.

In alkylaryl ethers only alkyl iodide and phenol are formed.



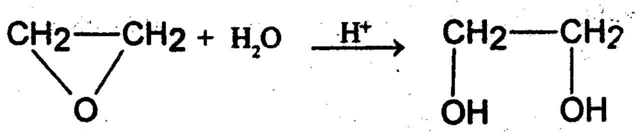
Anisole

Diphenyl ether does not give phenyl iodide even with excess of HI.

2.3.5 Ring opening of epoxides and orientation :

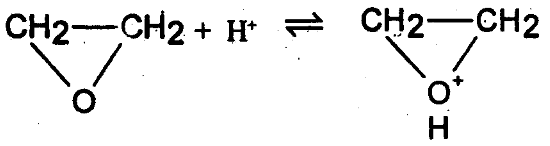
a) Acid catalysed ring opening and orientation :

When an epoxide is treated with a nucleophile like H_2O, ROH in the presence of an acid, it undergoes C – O cleavage.

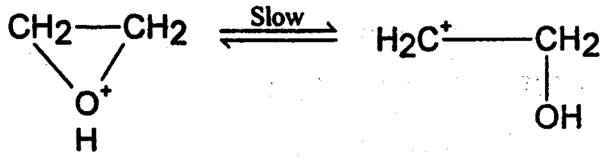


Mechanism :

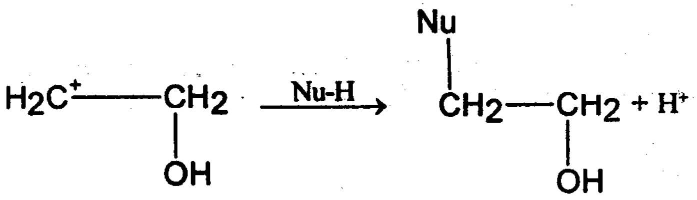
i) Protanation of epoxide.



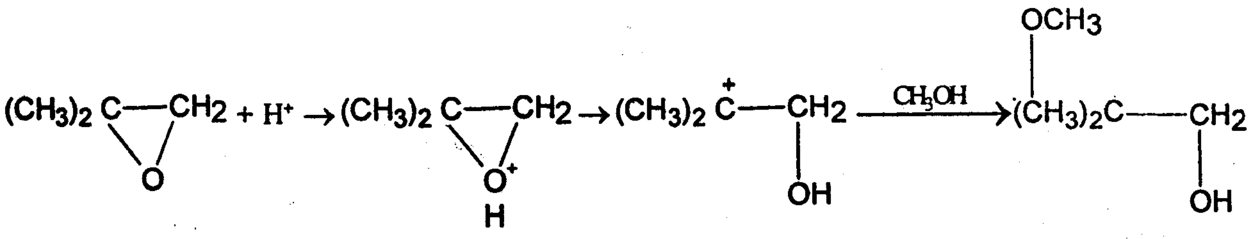
ii) Formation of carbocation.



iii) Nucleophilic attack by SN^1 mechanism.



In acid catalysed ring opening of unsymmetrical epoxides, ring opening is favoured in that direction which gives more stable carbocation.

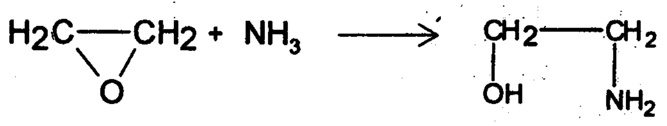


Orientation :

This is a stereo selective reaction. The 1,2 – diols formed correspond to anti addition to the carbon – carbon double bond.

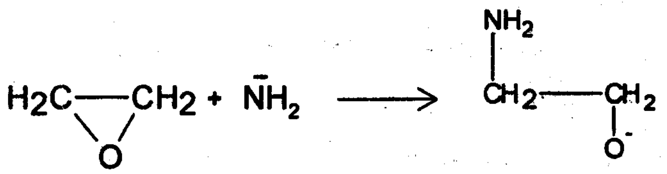
b) Base catalysed ring opening and orientation :

When an epoxides is treated with a strong nucleophilic reagent like NH_3, Amine the epoxide undergoes C – O cleavage.

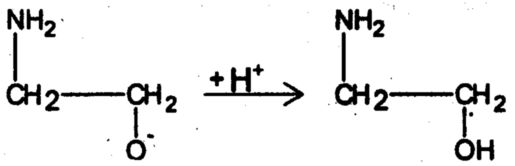


Mechanism :

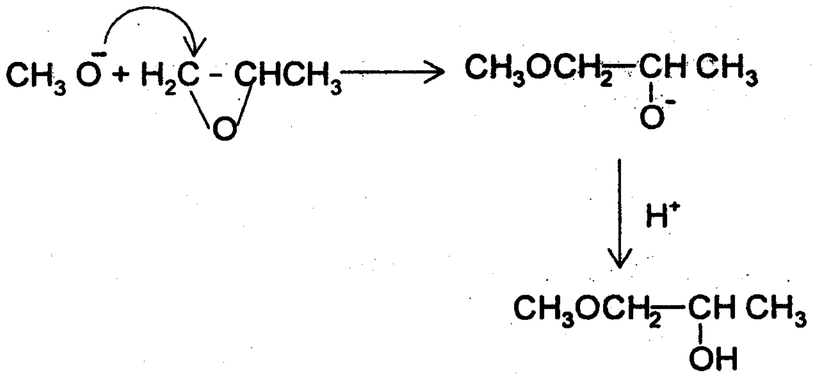
i) In this case the non – protonated epoxides is attacked by the strong nuclephile forming alkoxide ion.



ii) The alkoxide ion is then protonated forming the product.



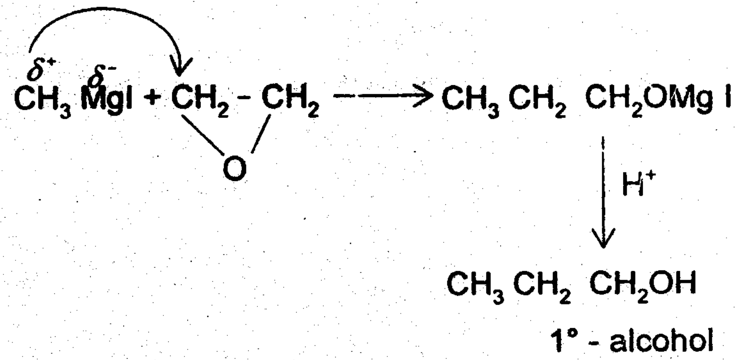
In base catalysed Unsymmetrical epoxides, the nucleophile attacks the less substituted carbon atom which is less hindered forming alkoxide ion which is then protonated.



1 - ethoxy - 2- Propanol

Action with Grignard reagent :

Grignard reagent react with ethylene oxide forming P – alcohol.



2.3.6. Model Questions :

1. Write different methods of preparation of ethers.
2. What is Williamson synthesis.
3. Discuss the reaction of HI with simple and mixed ethers in different conditions.
4. The boiling point of diethyl ether is considerably lower than that of ethyl alcohol. Explain.
5. Discuss acid and base catalysed ring opening of epoxides.

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UNIT - II

Lesson – IV

CARBONYL COMPOUNDS.

2.4.0

Nomenclature of aliphatic and aromatic carbonyl compounds and isomerism. Synthesis of aldehydes and ketones from acid chlorides. by using 1,3 – dithianes, nitriles and from carboxylic acids. Special methods for preparing aromatic aldehydes and ketones by –

a) Oxidation of arenes

b) Hydrolysis of benzyl halides.

Physical properties – absence of hydrogen bonding. Keto – enol tautomerism, polarisability of carbonyl groups. Reactivity of carbonyl group in aldehydes and ketones. Chemical reactivity – i) Addition of a) $NaHSO_3$ b) HCN C) RMgX d) NH_3 e) RNH_2 f) NH_2OH g) Ph $NHNH_2$ h) 2,4- DNP, Schiff's bases, addition of H_2O to form hydrate (unstable), comparison with chloral hydrate (Stable), addition of alcohols hemiacetal and acetal formation. Halogenation using PCl_5 with mechanism. Base catalysed reactions- with particular emphasis on Aldol, Cannizaro reaction, perkin reaction, Benzoin condensation, haloform reaction. Knovenagel condensation. Oxidation reaction – $KMnO_4$, Oxidation and autoxidation, reduction – catalytic hydrogenation, clemensen's reduction, Wolf – Kishner reduction, MPV reduction, reduction with LAH, $NaBH_4$ Analysis – 2,4 – DNP test, Tollen's test, Fehling's test, Schiff's test, haloform test (with equations). Introduction α, β - unsaturated carbonyl compounds.

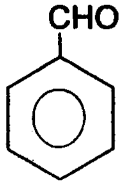
2.4.1 Nomenclature of aliphatic and aromatic carbonyl compounds :

a) Aldehydes : (R– CHO)

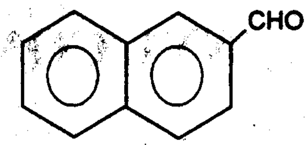
In IUPAC system aliphatic aldehydes are named as alkanals.

Formula	Common name	IUPAC name
H–CHO	formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$CH_3CH_2\ CH_2CHO$	n- butanaldehyde	Butanal
$C_6H_5CH_2\ CHO$	Phenyl acetaldehyde	Phenylethanal

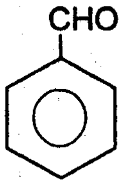
Aldehydes in which - CHO group is directly attached to the ring are named by adding the suffix carbaldehyde.



Benzene carbaldehyde
(common name : Benzaldehyde)



2- Naphthalene Carbaldehyde



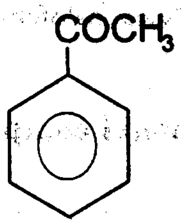
Cyclohexane Carbaldehyde

b) Ketones : (RCOR)

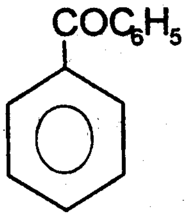
In IUPAC system, ketones are named as alkanones.

Formula	Common name	IUPAC name
$CH_3CH_2COCH_3$	Ethylmethyl ketone	Butanone
CH_3COCH_3	Acetone	Propanone
$C_6H_5CH_2COCH_3$	Benzyl methyl ketone	1-Phenyl-2-Propanone

Ketones in which >CO group is attached to the benzene ring are named as phenones.



Acetophenone



Benzophenone

2.4.2. Isomerism :

a) Aldehydes :

Aldehydes show chain and functional isomerism.

Chain isomers : $CH_3CH_2CH_2CHO$ $(CH_3)_2CHCHO$
n- butanal Isobutanal

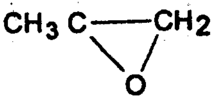
Functional isomers : CH_3CH_2CHO CH_3COCH_3
Propanal Acetone

$CH_2 = CH_2CH_2OH$

Allylalchohol

$CH_2 = CHOCH_3$

Methylvinyl ether



Propyleneoxide

b) Ketones : Ketones show chain, functional and metamerism.

Chain isomers : $CH_3CH_2COCH_3$ $(CH_3)_2CH_2COCH_3$

Methyl propylketone Methylisopropylketone

Metamers : $CH_3CH_2CH_2COCH_3$ $CH_3CH_2COCH_2CH_3$

Methyl propylketone diethylketone

2.4.3 Synthesis of Aldehydes and ketones :

2.4.3.1. From acidchlorides :

a) Rosenmund reduction :

Acid chlorides are reduced to aldehydes with hydrogen in the presence of palladium catalyst over barium sulphate.

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

To check further reduction of aldehyde the catalyst mixture is poisoned by adding a small amount of sulphur or quinoline. Formaldehyde and ketones cannot be prepared by this method.

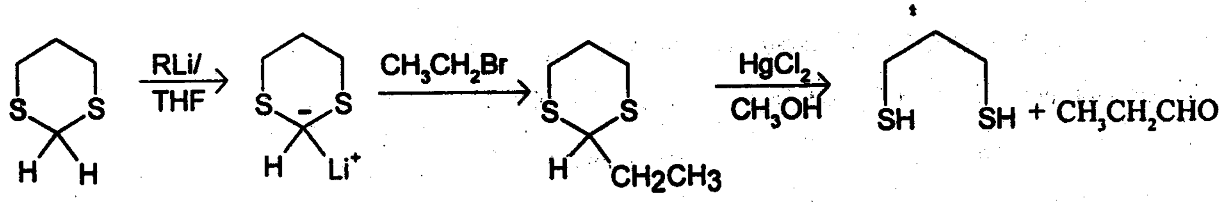
b) Acid Chlorides react with organocadmium compounds in the presence of dry ether forming ketones

$$2R'COCl + R_2Cd \xrightarrow[ether]{dry} 2\,R'COR + CdCl_2$$

$$2CH_3COCl + (C_2H_5)_2\,Cd \xrightarrow[ether]{dry} 2CH_3COC_2H_5 + CdCl_2$$

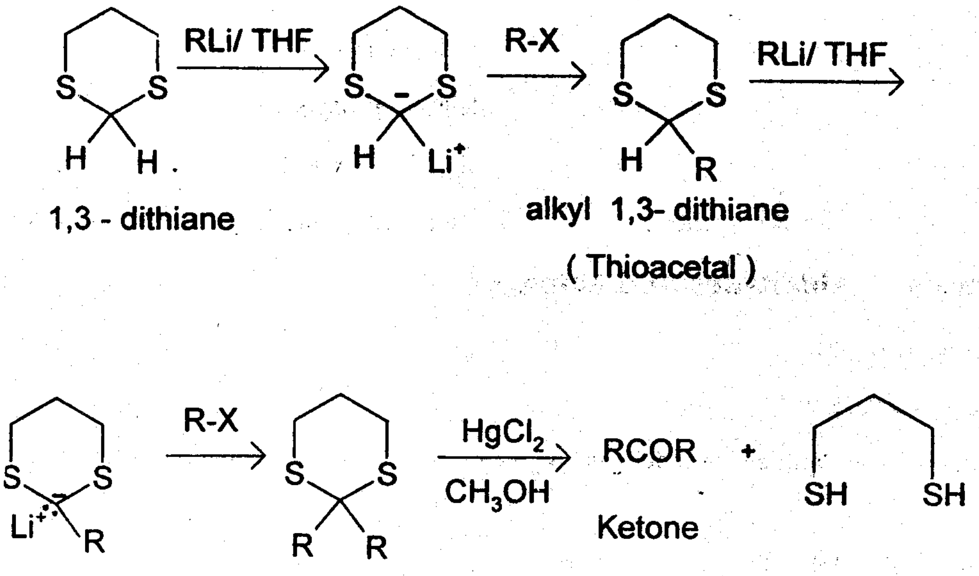
2.4.3.2. From 1,3 – dithianes :

a) 1,3– dithiane reacts with alkyllithum followed by alkyl 1,3– dithiane (thioacetal) which on hydrolysis with $HgCl_2$ in methanol form aldehyde.



1,3 - dithiane Thioacetal Aldehyde

b) 1,3 – dithiane reacts with excess of alkyllithium followed by alkyl halide forming dialkyl 1,3– dithiane (Thioketal) which on hydrolysis with $HgCl_2$ in methanol form aldehyde.

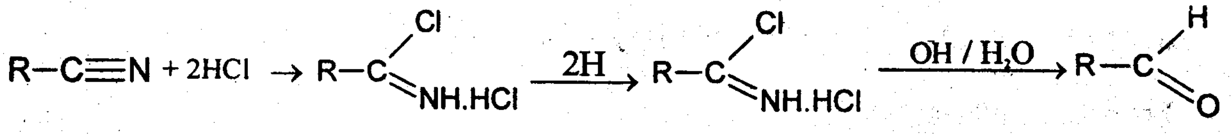


dialkyl 1,3 - dithiane
(Thioketal)

2.4.3.3. From Nitriles :

a) Stephen's method :

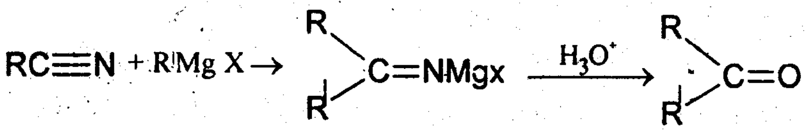
Alkyl or aryl cyanides on reduction with stannous chloride and hydrochloric acid in ether form aldehydes.



b) Hydrogen cyanide reacts with Grignand reagents followed by hydrolysis form aldehydes.

$$HC\equiv N + RMg\,X \rightarrow RCH = NMgx \xrightarrow{H_3O^+} RCHO$$

c) Alkyl cyanides react with Grignard reagents followed by hydrolysis form ketones.



$$RC\equiv N + R^IMg\,X \rightarrow \begin{matrix}R\\ \\ R^I\end{matrix}\!\!>C=NMgx \xrightarrow{H_3O^+} \begin{matrix}R\\ \\ R^I\end{matrix}\!\!>C=O$$

2.4.3.4. From carboxylic acids :

a) Calcium salt of the carboxylic acid on dry distillation with calcium formate forms aldehyde.

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} 2RCHO + 2CaCO_3$$

b) Calcium salt of carboxylic acid on dry distillation forms ketone.

$$(RCOO)_2Ca \xrightarrow{\Delta} RCOR + CaCO_3$$

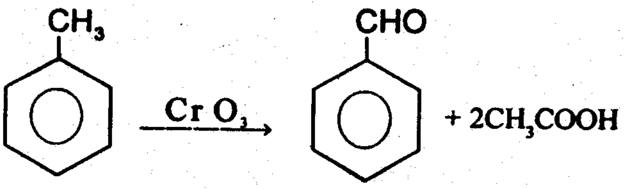
2.4.4. Special methods for the preparation of aldehydes and ketones :

2.4.4.1. Oxidation of arenes :

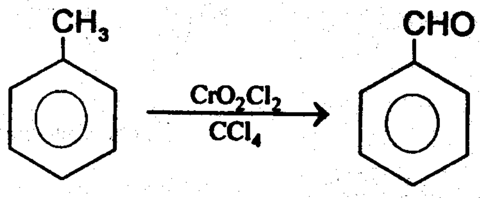
a) Aldehydes :

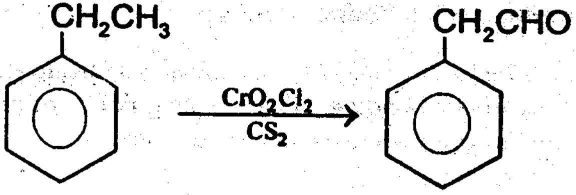
(i) Arenes with Alkyl side chain on the aromatic ring on oxidation with chromium trioxide and acetic anhydride give aldehyde.

The function of acetic anhydride is to prevent further oxidation of aldehyde to carboxylic acid.



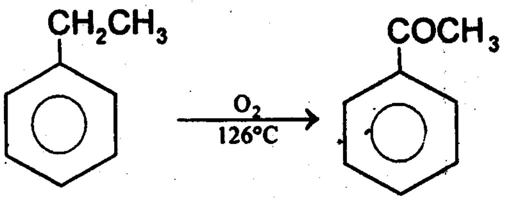
ii) **Etard's reaction :** Alkyl benzenes on oxidation with chromyl chloride in CCl_4 form aldehydes.





b) Ketones :

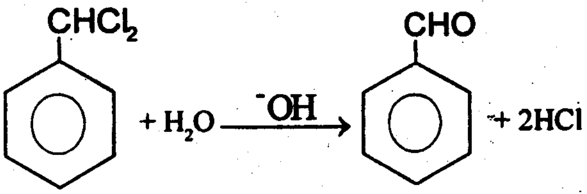
Ethyl benzene on oxidation with air at 126°c under pressure in the presence of manganese acetate catalyst gives acetophenone.



2.4.4.2. Hydrolysis of Benzal halides :

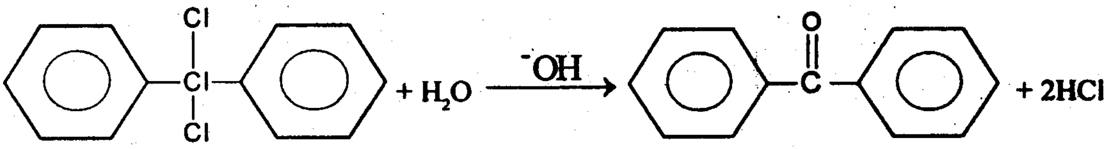
a) Aldehydes :

Benzal chloride on hydrolysis with alkali gives benzaldehyde.



b) Ketones :

Geminal dichloride on hydrolysis with alkali gives benzophenone.



Benzophenone

2.4.5. Physical Properties :

4.5.1. Absence of hydrogen bonding : (Boiling Points)

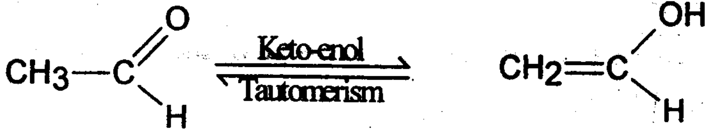
Examination of the structures of aldehydes and ketones indicate that they lack ' OH' group for molecular association through hydrogen bonding. Hence boiling points of aldehydes and ketones are less when compared to the corresponding alcohols and carboxylic acids.

4.5.2. Keto – enol Tautomerism :

All carbonyl compounds containing α – hydrogen atom undergo keto - enol tautomerism.

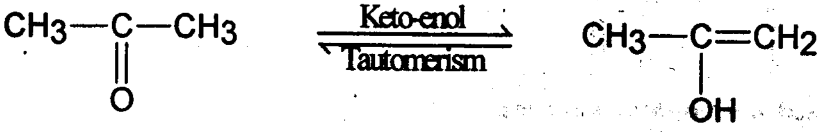
Interconvertable change in nature of the functional group due to the position of a mobile atom is called Tautomerism. In this if one is keto form and the other is enol form, it is called Keto - enol tautomerism.

Ex :



Acetaldehyde
Ketoform

Vinyl alcohol
Enol form



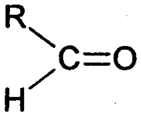
Ketoform
(Acetone)

enol form

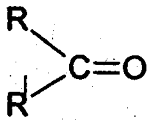
The structure in which – OH is attached to a doubly bonded carbon is called ' enol ' (ene + ol).

2.4.5.3. Polarisability of carbonyl group :

Aldehydes and ketones, both contain carbonyl group (>C = O).



Aldehyde

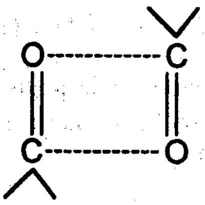


Ketone

In carbonyl group, electronegativity of oxygen is 3.5. electronegativity of carbon is 2.5. So, oxygen is more electronegative than carbon and π - electron cloud is displaced more towards oxygen. This cause polarisation of the carbonyl group.

$$>\overset{\delta^+}{C}=\overset{\delta}{O}$$

The polar nature of carbonyl group in aldehydes and ketones is suported by their large dipolemoments. The polar nature of carbonyl group causes intermolecular attraction i.e. dipole - dipole attraction in aldehydes and ketones.



Hence boiling points of aldehydes and ketones are high when compared to the corresponding alkanes.

2.4.5.4 Reactivity of carbonyl group in aldehydes and ketones (Chemical reactivity) :

a) Carbonyl group undergoes electromeric effect. So, nucleophilic addition takes place.

$$>\overset{\delta^+}{C}=\overset{\delta^-}{O} \rightleftharpoons >\overset{+}{C}-\overset{-}{O}$$

Electomeric effect in carbonyl group

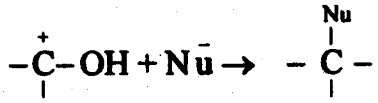
Mechanism :

a) Acid catalysed nucleophilic addition :

1) Formation of carbonium ion .

$$>C=O+H^+ \rightarrow -\underset{|}{\overset{+}{C}}-OH$$

2) Nucleophilic attack.

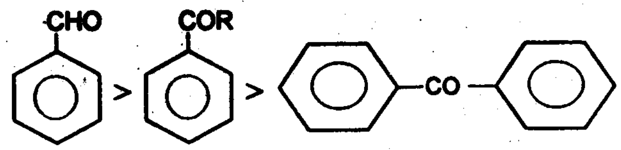


$$-\underset{|}{\overset{+}{C}}-OH+N\bar{u} \rightarrow -\underset{|}{\overset{\overset{Nu}{|}}{C}}-$$

b) Alkyl groups are electron releasing groups. They decrease the activity of carbonyl group. So, aldehydes are more reactive than ketones.

c) Benzene ring decreases the activity of carbonyl group due to mesomeric effect. So, aliphalic carbonyl compounds are more reactive than aromatic carbonyl compounds.

HCHO > RCHO> RCOR >

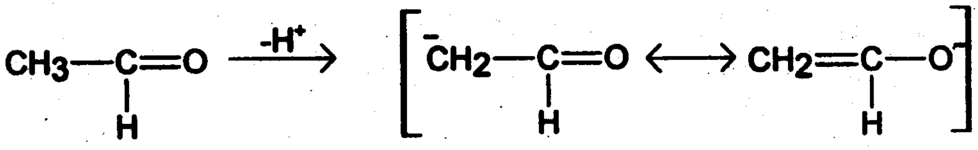


d) Electron with drawing group increases the activity of carbonyl compounds due to inductive effect.

∴ Chloroacetaldehye is more reactive than acetaldehyde.

$$ClCH_2CHO > CH_3CHO$$

e) **Activity of α – hydrogen** : In carbonyl compound α – hydrogen is more active. It can be removed easily because the intermediate ion has resonance stablisation.

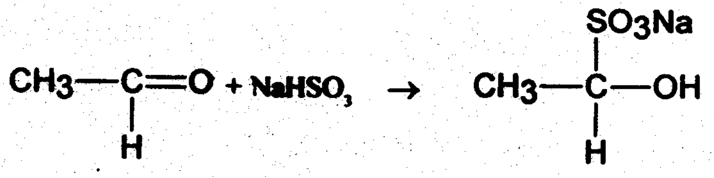


$$CH_3-\underset{\underset{H}{|}}{C}=O \xrightarrow{-H^+} \left[\overset{-}{C}H_2-\underset{\underset{H}{|}}{C}=O \longleftrightarrow CH_2=\underset{\underset{H}{|}}{C}-O^-\right]$$

2.4.5.5 Chemical properties : (Nucleophilic Addition reactions)

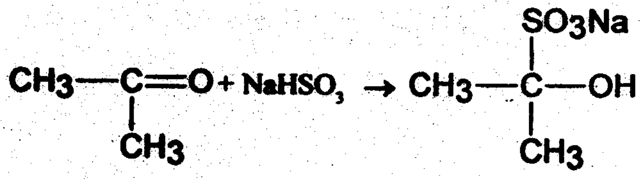
a) Adition of Sodium bisulphite :

Aldehydes and ketones react with sodium bisulphite. Crystalline addition products are formed.



$$CH_3-\underset{H}{C}=O + NaHSO_3 \rightarrow CH_3-\underset{H}{\overset{SO_3Na}{C}}-OH$$

Acetaldehyde Acetaldehyde sodium sulphite

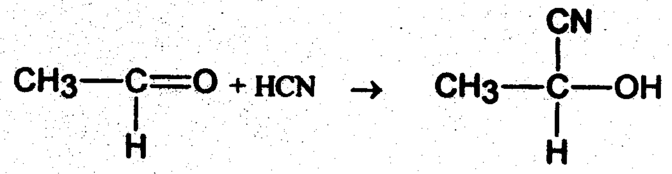


$$CH_3-\underset{CH_3}{C}=O + NaHSO_3 \rightarrow CH_3-\underset{CH_3}{\overset{SO_3Na}{C}}-OH$$

Acetone Acetone sodium sulphite

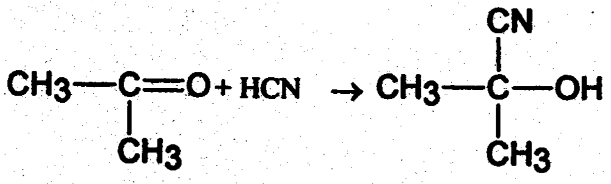
b) Addition of hydrogen cyanide :

Aldehydes and ketones react with hydrogen cyanide in the presence of a base forming cyanohydrins.



$$CH_3-\underset{H}{C}=O + HCN \rightarrow CH_3-\underset{H}{\overset{CN}{C}}-OH$$

Acetaldehyde Cyanohydrin

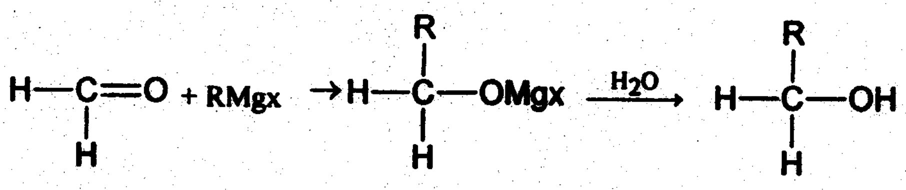


$$CH_3-\underset{CH_3}{C}=O + HCN \rightarrow CH_3-\underset{CH_3}{\overset{CN}{C}}-OH$$

Acetone Acetone Cyanohydrin

c) Addition of Grignard reagents :

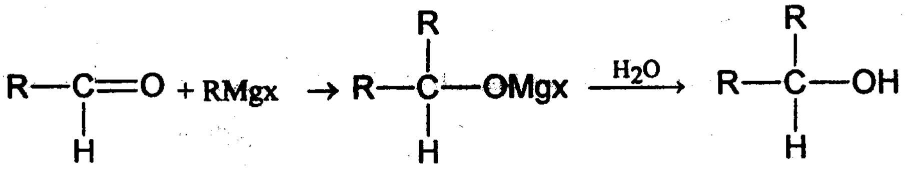
i) Formaldehyde reacts with Grignard reagents forming P- alcholols.



$$H-\underset{H}{C}=O + RMgx \rightarrow H-\underset{H}{\overset{R}{C}}-OMgx \xrightarrow{H_2O} H-\underset{H}{\overset{R}{C}}-OH$$

Formaldehyde P– alcohol

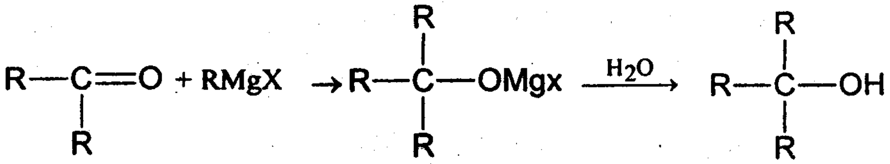
ii) Aldehydes except formaldehyde reacts with Grignard reagent forming s-alcohol



$$\mathrm{R-\underset{H}{C}=O + RMgx \rightarrow R-\overset{R}{\underset{H}{C}}-OMgx \xrightarrow{H_2O} R-\overset{R}{\underset{H}{C}}-OH}$$

S– alcohol

iii) ketones react with Grignard reagent forming t- alcohols.

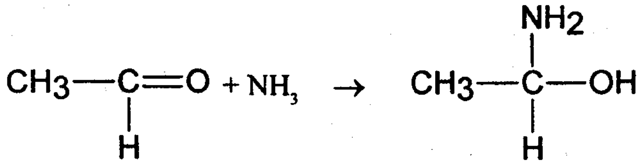


$$\mathrm{R-\underset{R}{C}=O + RMgX \rightarrow R-\overset{R}{\underset{R}{C}}-OMgx \xrightarrow{H_2O} R-\overset{R}{\underset{R}{C}}-OH}$$

t– alcohol

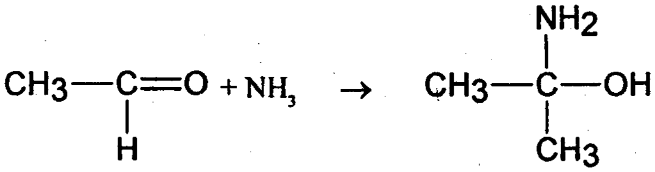
d) Addition with ammonia :

i) Aldehydes and ketones react with ammonia forming addition products.



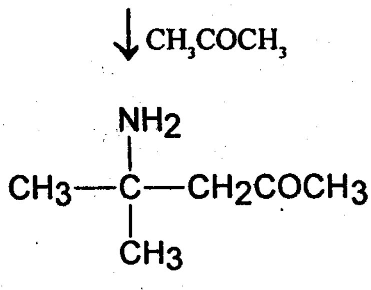
$$\mathrm{CH3-\underset{H}{C}=O + NH_3 \rightarrow CH3-\overset{NH2}{\underset{H}{C}}-OH}$$

Acetaldehyde ammonia



$$\mathrm{CH3-\underset{H}{C}=O + NH_3 \rightarrow CH3-\overset{NH2}{\underset{CH3}{C}}-OH}$$

Acetone ammonia

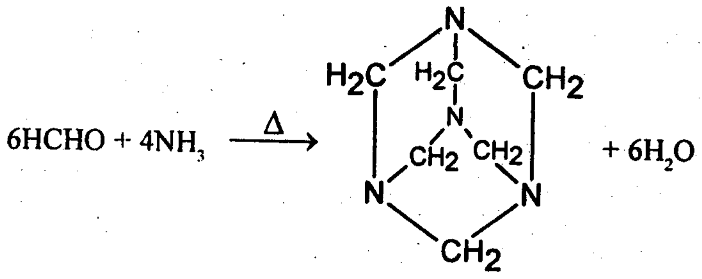


$$\mathrm{\downarrow CH_3COCH_3}$$

$$\mathrm{CH3-\overset{NH2}{\underset{CH3}{C}}-CH2COCH3}$$

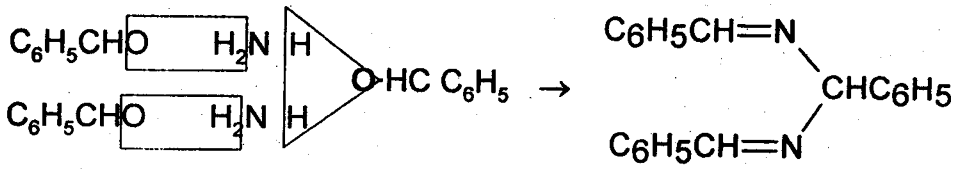
Diacetone amine

ii) 40% solution of formaldehyde reacts with ammonia forming hexa methylene tetramine.



hexamethylene
tetramine

iii) Benzaldehyde reacts with ammonia forming hydrobenzamide



hydrobenzamide

e) Addtion with amines :

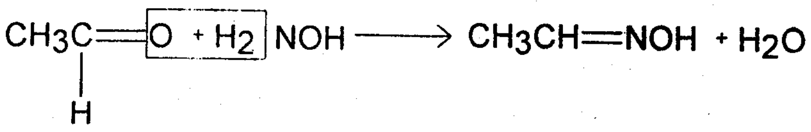
Carbonyl compounds react with p - amines forming Schiff's bases.

amine Schiff's base

2.4.5.6 Action with ammonia derivatives :

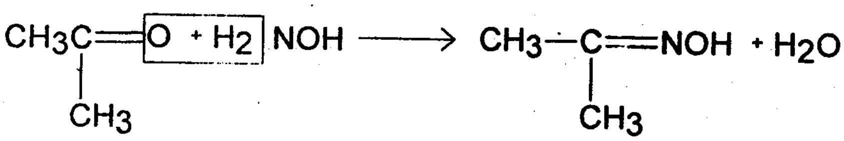
a)Action with hydrazine :

Aldehydes and ketones react with hydroxylamine forming oximes.



$$\underset{\substack{|\\ H}}{CH_3C}=\boxed{O + H_2}NOH \longrightarrow CH_3CH{=}NOH + H_2O$$

Acetaldoxime

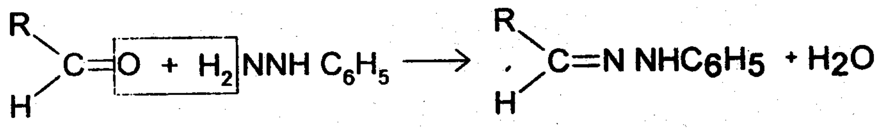


$$\underset{\substack{|\\ CH_3}}{CH_3C}=\boxed{O + H_2}NOH \longrightarrow CH_3-\underset{\substack{|\\ CH_3}}{C}{=}NOH + H_2O$$

Acetoneoxime

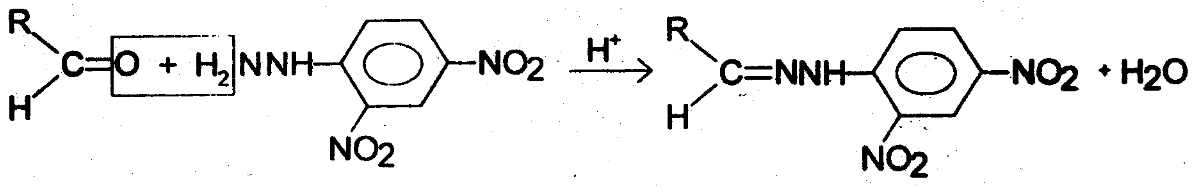
b) Action with phenyl hydrazine :

Aldehydes and ketones react with phenylhydrazine forming phenylhydrazone.



c) Action with 2,4 - dinitro phenylhydrazine (2,4-DNP) :

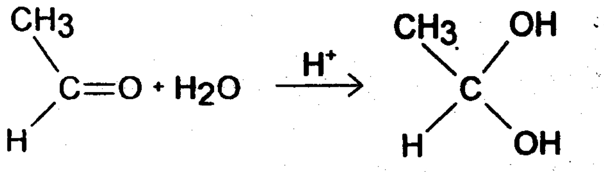
Aldehydes and ketones react with 2,4 - DNP forming yellow or red preeipitate of 2,4-dinitrophenyl hydrazone. It is used as qualitative test for the detection of aldehyde or ketone.



2,4 DNP

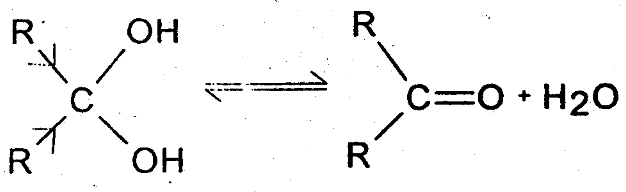
2.4.5.7 Addition of Water : (Hydration)

Aldehydes and ketones on hydration in the presence of acid or base form hydrates (gem-diols).



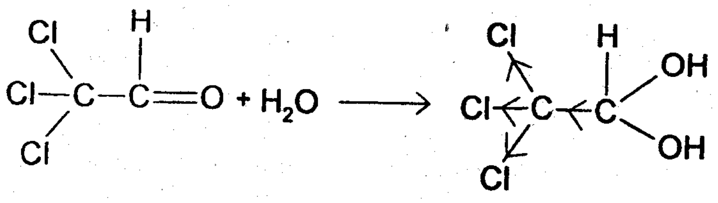
When two -OH group are attacthed to the same carbon, the compund should be unstable and should lose a molecule of water.

The stability of the hydrate decreases with the increase of electron donor groups like alkyls.



When electron withdrawing groups are introduced stability of the hydrate increases due to – I effect.

Ex : Chloral hydrate.



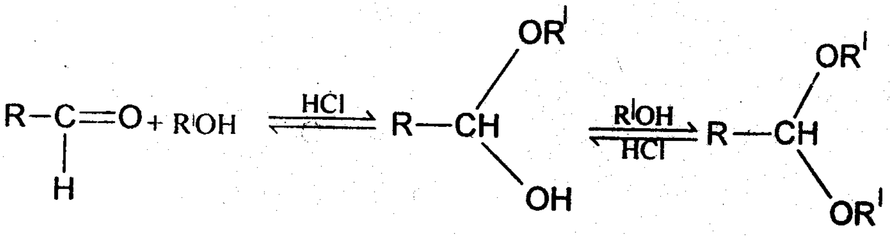
Chloral

Chloral hydrate stable

Here – Cl is electron with **drawing group.**

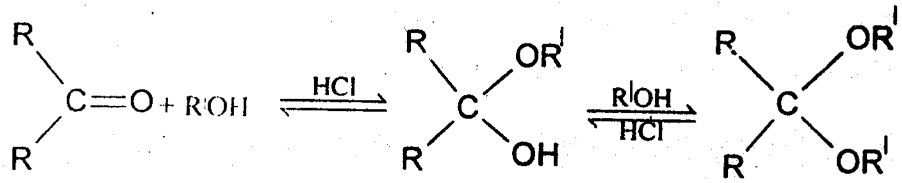
2.4.5.8. Addition of alcohols : (Formation of hemiacetals and acetals)

a) Aldehydes react with alcohols forming hemiacetals. Hemiacetal reacts with another molecule of alcohol forming acetal.



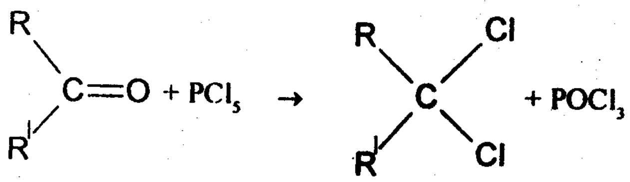
Hemiacetal has a – OH and a – OR group attached to the same carbon. Acetal has two – OR groups attached to the same carbon. Both compounds contain an ether linkage.

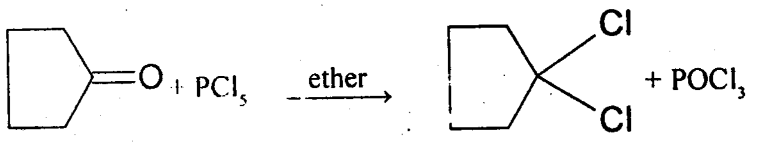
b) Ketones react with alcohol in the presence of HCl forming hemiketals and ketals.



2.4.5.9. Halogenation with PCl_5 :

Aldehydes and ketones react with phosphorus pentachloride forming dihalides.





Cyclopentanone

2.4.5.10 : Base Catalysed reactions (Carbanion addition to carbonyl groups)

a) Cannizzaro reaction :

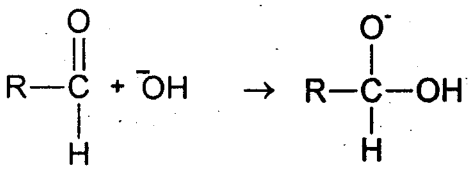
In the presence of concentrated alkali aldehydes and ketones without α – hydrogen undergo self oxidation and self reduction forming acids and alcohols.

$$2HCHO \xrightarrow{NaOH} HCOONa + CH_3OH$$

$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

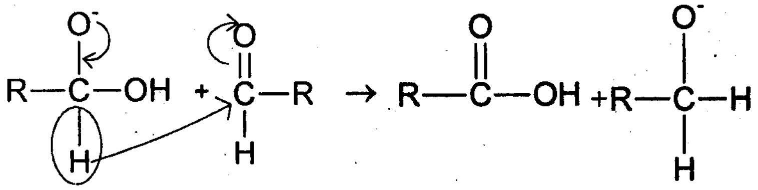
Mechanism :

(i) Hydroxide ion addition :



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}} + {}^{-}OH \rightarrow R-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

(ii) Transfer of hydride ion :



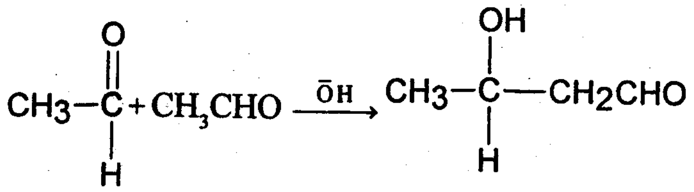
$$R-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH + \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{C}}-R \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R-\overset{\overset{\displaystyle O^{-}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

(iii) Proton transfer :

$$RCOOH + RCH_2O^{-} \rightarrow RCOO^{-} + RCH_2OH$$

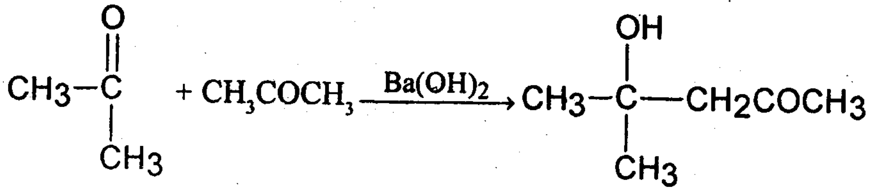
b) Aldol condensation :

In the presence of concentrated alkali aldehydes and ketones with α – hydrogen undergo aldol condensation forming β – hydroxy carbonyl compounds.



$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}} + CH_3CHO \xrightarrow{\bar{O}H} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO$$

Acetaldol.



$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}} + CH_3COCH_3 \xrightarrow{Ba(OH)_2} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2COCH_3$$

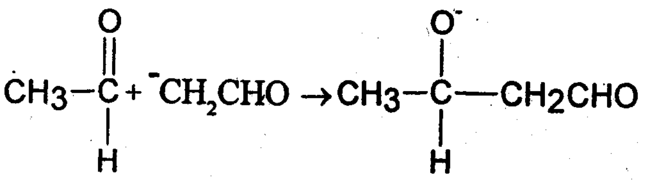
diacetone alcohol.

Mechanism :

(i) Formation of Carbanion :

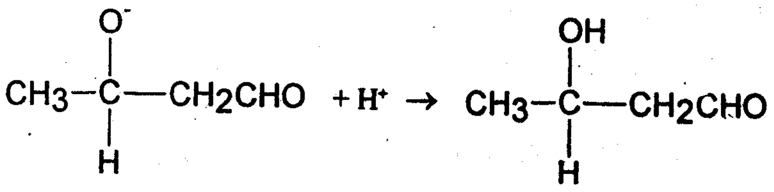
$$CH_3CHO \xrightarrow{\bar{O}H} {}^{-}CH_2CHO$$

(ii) Carbanion addition :



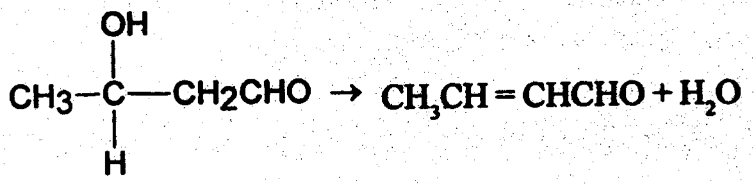
$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}} + {}^{-}CH_2CHO \rightarrow CH_3-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO$$

(iii) Proton addition :



$$CH_3-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO + H^+ \rightarrow CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO$$

(iv) Dehydration :

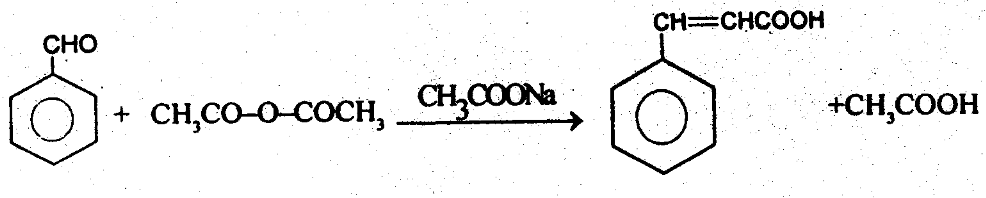


$$CH_3-\underset{H}{\overset{OH}{C}}-CH_2CHO \rightarrow CH_3CH=CHCHO+H_2O$$

Crotonaldehyde.

C) Perkin reaction :

In the presence of sodium acetate, aromatic aldehydes react with acetic anhydride forming α, β– unsaturated acids.



benzaldehyde

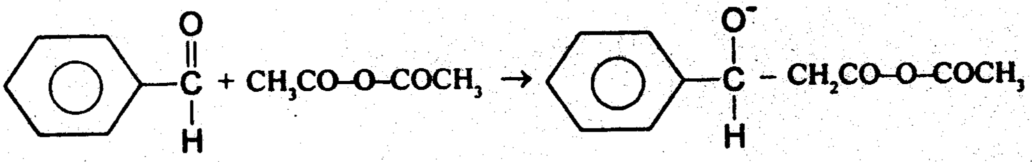
Cinnamic acid

Mechanism :

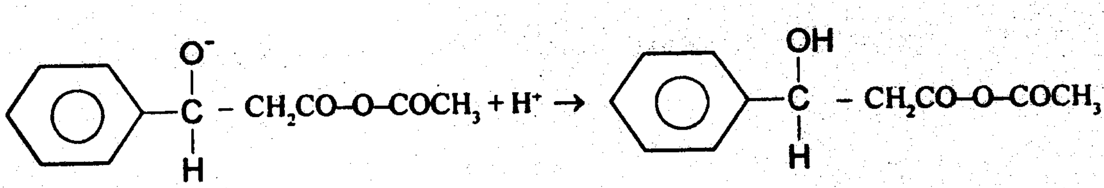
(i) Formation of Carbanion :

$$CH_3CO-O-COCH_3 \xrightarrow{CH_3COO^-} {}^-CH_2CO-O-COCH_3$$

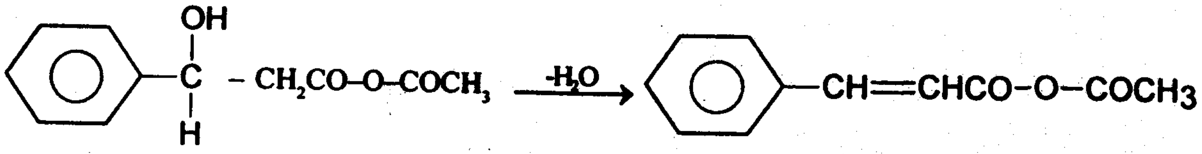
(ii) Carbanion addition :



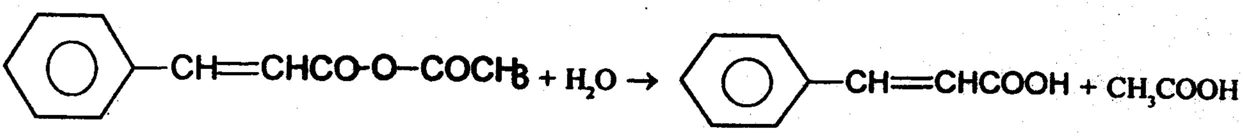
(iii) Proton addition :



(iv) Dehydration :

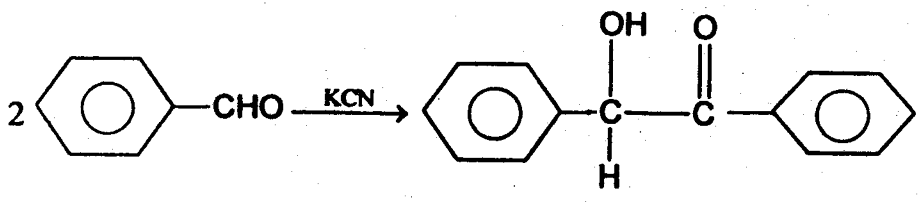


(v) Hydrolysis :



d) Benzoin condensation :

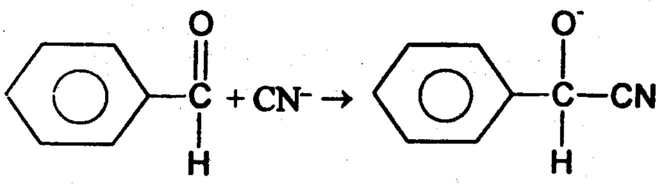
In the presence of alkalicyanide, aromatic aldehydes undergo benzoin condensation forming α-hydroxy ketones.



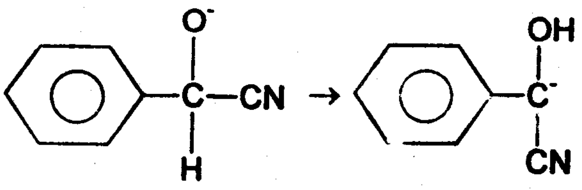
benzaldehyde benzoin

Mechanism :

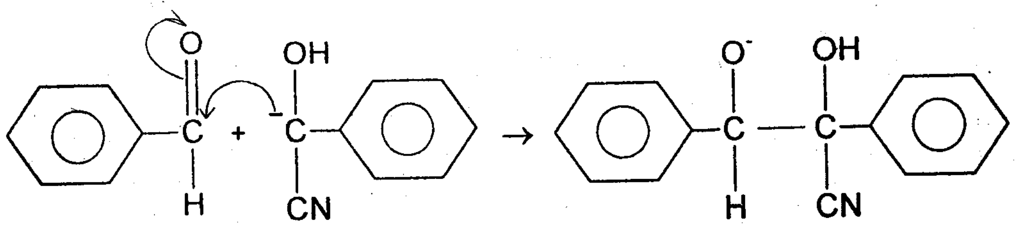
(i) Cyanide ion addition :



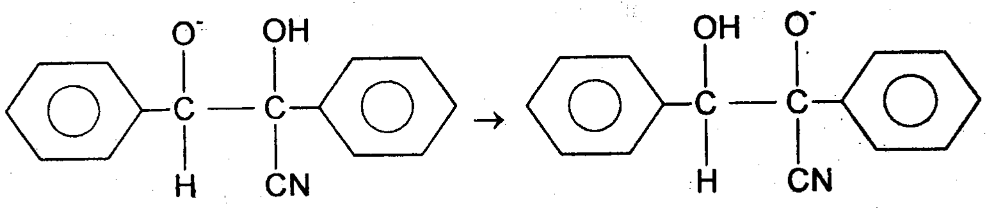
(ii) Formation of carbanion (proton shift) :



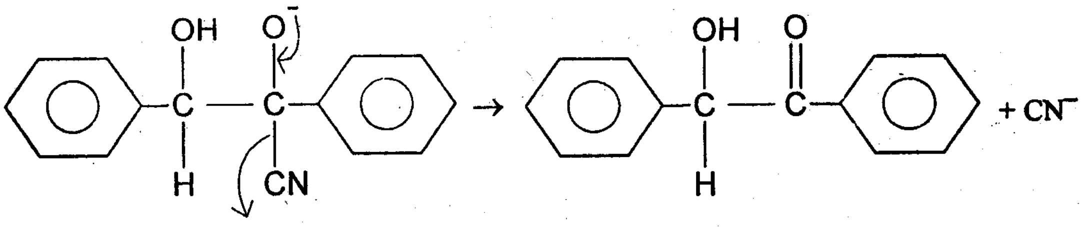
(iii) Carbanion attack :



(iv) Proton shift :



(v) Cyanide ion elimination :



e) Haloform reaction :

Acetaldehyde or Methyl ketones react with halogen in sodium hydroxide forming haloform.

$CH_3COCH_3 + 3X_2 + 4NaOH \rightarrow CH_3COONa + CHX_3 + 3\ NaX + 3H_2O$

Acetone Haloform

$CH_3CHO + 3X_2 + 4NaOH \rightarrow HCOONa + CHX_3 + 3\ NaX + 3H_2O$

Acetaldehyde

Mechanism :

i) Formation of trihalo compound :

$$\begin{tikzcd} \underset{\text{Acetone}}{CH_3COCH_3} \arrow[r, "Br_2", "^{-}OH"'] & CH_3COCH_2Br \arrow[r, "^{-}OH / Br_2", "fast"'] & CH_3COCHBr_2 \arrow[d, "^{-}OH/ Br_2\ fast"] \\ & & \underset{\text{tribromoacetone}}{CH_3COCBr_3} \end{tikzcd}$$

ii) Cleavage of carbon – carbon bond :

$$\begin{tikzcd} CH_3COCBr_3 + \overset{-}{O}H \arrow[r, shift left, "fast"] & CH_3COOH + \overset{-}{C}Br_3 \arrow[l, shift left] \arrow[d, shift left] \\ & \underset{\text{Bromoform}}{CH_3CO\overset{-}{O} + CHBr_3} \arrow[u, shift left] \end{tikzcd}$$

f) Knoevenagel reaction :

Aldehydes or ketones undergo condensation with compounds containing active methylene group in the presence of an organic base forming α, β – unsaturated compounds.

$$\begin{tikzcd} \text{(i)}\ CH_3CH\boxed{O + H_2}C(COOH)_2 \arrow[r] & CH_3CH = C(COOH)_2 + H_2O \arrow[d, "-CO_2", "\Delta"'] \\ \text{Malonic acid} & \underset{\text{Crotonic acid}}{CH_3CH = CHCOOH} \end{tikzcd}$$

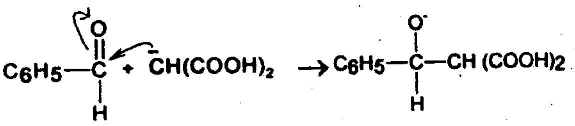
$$\begin{tikzcd} \text{(ii)}\ \underset{\text{benzaldehyde}}{C_6H_5CH}\boxed{O + H_2}\underset{\text{Malonic acid}}{C(COOH)_2} \arrow[r] & C_6H_5CH = C(COOH)_2 + H_2O \arrow[d, "-CO_2", "\Delta"'] \\ & \underset{\text{Cinnamic acid}}{C_6H_5CH = CHCOOH} \end{tikzcd}$$

Mechanism :

(i) Formation of carbanion.

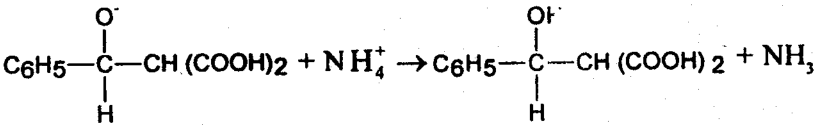
$$CH_2(COOH)_2 + NH_3 \rightleftharpoons NH_4^+ + {}^-CH(COOH)_2$$

(ii) Carbanion attack.



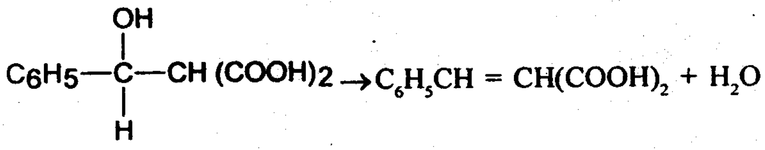
$$C_6H_5-\underset{H}{\overset{\overset{O}{\|}}{C}} + \bar{C}H(COOH)_2 \rightarrow C_6H_5-\underset{H}{\overset{O^-}{C}}-CH(COOH)2$$

(iii) Protonation.



$$C_6H_5-\underset{H}{\overset{O^-}{C}}-CH(COOH)2 + NH_4^+ \rightarrow C_6H_5-\underset{H}{\overset{OH}{C}}-CH(COOH)2 + NH_3$$

(iv) Dehydration.



$$C_6H_5-\underset{H}{\overset{OH}{C}}-CH(COOH)2 \rightarrow C_6H_5CH = CH(COOH)_2 + H_2O$$

(v) Decarboxylation.

$$C_6H_5\,CH = CH(COOH)_2 \xrightarrow{\Delta} C_6H_5\,CH = CHCOOH + CO_2$$

cinnamic acid

2.4.5.11. Oxidation reactions :

a) Oxidation with potassium permanganate :

Aldehydes on oxidation with acidified $KMnO_4$ form carboxylic acids containing same number of carbonatoms.

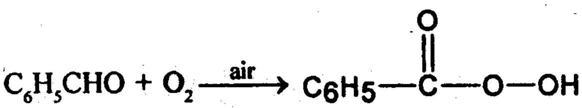
$$CH_3CHO + (O) \xrightarrow{KMnO_4/H^+} CH_3COOH$$

Ketones on oxidation with acidified $KMnO_4$ form carboxylic acids containing less no. of carbon atoms.

$$CH_3COCH_3 + 4(O) \xrightarrow{KMnO_4/H^+} CH_3COOH + CO_2 + H_2O$$

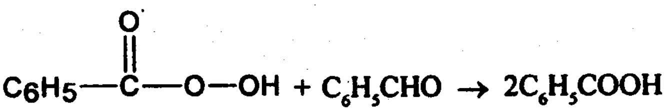
b) Autoxidation :

Aromatic aldehydes undergo auto - oxidation when exposed to air forming carboxylic acids.



$$C_6H_5CHO + O_2 \xrightarrow{air} C_6H_5-\overset{\overset{O}{\|}}{C}-O-OH$$

Perbenzoic acid



$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-OH + C_6H_5CHO \rightarrow 2C_6H_5COOH$$

benzoic acid

The auto - oxidation of benzaldehyde can be prevented by the addition of traces of pyrogallol or hydroquinone.

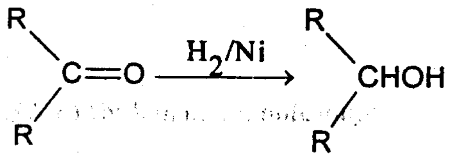
2.4.5.12. Reduction reactions :

a) Catalytic hydrogenation :

Aldehydes on catalytic hydrogenation with hydrogen in the presence of Ni form primary alcohols.

$$RCHO \xrightarrow{H_2/Ni} RCH_2OH$$

Ketones on catalytic hydrogenation form Secondary alcohols.



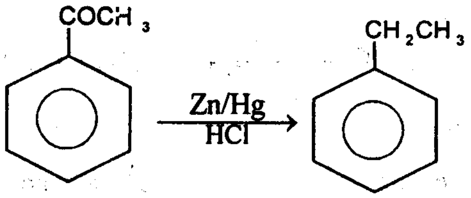
b) Clemenson reduction :

Aldehydes and ketones on reduction with amalgamated Zinc and hydrochloric acid form hydrocarbons.

$$RCOR \xrightarrow[HCl]{Zn/Hg} RCH_2R$$

$$CH_3CHO \xrightarrow[HCl]{Zn/Hg} CH_3 - CH_3$$

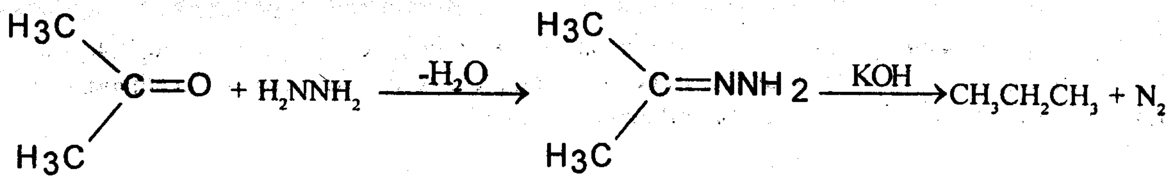
ethane



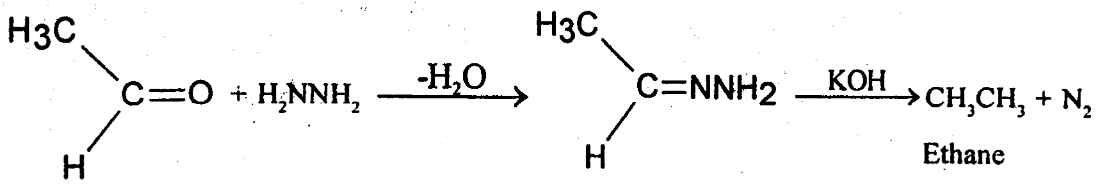
Acetophenone Ethylbenzene

c) Wolf – Kishner reduction :

Aldehydes and ketones on reduction with hydrazine and strong base like KOH form alkanes.



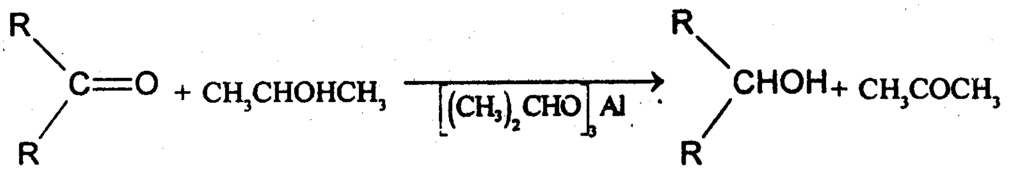
Acetone Acetonehydrazone



Acetaldehyde

d) Meerwein - pondorf - verly (MPV) reduction :

Carbonyl compounds on reduction with Isopropyl alcohol in the presence of Aluminium isopropoxide form alcohols.



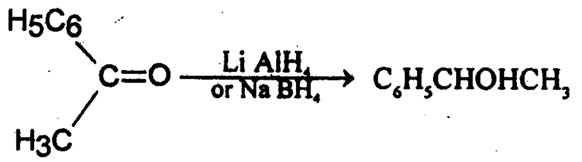
e) Reduction with LAH, $NaBH_4$:

Aldehydes on reduction with lithium aluminium hydride (LAH) or with sodium borohydride form P– alcohols.

$$CH_3CH_2CHO \xrightarrow[\text{or Na BH}_4]{\text{Li AlH}_4} CH_3CH_2CH_2OH$$

Propanal 1– Propanol
(1° – alcohol)

Ketones on reduction with lithium aluminium hydride or with sodium borohydride form S– alcohols.



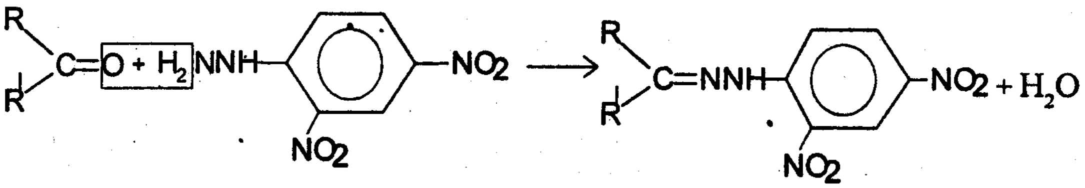
Acetophenone 2° – alcohol

LAH is more powerful reducing agent than $NaBH_4$.

2.4.6. Analysis of aldehydes and ketones :

a) 2,4 – DNP Test :

It is a qualitative test to detect aldehyde or ketone. if the given sample is liquid, 2,4 – dinitrophenyl hydrazine (2,4– DNP) reagent is added. If the given sample is solid, it is dissolved in ethanol and 2,4 - DNP reagent is added. An yellow or red precipitate is formed.



b) Tollen's Test :

Aldehydes give positive test with Tollen's reagent but ketones do not.

2ml of Tollen's reagent A (dilute silver nitrate solution) is added to Tollen's reagent B (ammonica. aqueous sodium hydroxide) drop wise until a precipitate formed is just dissolved. Then the sample is added and heated gently on a water both. A black colloidal precipitate of metallic silver or shiny silver mirror is formed on the inner sides of the test tube.

$$CH_3CHO + 2[\,Ag\,(NH_3)_2]^+ + 3\overset{-}{O}H \rightarrow CH_3CO\overset{-}{O} + 2Ag + 4\,NH_3 + 2H_2O$$

c) Fehling's test :

Fehlings reagent is a good oxidising agent but not that powerful as Tollen's reagent.

Aliphatic aldehydes give positive test with Fehling's reagent but ketones and certain aromatic aldehydes like benzaldehyde do not.

The sample is added to fehling's solution and heated. A red precipitate of cuprous oxide is formed.

Rochelle salt is used to prepare fehling's solution. It contains a complex cupric ion with tartaric acid in basic medium.

$$2RCHO + [\ Cu\ (\ tartrate\ )_2\ ]^{-2} \xrightarrow{base} 2RCOOH + Cu_2O$$

$$CH_3CHO + 2Cu^+ + 5\overset{-}{O}H \rightarrow CH_3CO\overset{-}{O} + Cu_2O\downarrow + 3H_2O$$

d) Schiff's Test :

This is a highly sensitive test for aldehydes. Ketones do not show this test. Schiff's reagent is a dilute solution of fuschen hydrochloride (P- rosaniline) which is decolourised by SO_2.

The sample is added to schiff's reagent. Aldehydes form a characteristic magenta colour.

e) Haloform Test : (Iodoform test)

Methyl ketones are characterised by this test.

$$CH_3CHO + 3I_2 + 4NaOH \rightarrow HCOONa + CHI_3 + 3NaI + 3H_2O$$

$$CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CH_3COONa + CHI_3 + 3NaI + 3H_2O$$

Acetaldehyde or methyl ketones react with iodine in sodium hydroxide forming yellow needles of iodoform.

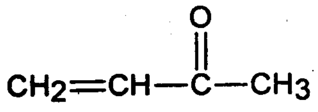
Compounds containing CH_3CO group gave haloform test.

2.4.7 $\alpha, \beta-$ unsaturated carbonyl compounds :

The $\alpha, \beta-$ unsaturated carbonyl compounds contain a carbon - carbon double bond as well as a carbonyl group.

$CH_2 = CHCHO$
acrolein

$CH_3CH = CHCHO$
Crotonaldehyde



$$CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

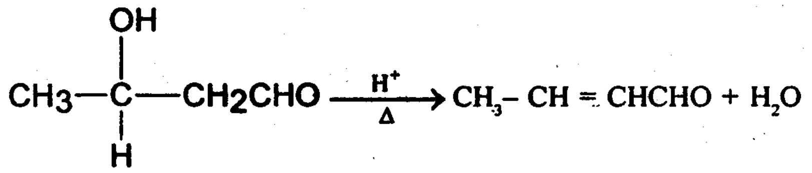
methylvinyl kelone

$(CH_3)_2C = CHCOCH_3$
Mesityl oxide

$C_6H_5CH = CHCHO$
Cinnamaldehyde.

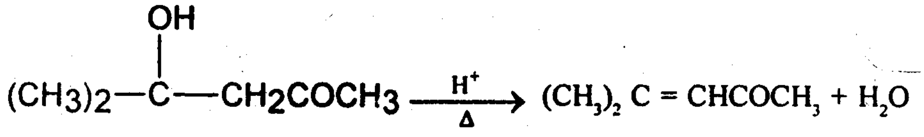
2.4.7.1. Preparation :

a) crotonaldehyde is prepared by heating aldol in the presence of acid.



$$CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}CH_2CHO \xrightarrow[\Delta]{H^+} CH_3{-}CH = CHCHO + H_2O$$

b) Misityl oxide is prepared by heating diacetone alcohol in the presence of acid.



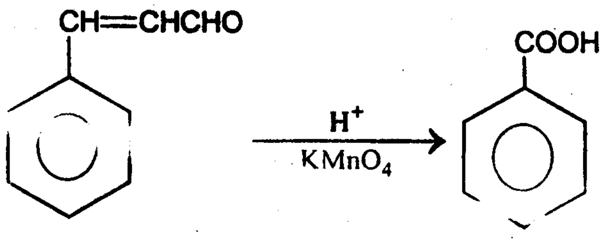
$$(CH_3)_2{-}\overset{\overset{\displaystyle OH}{|}}{C}{-}CH_2COCH_3 \xrightarrow[\Delta]{H^+} (CH_3)_2\,C = CHCOCH_3 + H_2O$$

2.4.7.2. Properties :

These compounds give all the reactions of C=C and >C=O.

a) oxidation:

α, β – unsaturated carbonyl compounds on oxidation with acidified $KMnO_4$ form carboxylic acids.



Cinnamaldehyde Benzoicacid

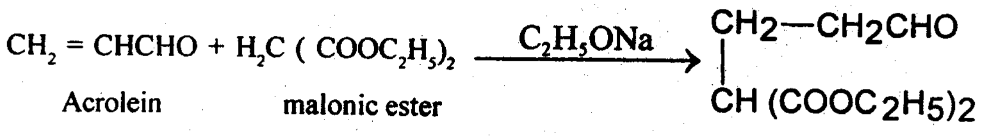
b) MPV reduction :

α, β – unsaturated carbonyl compounds on MPV reduction form α, β – unsaturated alcohols.

$$C_6H_5CH = CHCHO + CH_3CHOHCH_3 \xrightarrow{[(CH_3)_2CHO]_3Al} C_6H_5CH = CHCH_2OH + CH_3COCH_3$$

c) Michael addition : (addition of carbanions to $\alpha, \beta-$ unsaturated carbonyl compounds)

$\alpha, \beta-$unsaturated carbonyl compounds react with compounds like malonic ester, acetoacetic ester in the presence of C_2H_5ONa.



$$\underset{\text{Acrolein}}{CH_2 = CHCHO} + \underset{\text{malonic ester}}{H_2C(COOC_2H_5)_2} \xrightarrow{C_2H_5ONa} \begin{array}{l} CH_2-CH_2CHO \\ | \\ CH(COOC_2H_5)_2 \end{array}$$

2.4.8. Model Questions :

1. What is 2,4 – diphenyl hydrazine? How is it useful in the identification of carbonyl group? Explain with equation.
2. Explain cannizzaro and haloform reactions.
3. Discuss with example the process of self oxidation and reduction of an aldehyde having no α - hydrogen by the action of strong alkali.
4. How aldehyde can be distinguished from ketone.
5. Complete the following reactions and name them.
   - i) $C_2H_5CONH_2 + Br_2 + 4KOH \rightarrow$
   - ii) $CH_2O + CH_2O \xrightarrow{50\%aqKOH}$
   - iii) Trimethyl acetaldehyde + strong NaOH →
   - iv) $CH_3COOH \xrightarrow{CaCO_3} A \xrightarrow{Pyrolysis} B \xrightarrow{NH_2OH} C$
   - v) $CH_3CHO + Cl_2 + 4NaOH \rightarrow$
   - vi) $CH_3COCH_3 + I_2 + Na_2CO_3 \rightarrow$
   - vii) $CH_3CHO \xrightarrow{\bar{O}H}$
   - viii) $C_6H_5CHO \xrightarrow{\bar{O}H}$
6. Write balanced equations for the following –
   - i) Diethyl ketone + Hydroxylamine
   - ii) Methylethyl ketone + HCN
   - iii) Acetone + HCN
   - iv) Benzophenone + hydroxylamine
7. Both $>C = O$ and $>C = C<$ contain double bond. But they show different types of reactions. Explain.
8. Formaldehyde does not give aldol condensation reaction, it rather gives cannizzaro reaction.

9. Write notes on the following with mechanisms –
   i) Aldol condensation
   ii) Benzoin condensation
   iii) Cannizzaro reaction
   iv) Haloform reaction
   v) Perkin reaction
   vi) Knoevenagel reaction

10. Write notes on the following –
    i) Clemenson reduction
    ii) Wolf – kishner reduction
    iii) MPV reduction
    iv) Rosenmund reduction.

11. Explain the products formed with equation when acetaldehyde and acetone are treated with.
    a) $NaHSO_3$
    b) NH_3
    c) $C_6H_5NHNH_2$

12. Discuss keto – enol tautomerism with example.

13. How do you convert benzaldehyde to cinnamic acid.

14. How chloral hydrate is stable.

15. What are hemiacetals and acetals ?

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UNIT – II

Lesson - V

CARBOXYLIC ACIDS AND DERIVATIVES

2.5.0

Nomenclature, Classification and methods of preparation a) Hydrolysis of nitriles, amides and esters b) Carbonation of Grignand reagents. Special methods of preparation of aromatic acids a) Oxidation of the side chain b) Hydrolysis of benzotrichlorides c) Kolbereaction. Physical properties - hydrogen bonding dimeric association, Acidity - Strength of acids with the examples of trimethylacetic acid and trichloracetic acid, relative differences in the acidity of aromatic and aliphatic acids. Chemical properties - reactions involving H, –OH and – COOH groups - salt formation, anhydride formation, acid halide formation.

Esterification (mechanism) and amide formation. Reduction of the acid to the corresponding P - alcohol - via ester or acid chloride. Degradation of Carboxylic acids by Hunsdiecker reaction, Schmidt reaction (decarboxylation) . Arndt - Eistert synthesis. Halogenation by Hell - Volhard - Zelinsky reaction. Carboxylic acid derivatives - reactions of acid halides, acid anhydrides, acid amides and esters (mechanism of ester hydrolysis by base and acid).

2.5.1 Nomenclature :

In IUPAC system, carboxylic acids are named as alkanoic acids. Thus the name of an individual acid is derived by replacing the end letter 'e' of the corresponding alkane by - oic acid. While numbering the acid the carboxyl carbon is always given number1. $C^5 - C^4 - C^3 - C^2 - C^1OOH$.

Formula	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
C_3H_7COOH	Butyric acid	Butanoic acid

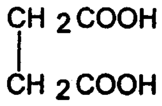
2.5.2 Classification :

Carboxylic acids are classified into monocarboxylic acids, dicarboxylic acids, Tri carboxylic acids etc. according to the number of – COOH groups present in the compound.

Mono carboxylic acid CH_3COOH

Acetic acid

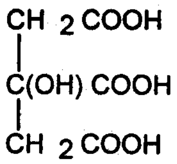
Dicarboxylic acid



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

Succinic acid

Tri carboxylic acid



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)\,COOH \\ | \\ CH_2COOH \end{array}$$

Citric acid.

Monocarboxylic acids are also known as fatty acids because many of them are obtained from fatt.

Monocarboxylic acids may be saturated or unsaturated.

Saturated CH_3CH_2COOH

Propionic acid

Unsaturated $CH_2 = CHCOOH$

Acrylic acid.

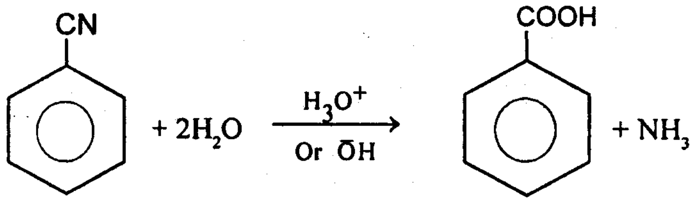
2.5.3 Methods of Preparation :

a) Hydrolysis :

i) Hydrolysis of nitriles :

Organic cyanides are called nitriles. Nitriles on hydrolysis with acid or base form carboxylic acids.

$$RCN + 2H_2O \xrightarrow{H_3O^+} RCOOH + NH_3$$

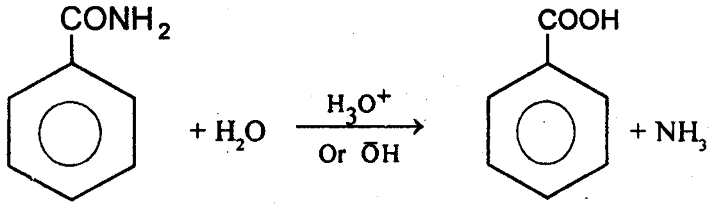


benzonitrile benzoic acid

ii) Hydrolysis of amides :

Amides on hydrolysis with acid or base form carboxylic acids.

$$CH_3CONH_2 + H_2O \xrightarrow[\text{Or } \bar{O}H]{H_3O^+} CH_3COOH + NH_3$$



benzanide benzoic acid

iii) Hydrolysis of esters :

Ester on boiling with alkali form salt of carboxylic acid which on treatment with acid gives carboxylic acid.

$$CH_3COOC_2H_5 + KOH \xrightarrow{heat} CH_3COOK + C_2H_5OH$$

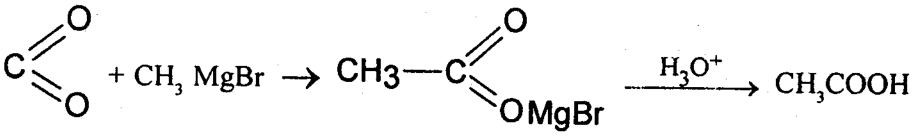
Ethylacetate Potassium acetate.

$$CH_3COOK + HCl \rightarrow CH_3COOH + KCl$$

Acetic acid

b) Carbonation of Grignard reagents :

Grignard reagents react with carbondioxide forming addition product which on hydrolysis form carboxylic acids.

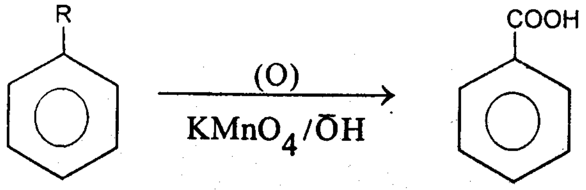


Carbon dioxide Methylmagnesium bromide acetic acid.

2.5.4 Special methods of preparation of aromatic acids :

a) Oxidation of the side chain :

Aromatic compounds with alkyl side chain on Vigorous oxidation with alkaline $KMnO_4$ or acidified potassium dichromate or dilute nitric acid form aromatic carboxylic acids.

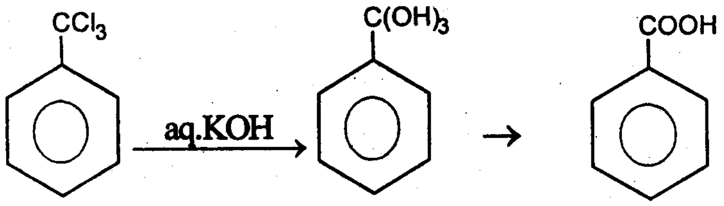


alkyl benzene benzoic acid

Irrespective of number of carbons present in the side chain, only -COOH is formed.

b) Hydrolysis of benzotrichlorides :

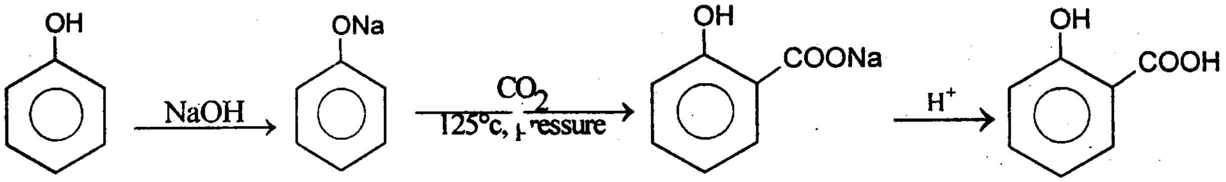
Trihalogen derivatives containing three halogen atoms on the same carbon atom on hydrolysis with aqueous alkali form carboxylic acids



benzotrichloride benzoic acid

c) Kolbereaction :

Sodium phenoxide reacts with CO_2 at 125°c under pressure forming salicylic acid.



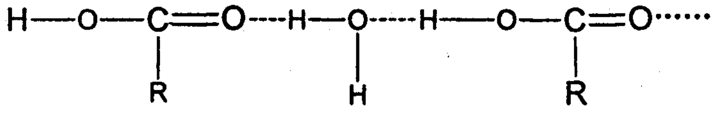
2.5.5 Physical properties :

a) Hydrogen bonding :

Carboxylic acids are polar in nature. They form hydrogen bonds with each other and with other molecules.

i) Solubility :

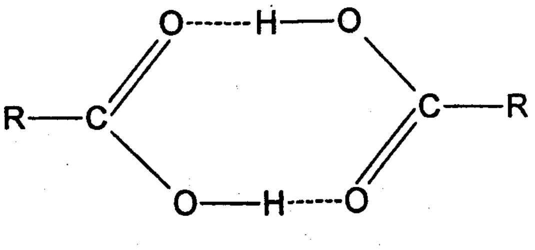
Carboxylic acids upto C_4 are freely soluble in water due to hydrogen bonding with water molecules.



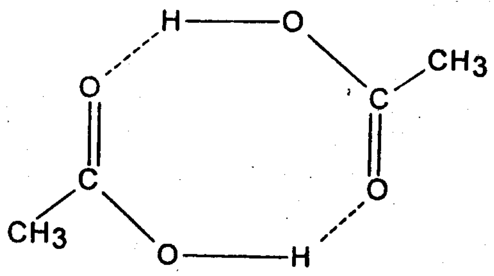
$$H-O-\underset{R}{\underset{|}{C}}=O\cdots H-\underset{H}{\underset{|}{O}}\cdots H-O-\underset{R}{\underset{|}{C}}=O\cdots\cdots$$

ii) Boiling Points :

Boiling points of carboxylic acids are higher than that of the corresponding alcohols. This is due to the fact that hydrogen bonding in carboxylic acids is stronger than those in alcohols, This is because carboxylic acids exist as dimers with the formation of a ring.



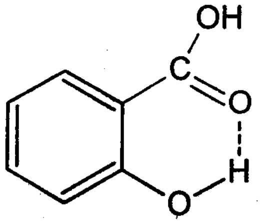
Dimeric carboxylic acid



Dimeric acetic acid

iii) Intramolecular hydrogen bonding is also noticed in orthohydroxy carboxylic acids.

Ex : Salicylic acid.



Intramolecular hydrogen bonding

b) Acidity :

i) Carboxylic acids are more acidic than alcohols. Alcohol ionises as

$$R\text{–}OH \rightleftharpoons RO^- + H^+$$

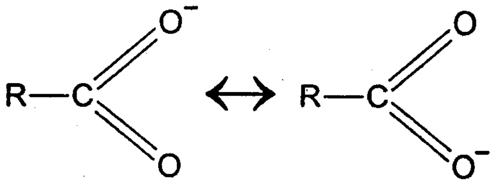
Alkoxide ion has no resonance stabilisation.

carboxylic acid ionises as

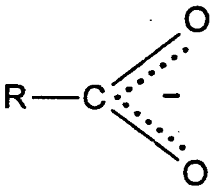
$$RCOOH \rightleftharpoons RCOO^- + H^+$$

Carboxylation

Carboxylate ion is stabilised by resonance.



Resonance in Carboxylate ion

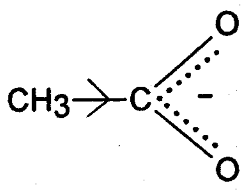


Resonance hybrid

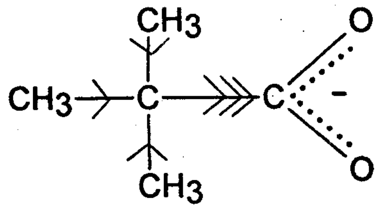
Hence carboxylateion is more stabilised and carboxylic acids are more acidic.

ii) Effect of electron releasing group :

Trimethylacetic acid is less acidic than acetic acid. Methyl group is electron releasing group. Electron releasing substituent in carboxylic acid increases negative charge due to +I effect. Hence stability of the carboxylate ion there by acidity of the carboxylic acid decreases.



Acetate ion

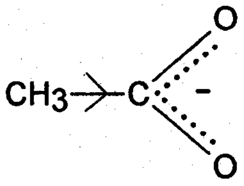


Trimethyl acetateion

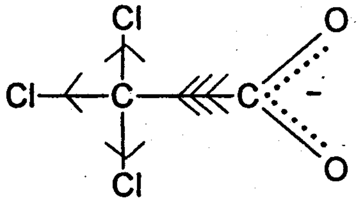
CH_3COOH > $(CH_3)_3\ CCOOH$

Pka = 4.76 Pka = 5.02

iii) Trichloroacetic acid is more acidic than acetic acid. Cl^- group is electron with drawing group. Electron with drawing substituent in carboxylic acid disperse negative charge due to - I effect. Hence stability of the carboxylate ion there by acidity of carboxylic acid increases.



Acetate ion



Trichloro acetateion

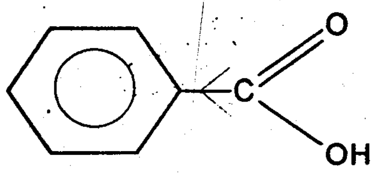
CH_3COOH < $Cl_3\ CCOOH$

Pka = 4.76 Pka = 0.08

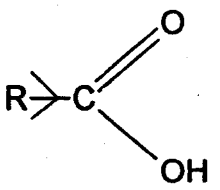
Actually, trichloro acetic acid is as strong as mineral acid.

iv) Relative acidity of aromatic and aliphatic acids:

Aromatic carboxylic acids are stronger than the simple aliphatic carboxylic acids.



Aromatic acid

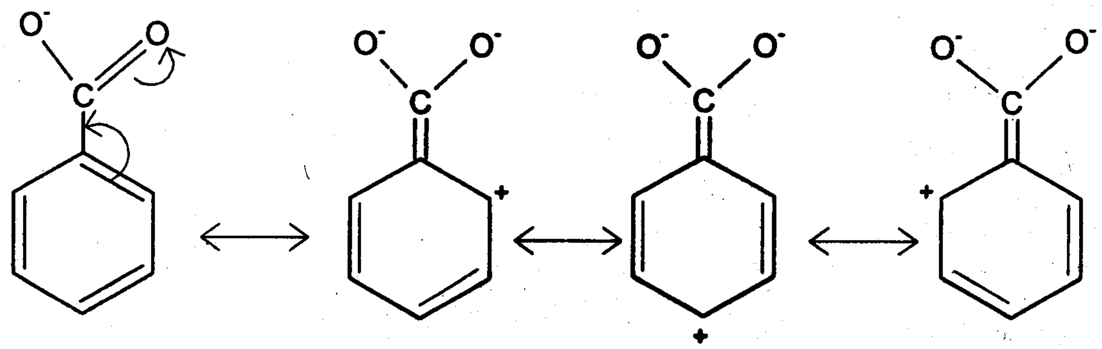


In aromatic carboxylic acids, the **carboxylate group is attached** to more **electronegative** Sp^2 hybridised carbon.

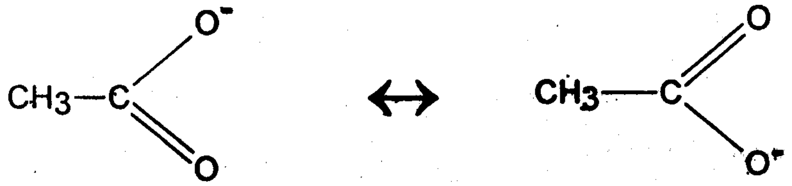
∴ benzene ring acts as electron with **drawing substituent** on the α - carbon and acid strength increases.

In aliphatic carboxylic acids, the **carboxylate group is attached** to sp^3 hybridised carbon which is less electronegative than sp^2 hybridised carbon. ∴ **alkyl group acts as electron** releasing group on the α - carbon and acid strength decreases.

Also benzoate ion is more stable than **acetate ion because benzoate ion has** more number of resonating structures.

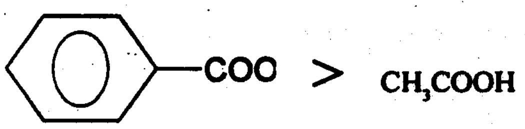


Resonance in **benzoate ion** **more number of resonating** structures. More stable.



Resonance in **acetation** **less number of resonating** structures. Less stable.

Thus benzoic acid is more acidic than **aceticacid.**



Benzoic acid Acetic acid

2.5.6 Chemical properties :

a) Reactions involving -H :

(Salt formation)

i) carboxylic acids form salts with active metals like Mg, Ca, Zn etc liberating hydrogen.

$$2RCOOH + Ca \rightarrow (RCOO)_2Ca + H_2$$

ii) Carboxylic acids form salts with metal hydroxides

$$RCOOH + NaOH \rightarrow RCOO\,Na + H_2$$

iii) carboxylic acids form salts with bicarbonates liberating Co_2 with quick effervescene (test for acids)

$$RCOOH + NaHCO_3 \rightarrow RCOO\,Na + CO_2\uparrow + H_2$$

b)Reactions involving -OH : (Acid derivatives)

i) Formation of anhydrides :

Carboxylic acids on heating with P_2O_5 form anhydrides.

ii) Formation of acid halides :

Carboxylic acids react with phosphorus halides or thionyl chloride forming acid halides.

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl + POCl_3$$

$$3\,CH_3COOH + PCl_3 \rightarrow 3\,CH_3COCl + H_3PO_3$$

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + HCl + SO_2$$

iii) Formation of Amides :

Carboxylic acids react with ammonia forming ammonum salts which on heating decomposes to amides.

$$RCOOH + NH_3 \rightarrow RCOONH_4 \xrightarrow{heat} RCONH_2 + H_2O$$

iv) Formation of esters (esterification) :

The reaction of carboxylic acids with alcohol forming ester and water is called esterification. It is a revessible reaction.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R^{\prime}-OH} \xrightleftharpoons{\text{esterification}} \underset{\text{ester}}{RCOOR^{\prime}} + H_2O$$

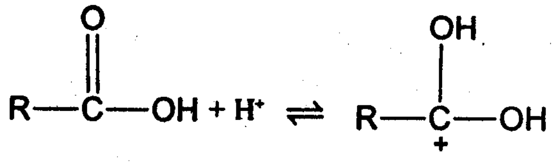
The reaction of an ester with water forming carboxylic acid and alcohol is called esterhydrolysis.

$$RCOOR^{I} + H_2O \xrightleftharpoons{\text{esterification}} RCOOH + R^{I}OH$$

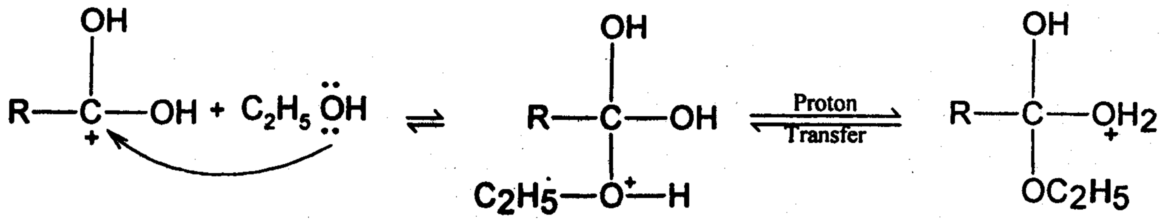
Ester hydrolysis catalysed by a base is irreversible. It is called saponification.

Mechanism :

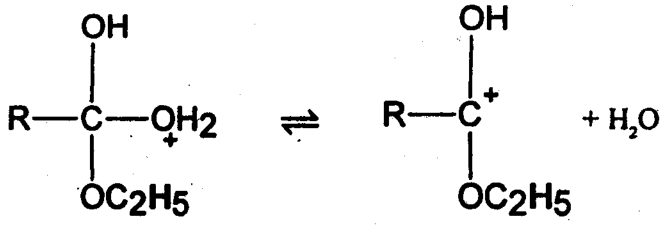
Protonation :



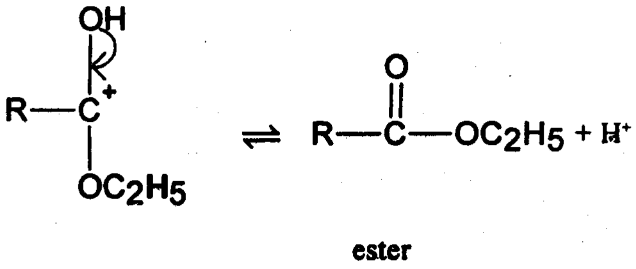
Nucleophilic attack :



Loss of water :



Proton elimination :



C) Reactions involving – COOH group :

i) Reduction to primary alcohol :

Carboxylic acids on reduction with lithium aluminium hydride form P – alcohols.

$$RCOOH \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} R-CH_2OH$$

ii) Reduction to P – alcohol via ester :

Carboxylic acids react with alcohol forming ester which on reduction with Sodium and ethanol form P – alcohols.

$$RCOOH + R^{I}OH \xrightarrow{H^+} RCOOR^{I} + H_2O$$

$$\downarrow Na,\ C_2H_5OH$$

$$R-CH_2OH$$

P - alcohol

iii) Reduction to P – alcohol via acid chloride :

Carboxylic acids react with PCl_5 forming acid chlorides. These on reduction with hydrogen in the presence of a catalyst form aldehydes. Aldehydes on reduction with Fe and CH_3COOH form P – alcohols.

$$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

$$\downarrow H_2/Pd$$

$$RCHO$$

$$\downarrow \text{Fe, Acetic acid}$$

$$R-CH_2OH$$

P - alcohol

d) Degradation of Carboxylic acids : (decarboxylation)

i) Hunsdiecker reaction :

Heavy metal salts of carboxylic acids on heating with a halogen in carbonterachloride form alkylhalides.

$$RCOOAg + X_2 \xrightarrow[\Delta]{CCl_4} R-X + CO_2 + AgX$$

alkylhalide

ii) Schmidt reaction :

Carboxylic acids react with hydrazoic acid in the presence of Conc. H_2SO_4 forming amines.

$$RCOOH + N_3H \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{amine}}{RNH_2} + CO_2 + N_2$$

e) Arndt - Eistert synthesis : (conversion to next higher homologue)

Carboxylic acid is first converted to acid chloride which on treatment with excess of diazomethane gives diazoketone. Diazoketone decomposes in the presence of moist silver oxide forming next higher homologue.

$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow[H_2O]{Ag_2O} RCH_2COOH + N_2$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{CH_2N_2} C_6H_5COCHN_2 \xrightarrow[H_2O]{Ag_2O} \underset{\text{Phenyl acetic acid}}{C_6H_5CH_2COOH} + N_2$$

f) Halogenation (Hell - Volhard - zelinsky reaction)

Fatty acids react with halogens in the presence of a catalyst in sunlight or on heating to form α - haloacids.

$$\underset{\text{acetic acid}}{CH_3COOH} \xrightarrow{Cl_2/P} \underset{\text{monochloroacetic acid}}{ClCH_2COOH} \xrightarrow{Cl_2/P} \underset{\text{dichloroacetic acid}}{Cl_2CHCOOH}$$

$$\downarrow Cl_2/P$$

$$\underset{\text{Trichloroacetic acid}}{Cl_3CCOOH}$$

2.5.7. Carboxylic acid derivatives :

If - OH group in the carboxylic acid $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$ is replaced by –X, - OCOOR, - NH_2, - OR, acid halides, anhydrides, amides and esters are obtained. These are called carboxylic acid derivatives.

a) Acid Halides (RCOX) :

Preparation :

Carboxylic acids react with phosphorus pentahalide, phosphorus trihalide forming acid halides.

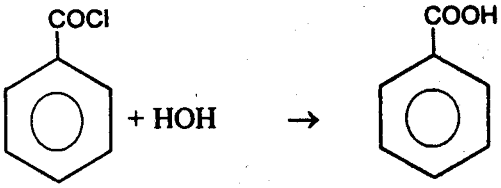
$$RCOOH + PX_5 \rightarrow RCOX + HX + POX_3$$

$$3RCOOH + PX_3 \rightarrow 3RCOX + H_3PO_3$$

Properties :

1. **Hydrolysis :** Acid chlorides undergo hydrolysis forming acids.

$$RCOCl + HOH \rightarrow RCOOH + HCl$$



Benzoyl chloride benzoic acid

2. **Ammonolysis :** Acid chlorides react with ammonia forming amides.

$$RCOCl + 2NH_3 \rightarrow RCOONH_2 + NH_4Cl$$

Alcoholysis : Acid chlorides react with alcohols forming esters.

$$RCOCl + R^{l}OH \rightarrow RCOOR^{l} + HCl$$

Rosenmund reduction : Acid chlorides on reduction with hydrogen in the presence of Pd form alcohols.

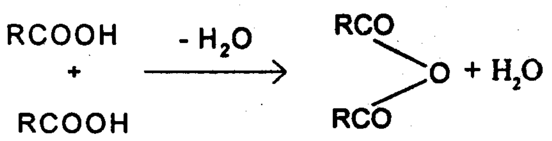
$$RCOCl + H_2 \xrightarrow{Pd} RCHO + HCl$$

Friedel crafts acylation : Acid chlorides react with benzene in the presence of anhydrous $AlCl_3$ forming ketones.

$$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$$

b) Acidanhydrides : (RCO–O–COR)

Anhydrides are regarded as derived from two molecules of acids with the elimination of water molecule.



Preparation :

i) Acid chlorides react with salts of carboxylic acids forming anhydrides.

$$CH_3COCl + CH_3COONa \xrightarrow{heat} CH_3CO\text{–}O\text{–}COCH_3 + NaCl$$

Acetic anhydride.

ii) Carboxylic acids on dehydration with P_2O_5 form anhydrides.

$$CH_3COOH \xrightarrow[heat]{P_2O_5} CH_3CO\text{–}O\text{–}COCH_3 + H_2O$$

Properties :

Hydrolysis : Anhydrides on hydrolysis form carboxylic acids.

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

Ammonolysis : Anhydrides react with ammonia forming amides.

$$(CH_3CO)_2O + 2NH_3 \rightarrow \underset{\text{Amide}}{CH_3CONH_2} + \underset{\text{Ammonium acetate}}{CH_3COONH_4}$$

Alcoholysis : Anhydrides react with alcohols forming esters.

$$(CH_3CO)_2O + CH_3OH \rightarrow \underset{\text{Methyl acetate}}{CH_3COOCH_3} + CH_3COOH$$

Friedel crafts reaction : Anhydrides react with benzene in the presence of Al Cl_3 forming ketones.

$$C_6H_6 + (CH_3CO)_2O \rightarrow \underset{\text{acetophenone}}{C_6H_5COCH_3} + CH_3COOH$$

c) Amides : ($RCONH_2$)

Acid chlorides, anhydrides or esters react with ammonia forming amides.

$$RCOCl + NH_3 \xrightarrow{AlCl_3} RCONH_2 + HCl$$

$$(CH_3CO)_2O + 2NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4$$

$$CH_3COOC_2H_5 + NH_3 \rightarrow CH_3CONH_2 + C_2H_5OH$$

Properties :

Hydrolysis : Amides on hydrolysis form acids liberating NH_3.

$$RCONH_2 + H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

$$RCONH_2 + H_2O \xrightarrow{^-OH} RCOO^- + NH_3$$

Hofmanndegradation :

Amides react with bromine in alkali forming amines.

$$RCONH_2 + Br_2 + 4KOH \rightarrow \underset{\text{Amine}}{RNH_2} + 2KBr + K_2CO_3 + H_2O$$

Dehydration :

Amides on dehydration with P_2O_5 form alkyl cyanides.

$$RCONH_2 \xrightarrow{P_2O_5} RCN + H_2O$$

Esters : (RCOOR^{1})

Preparation :

i) Esterification :

Carboxylic acids react with alcohols in the presence of Conc. H_2SO_4 forming esters.

$$CH_3COOH + C_2H_5OH \xrightarrow{Conc.H_2SO_4} CH_3COOC_2H_5 + H_2O$$

ii) Acid chlorides or anhydrides react with alcohols forming esters.

$$CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl$$

$$(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH$$

Properties :

Hydrolysis in the presence of acid :

Esters on hydrolysis in the presence of acid form carboxylic acid and alcohol. It is a reversible reaction.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Hydrolysis in the presence of a base : (Saponification)

Esters on hydrolysis in the presence of a base form carboxylic acid and alcohol. It is irreversible reaction.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Ammonolysis : Esters react with ammonia forming amides.

$$CH_3COOC_2H_5 + NH_3 \rightarrow CH_3CONH_2 + C_2H_5OH$$

Alcoholysis : Esters undergo transesterification with alcohols.

$$CH_3COOC_2H_5 + C_3H_7OH \rightarrow CH_3COOC_3H_7 + C_2H_5OH$$

Bouveault - Blanc reduction :

Esters on reduction with sodium and ethanol form P – alcohols.

$$CH_3COOC_2H_5 + 4[H] \xrightarrow{Na/\ C_2H_5OH} CH_3CH_2OH + C_2H_5OH$$

2.5.8. Mechanism of Ester hydrolysis by base and acid :

The reaction of an ester with water forming carboxylic acid and alcohol is called ester hydrolysis.

$$RCOOR^{I} + H_2O \overset{H^+}{\rightleftharpoons} RCOOH + R^{I}OH$$

Ester hydrolysis catalysed by a base is irreversible. It is called Saponification.

$$RCOOR^{I} + NaOH \xrightarrow{\text{Saponification}} RCOONa + R^{I}OH$$

Mechanism of ester hydrolysis :

a) Acid catalysed mechanism :

Protonation :

$$RCOOR^{I} + H^+ \rightleftharpoons RCO\underset{H}{\overset{+}{O}}R^{I}$$

Acyloxygen fission :

$$RCO\underset{H}{\overset{+}{O}}R^{I} \rightleftharpoons RCO^+ + R^{I}OH$$

Hydration :

$$RCO^+ + H_2O \rightleftharpoons RCOOH + H^+$$

ESTER HYDROLYSIS

b) Base catalysed mechanism :

Alkyl - Oxygen fission :

$$RCOOR^{I} \rightleftharpoons RCOO^- + R^{I+}$$

Hydration :

$$R^{I} + H_2O \rightleftharpoons R\overset{+}{O}H_2$$

Protontransfer (irreversible) :

$$RCOO^- + R^{I}\overset{+}{O}H_2 \longrightarrow RCOOH + R^{I}OH$$

SAPONIFICATION

2.5.9. Model Questions :

1. What are the effects of substituents on the acidity of carboxylic acids and phenols ?
2. Explain HVZ reaction. Why α– chloropropionic acid is more acidic than propionic acid.
3. Write mechanism of acid catalysed esterification.
4. Write an account on the mechanism of ester hydrolysis

5. What happens when –
   a. Calcium formate and calcium acetate are dry distilled.
   b. Calcium acetate is heated.
   c. Acetamide reacts with bromine and caustic potash
   d. Ammonium acetate is heated with P_2O_5
6. How is acetic acid converted to.
   a. Methane
   b. Ethanol
   c. Acetyl chloride. Give equations.
7. Formic acid is stronger than acetic acid.
8. Propionic acid is weaker than acetic acid.
9. Trichloroacetic acid is stronger than acetic acid.
10. Write down the preparation of acetamid
11. Explain acidic nature of - COOH grou
12. Write a brief note on the following –
    a. Kolbe reaction
    b. Hunsdiecker reaction
    c. HVZ reaction
13. What are carboxylic acid derivatives ? Write their structures and name them.
14. Write dimmer structure of acetic acid.
15. What for Arndt – Eistert synthesis is useful. Explain with example.
16. Write notes on Rosenmund reduction.

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UNIT – II

Lesson – VI

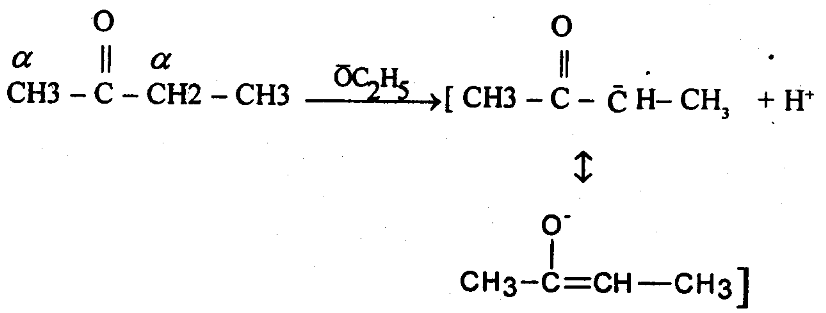
SYNTHESIS BASED ON CARBANIONS

2.6.0

Acidity of hydrogens, structure of carbanion. Preparation of acetoacetic ester - claisen condensation and synthetic applications of acetoacetic ester a) acid hydrolysis and ketonic hydrolysis, preparation of (i) mono carboxylic acids (ii) dicarboxylic acids. Malonic ester synthetic applications i) substituted mono carboxylic acids (ii) substituted dicarboxylic acids (iii) di - alkylacetic acid.

2.6.1 Acidity of α – hydrogens : (active methylene group)

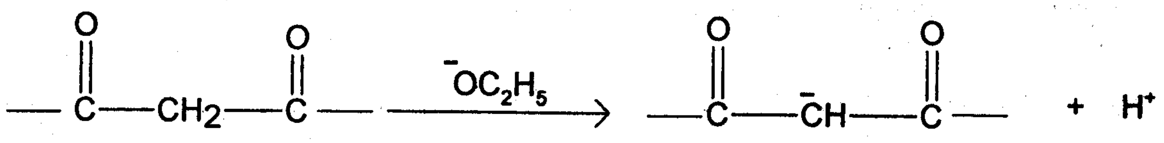
The hydrogen atoms on a carbon atom α – to a carbonyl group are acidic. This is because ionisation of an α – hydrogen gives a carbanion is stabilised by resonance.



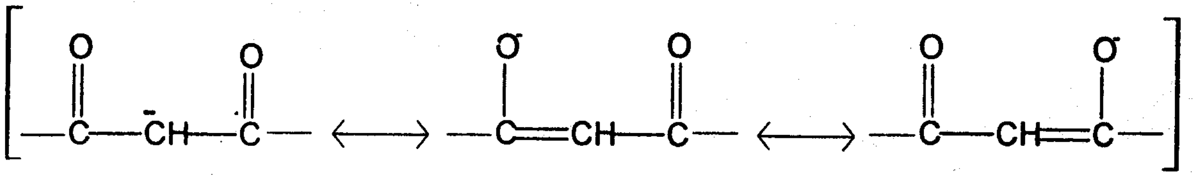
Carbanion stabilised by resonance

α – hydrogen atom from such compounds can be easily removed by a strong base like ethoxide ion.

Similarly when a methylene group is flanked by two carbonyl groups, the hydrogen atom of the methylene group is more acidic because the resulting carbanion is stabilised by resonance to a greater extent.

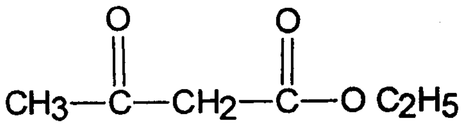


Carbanion



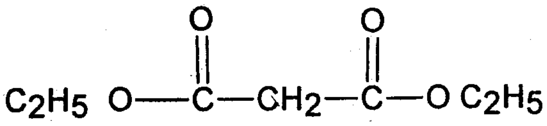
Carbanion stabilised by more resonance.

Such a methylene group is called active methylene group. Compounds containing active methylene group are



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

Acetoacetic ester



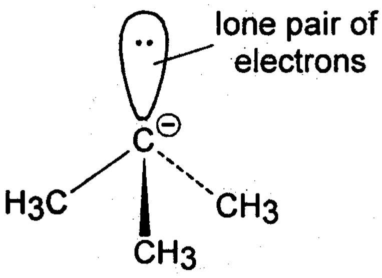
$$C_2H_5O-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

Malonic ester

2.6.2 Structure of Carbanion :

Carbanion is an ion in which the carbon carries negative charge $-\overset{|}{\underset{|}{C}}\overset{\ominus}{:}$

The negatively charged carbon atom of the carbanion is SP^3 hybridised. The three SP^3 orbitals form three bonds with the alkyl groups or hydrogen atoms. The fourth SP^3 orbital is filled with a pair of electrons and unused. This makes carbon atom electron [illegible] and gives negative charge to it.



Structure of Carbanion

Carbanion has a pyramidal structure, similar to that of ammonia. In fact, a carbanion and ammonia are isoelectronic species.

2.6.3. Preparation of acetoacetic ester (Claisen condensation) :

Two molecules of ethyl acetate undergo condensation when refluxed with sodium and ethanol forming acetoacetic ester.

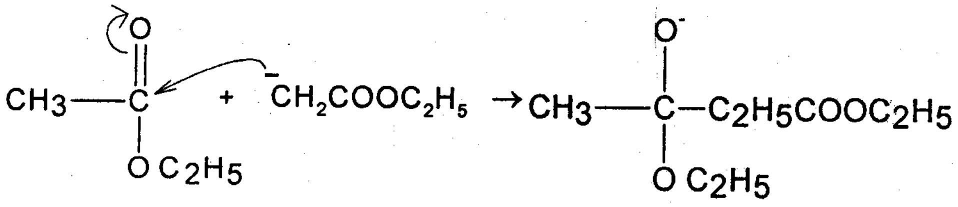
$$CH_3CO\boxed{OC_2H_5 + H}CH_2\ COOC_2H_5 \xrightarrow[C_2H_5ONa]{Na} CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

Mechanism :

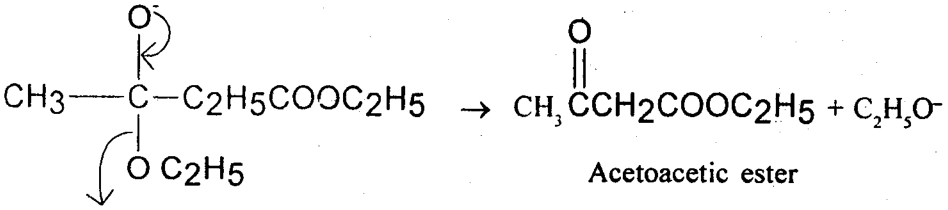
Formation of carbanion :

$$CH_3\ COOC_2H_5 \xrightarrow{C_2H_5ONa} \bar{C}H_2COOC_2H_5$$

Carbanion addition :



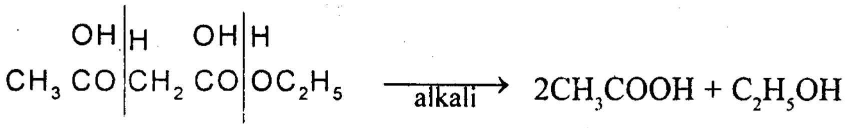
Ethoxide ion elimination :



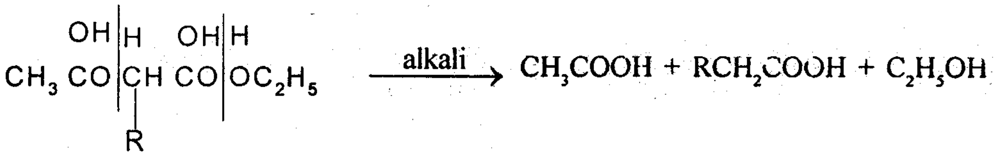
2.6.4 Synthetic applications of acetoacetic ester :

2.6.4.1. Acid hydrolysis : (Preparation of monocarboxylic acids)

Acetoacetic ester undergoes hydrolysis with alkali forming acids.



$$\overset{OH}{CH_3CO}\,|\,\overset{H}{CH_2}\,\overset{OH}{CO}\,|\,\overset{H}{OC_2H_5} \xrightarrow{alkali} 2CH_3COOH + C_2H_5OH$$



$$\overset{OH}{CH_3CO}\,|\,\underset{R}{\overset{H}{CH}}\,\overset{OH}{CO}\,|\,\overset{H}{OC_2H_5} \xrightarrow{alkali} CH_3COOH + RCH_2COOH + C_2H_5OH$$

Alkylacetoacetic ester

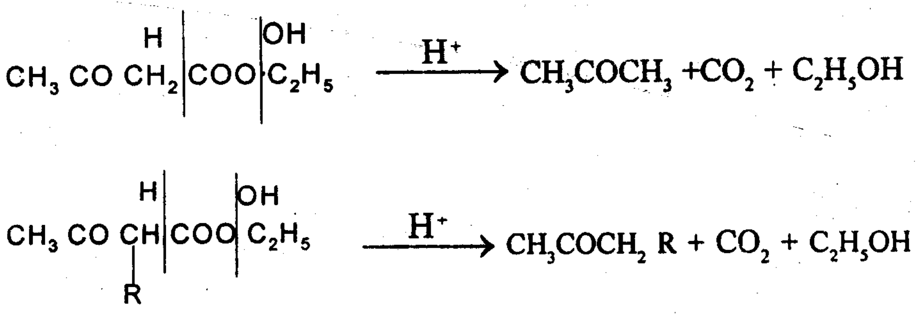
R = CH_3 Propionic acid

R = CH_3CH_2 n – butyric acid

R = $CH_3CH_2CH_2$ n – valeric acid

2.6.4.2. Ketonic hydrolysis :

Acetoacetic ester undergoes hydrolysis with dil. HCl forming Ketones.



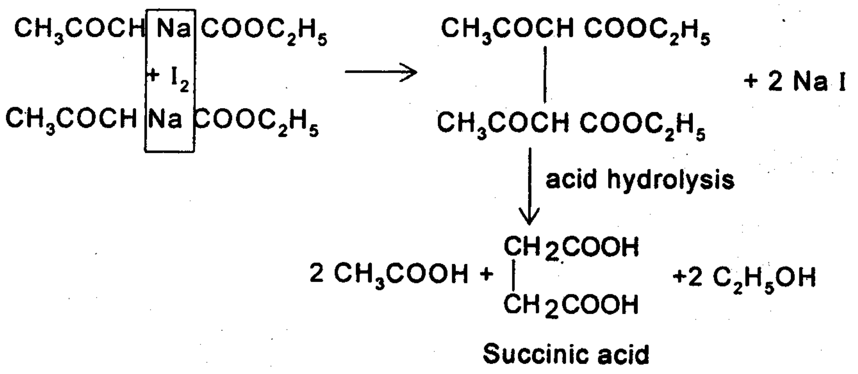
$$CH_3\,CO\,CH_2 \mid COO \mid C_2H_5 \xrightarrow{H^+} CH_3COCH_3 + CO_2 + C_2H_5OH$$

$$CH_3\,CO\,\underset{R}{CH} \mid COO \mid C_2H_5 \xrightarrow{H^+} CH_3COCH_2\,R + CO_2 + C_2H_5OH$$

2.6.4.3. Preparation of dicarboxylic acids :

In the presence of sodium ethoxide acetoacetic ester reacts with Iodine followed by acid hydrolysis gives succinic acid.

$$CH_3COCH_2\,COOC_2\,H_5 \xrightarrow{C_2H_5ONa} CH_3COCH\,Na\,COOC_2H_5$$



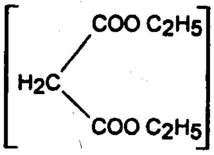
$$\begin{matrix} CH_3COCH\,Na\,COOC_2H_5 \\ + I_2 \\ CH_3COCH\,Na\,COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} CH_3COCH\,COOC_2H_5 \\ | \\ CH_3COCH\,COOC_2H_5 \end{matrix} + 2\,Na\,I$$

$$\downarrow \text{acid hydrolysis}$$

$$2\,CH_3COOH + \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + 2\,C_2H_5OH$$

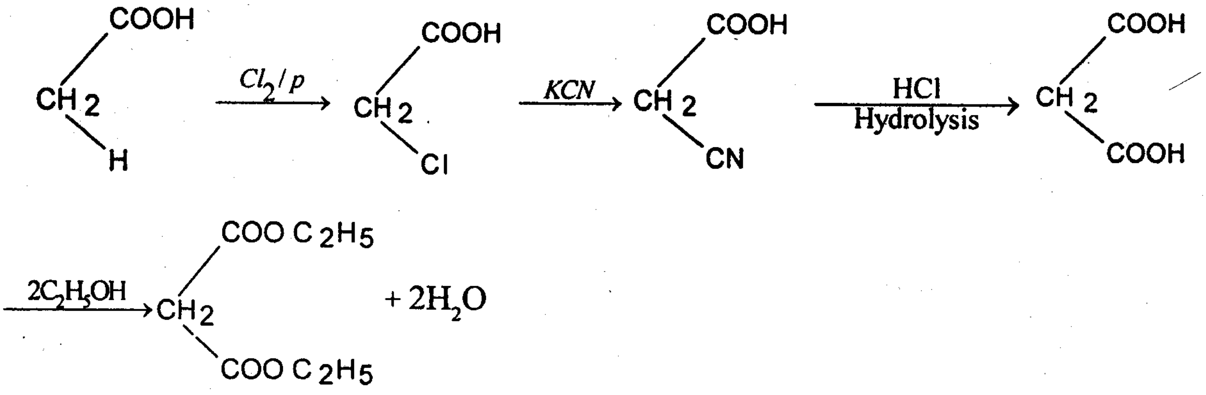
Succinic acid

2.6.5. Preparation of Malonic ester :



$$\left[H_2C \begin{matrix} COO\,C_2H_5 \\ COO\,C_2H_5 \end{matrix} \right]$$

Malonic ester is prepared from acetic acid.



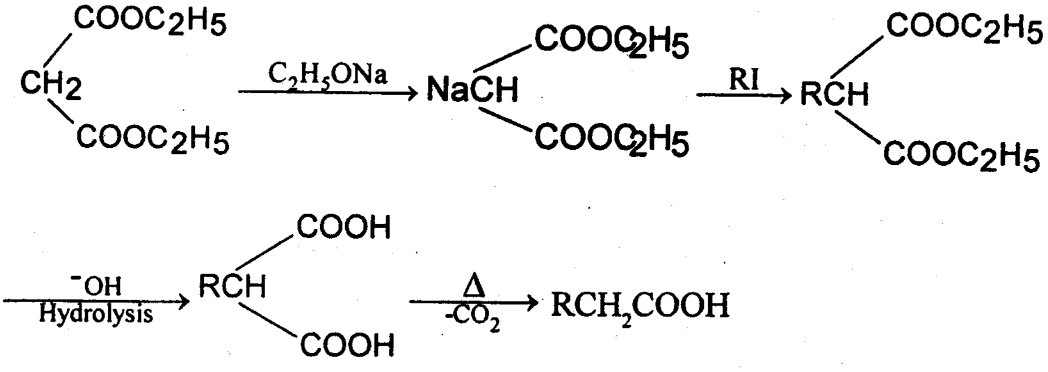
$$CH_2\begin{matrix} COOH \\ H \end{matrix} \xrightarrow{Cl_2/p} CH_2\begin{matrix} COOH \\ Cl \end{matrix} \xrightarrow{KCN} CH_2\begin{matrix} COOH \\ CN \end{matrix} \xrightarrow[\text{Hydrolysis}]{HCl} CH_2\begin{matrix} COOH \\ COOH \end{matrix}$$

$$\xrightarrow{2C_2H_5OH} CH_2\begin{matrix} COO\,C_2H_5 \\ COO\,C_2H_5 \end{matrix} + 2H_2O$$

2.6.6. Synthetic applications of malonic ester :

2.6.6.1 Substituted monocarboxylic acids :

In the presence of sodium ethoxide and alkylhalide malonic ester gives substituted molonic ester. This on hydrolysis followed by decarboxylation gives substituted mono carboxylic acids.



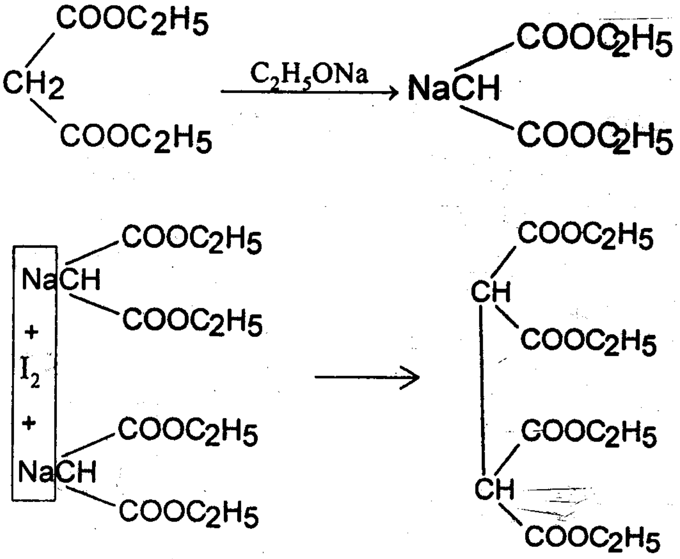
R = CH_3 Propionic acid

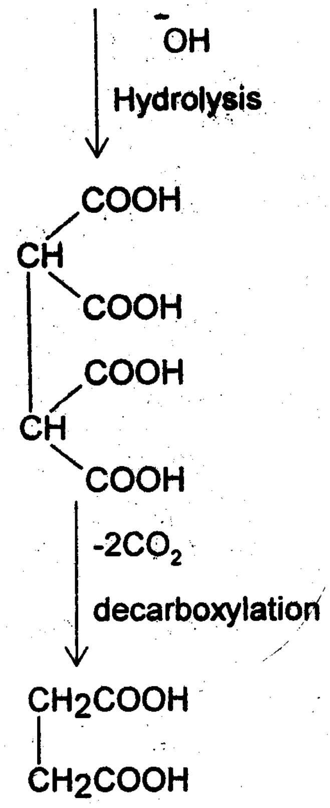
R = CH_3CH_2 n – butyric acid

R = $CH_3CH_2CH_2$ n – valeric acid

2.6.6.2. Substituted dicarboxylic acids :

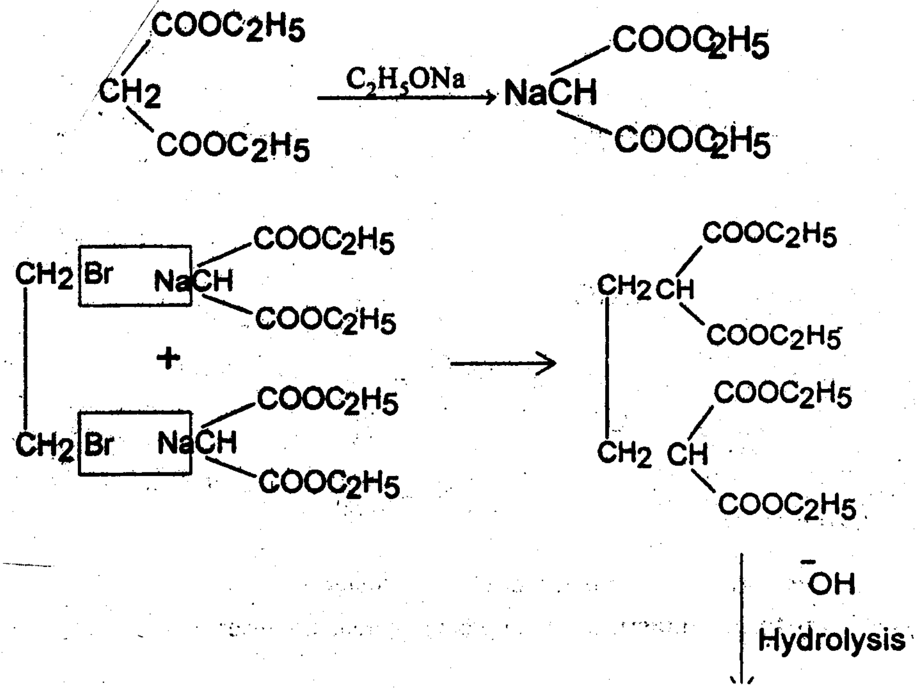
a) In the presence of sodium ethoxide malonic ester reacts with iodine followed by hydrolysis and decarboxylation gives succinic acid.

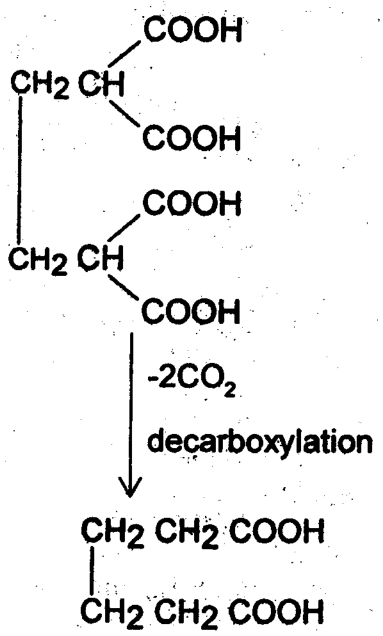




Succinic acid

b) In the presence of sodium ethoxide malonic ester reacts with ethylene dibromide followed by hydrolysis and decarboxylation gives adipic acid.

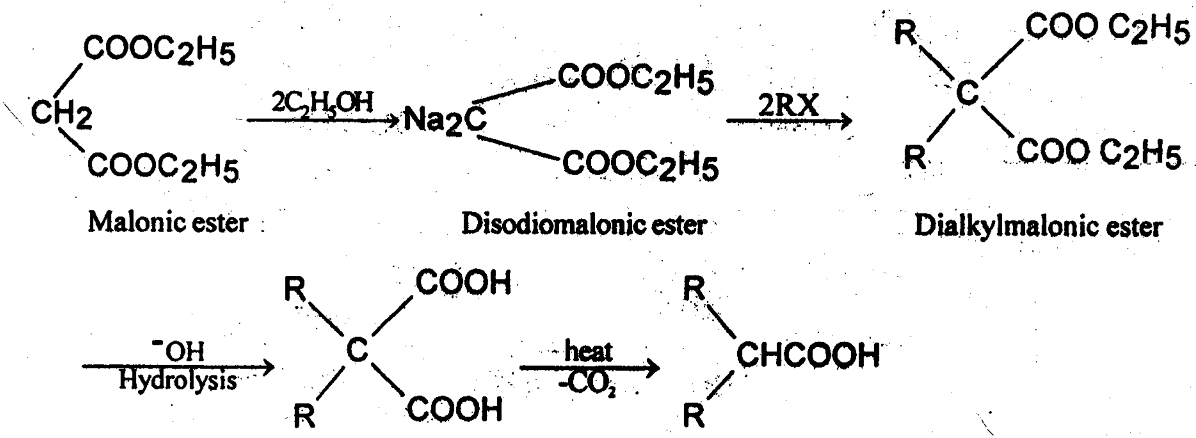




Adipic acid

c) dialkylacetic acid :

Malonic ester on heating with two equivalents of sodium ethoxide and then with two equivalents of alkyl halide forms dialkymalonic ester. Dialkyl malonic ester on hydrolysis followed by decarboxylation gives dialkylacetic acid.



Malonic ester

Disodiomalonic ester

Dialkylmalonic ester

Dialkylacetic acid

2.6.7. Model Questions :

1. a) Give mechanism for the preparation of acetoacetic ester.
   b) Give any three synthetic applications of acetoacetic ester.

2. a) How do you prepare diethylmalonate ?
   b) Explain any four synthetic uses of diethyl malonate.
3. What are active methylene compounds ? Give an example. Discuss how is it useful in the synthesis of organic compounds.
4. What is claisen condensation ?
5. What is carbanion ? How is it produced from active methylene compounds ?
6. Starting from acetoacetic ester how can you bring out the following –
   a) Acetone
   b) Succinic acid
7. Explain acidity of α– hydrogen
8. Explain acid hydrolysis and ketonic hydrolysis of acetoacetic ester.
9. Write notes on the structure of carbanion.
10. Starting from malonic ester how can you bring out the following –
    a) Propionic acid
    b) Succinic acid
    c) Adipic acid.

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Unit - III **Physical Chemistry**

Lesson - I

PHASE RULE

3.1.1 Introduction :

Statement and meaning of the terms - phase, component and degrees of freedom, Gibb's Phase Rule, phase equilibria of one component system - water system. Phase equilibria of two - component system - solid liquid equilibria, simple eutectic - Pb - Ag system, desilverisation of lead. Solid solutions - compound with congruent melting point (Mg- Zn) system and in congruent melting point - ($NaCl-H_2O$) system. Freezing mixtures.

3.1.2 Introduction :

Statement and meaning of the terms - phase, component and degrees of freedom, Gibb's Phase Rule.

The Phase Rule is the generalisation dealing with the behaviour of heterogeneous systems at equilibrium, With the application of Phase Rule, it is possible to predict, the effect of change in temperature, pressure and concentration on a heterogeneous system in equilibrium. A system consisting of only one phase is called a homogeneous system where as a system containing more than one phase is called as heterogeneous system. The Phase rule was formulated by an American physicist Willard Gibbs in 1874.It may be stated mathematically as follows.

$$F = C - P + 2$$

Where ' F ' is the number of degrees of freedom, 'C' is the number of components and 'P' is the number of Phases in equilibrium.

Explanation of the terms :

Since, Phase rule is an important generalisation. it is necessary to it understand thoroughly, the various terms involved in it

Phase :

It is denoted by letter 'P'. Any homogeneous part of a system physically distinct by a boundary surface and mechanically separable from other parts of the system is called as a phase. A phase has same physical and chemical properties through out. A system containing only liquid water, is called one phase system. If there is both liquid water and water vapour, it is called a two phase system. In a similar way, if a system consists of ice, liquid water and water vapour, the system is said to be consisting of three phases.

A Solid, a liquid or a gas (any pure substance) made up of by one chemical substance is considered as one phase. The substance in a phase may be in small size or in bulk, it belongs to single phase only. For example, whether ice is in the form of single piece or many pieces, it is considered as only one phase. Each substance in a homogeneous mixture cannot be taken as a separate phase. For example a mixture of gases i.e. oxygen and nitrogen must be taken as a single phase. Only miscible liquids always form a single phase. Eg : - Ethanol and water system. A mixture of two immiscible liquids form two separate phases. Eg : water and benzene system.

Aqueous solutions are considered as single phase. However, a saturated solution of sugar in contact with excess of sugar is considered as a two phase system.

A mixture of two solids is considered as a two phase system. Thus a mixture of calcium carbonate and calcium oxide is a two phase system.

Component :

It is denoted by letter 'C'. The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase can be expressed with the help of a chemical equation.

For example

(1) in water system, there are three phases namely ice, water and water vapour and the composition of all these three phases can be expressed only in terms of only chemical individual H_2O. Hence water system has only one component and hence is called a one component system. So, any system which consists only one chemical individual is known as a one component system.

(2) Sulphur system has four phases namely rhombic sulphur, monoclinic sulphur, liquid sulphur and sulphur vapour. The composition of all these four phases can be expressed by only sulphur and hence sulphur system is a one component system.

(3) Decomposition of calcium carbonate is another example constituting two solids and one gas. Calcium carbonate, when heated in a closed vessel, exists in equilibrium with its products, calcium oxide and carbon dioxide.

$$\underset{\text{Solid}}{CaCO_3} \rightleftharpoons \underset{\text{Solid}}{CaO} + \underset{\text{Gas}}{CO_2}$$

These three constituents are not independent of one another and thus the composition of all the phases can be expressed in terms of any two of the three chemical substances present in equilibrium. Hence, the decomposition of calcium carbonate is a two component system.

a) If CaO and CO_2 are considered as the components.

Phase		**Components**
$CaCO_3$	=	$CaO + CO_2$
CaO	=	$CaO + OCO_2$
CO_2	=	$OCaO + CO_2$

b) If $CaCO_3$ and CO_2 are considered as the two components.

Phase		**Components**
$CaCO_3$	=	$CaCO_3 + OCO_2$
CaO	=	$CaCO_3 - CO_2$
CO_2	=	$O\,CaCO_3 + CO_2$

c) If $CaCO_3$ and CaO are considered as the two components.

Phase		Components
$CaCO_3$	=	$CaCO_3 + OCaO$
CaO	=	$OCaCO_3 + CaO$
CO_2	=	$CaCO_3 - CaO$

(4) Ammonium chloride when heated in a closed vessel exists in equilibrium with the products i.e. ammonia and hydrogen chloride gas.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Solid Gas Gas

The system consists of two phases namely solid NH_4Cl and gaseous mixture containing NH_3 and HCl in the same proportion as they are combined in solid NH_4Cl. The composition of both the phases can be expressed in terms of NH_4Cl only.

Phase		Components
Solid	=	NH_4Cl
Gaseous	=	$xNH_3 + xHCl$ or xNH_4Cl

Hence the dissociation of NH_4Cl is a one component system.

Degrees of freedom :

It is denoted by letter 'F'. It is the number of independent variables such as pressure, temperature and concentration which must be specified in order to define the system at equilibrium completely. In the system, the remaining variables are automatically fixed. For example.

The equilibrium between water and its vapour, depends only on pressure or temperature and hence the system has only one degree of freedom and the system is said to be univariant (F=1). Consider a one component system with three phases. Ice, water (liquid) and vapour are co existing at the freezing point of water. These three phases can co exist only at a particular temperature under one particular pressure. If either pressure or temperature is varied one of the phases immediately disappears. Hence the system has no degrees of freedom and is known as non variant or invariant (F=0). A system containing pure gas has two degrees of freedom. If the values of pressure and temperature are specified, the volume is fixed automatically (F=2). A system containing a mixture of two or more gases is completely defined when temperature, pressure and concentration are specified. All the three variables are specified, to define the system and hence the system has three degrees of freedom (F=3).

3.1.3 Phase Diagrams :

The diagram with the help of which the co-existence of different phases in a multiphase system can be studied is called a phase diagram. It is a graph showing the conditions of pressure and temperature under which different phases can exist together in a state of dynamic equilibrium. The phase diagram consists of areas, curves and triple points.

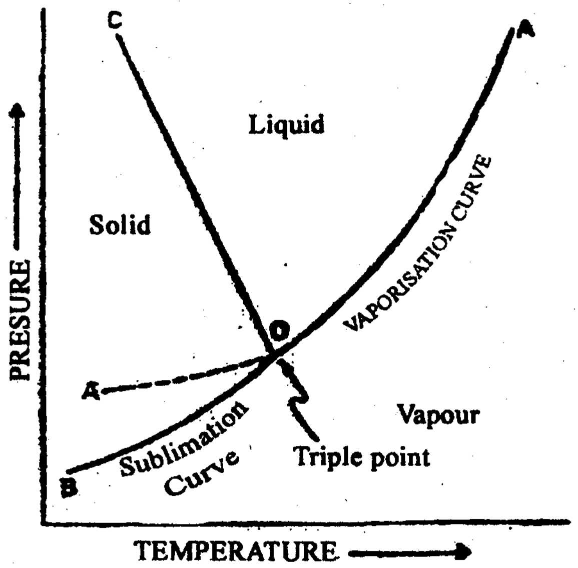


Fig : A Typical Phase diagram of a one - component system

a) The above given diagram which represents one component system is divided into three areas namely solid, liquid and vapour. Each area indicates the conditions of temperature and pressure under which that particular phase can exist. In a system when there is only one phase, on applying phase rule, indicates the number of degrees of freedom as '2' and hence each area of phase diagram represents a bivariant system.

$F = C - P + 2$

$F = 1 - 1 + 2 = 2$

In order to define the condition of the phase, both temperature and pressure must be stated.

b) There are three curves in the phase diagram, indicating the separation of areas. The curves indicate the conditions of equilibrium between any two of the three phases.

Along any of the above three curves on the phase diagram, when temperature or pressure is specified, the other is fixed automatically. On applying phase rule, it indicates, that on any curve, the system is univariant and has one degree of freedom.

$F = C - P + 2$

$F = 1 - 2 + 2 = 1$

Triple Point :

The three curves, enclosing the three areas on the phase diagram intersect at a point called Triple Point. At triple point, since both temperature and pressure are fixed the system has Zero degrees of freedom and hence is called non - variant or invariant.

Solid $\rightleftharpoons$ liquid $\rightleftharpoons$ vapour

$F = C - P + 2 = 1 - 3 + 2 = 0$

Metastable equilibrium :

By careful cooling of the liquid, the vapour pressure curve AO can be extended to A^1 without terminating at 'O'. It means, the liquid can be cooled far below the freezing point or super cooled without separation of the crystals. The super cooled liquid is unstable and by the addition of a seed crystal the liquid solidifies completely. Thus the curve ' OA^1' represents a metastable equilibrium. The vapour pressure of the metastable phase is always higher than the stable phase at a given temperature.

Super cooled liquid $\rightleftharpoons$ vapour

3.1.4. Phase equilibria of one component system - water system :

The water system is an example for one component system. All the three phases i.e. ice, liquid water and water vapour present in the water system are represented by one chemical individual H_2O and hence is a one component system. In the phase diagram of water system.

There are (a) three curves namely OA, OB and OC (b) Three areas namely AOC,AOB and BOC and (c) the triple point 'O'.

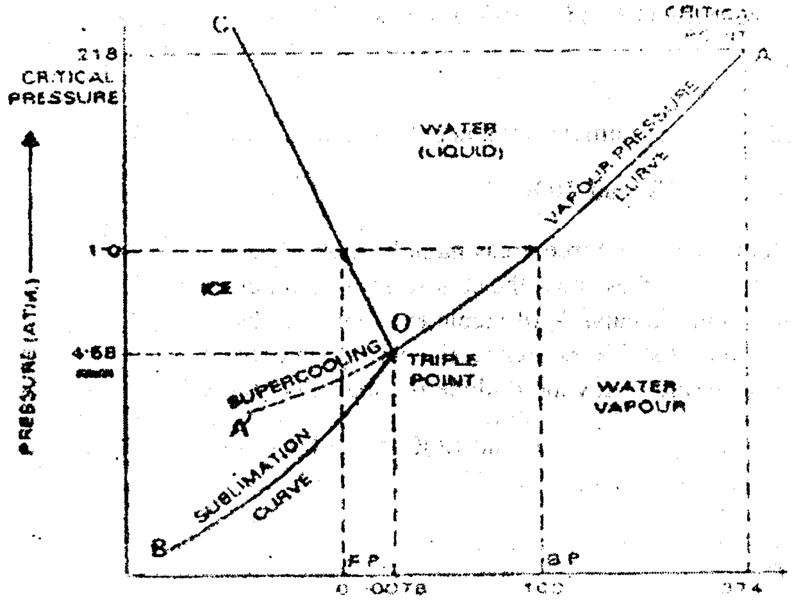


Fig : The Phase diagram of Water System

1) Importance of the curves OA,OB and OC :

The three curves OA, OB and OC meet at point 'O' and divide the phase diagram into three areas.

The curve OA known as vapour pressure curve of water represents the equilibrium between liquid water and vapour at different temperatures. The system is univariant and the number of degrees of freedom is only one.

Liquid water $\rightleftharpoons$ vapour

$F = C - P + 2 = 1 - 2 + 2 = 1$

The temperature at which the vapour pressure of water is equal to one atmosphere is called as the boiling point of water (100°c). The curve OA terminates at 'A', the critical point (at pressure 218 atmosphere, and temperature 374°c) above which liquid water can not exist.

The curve 'OB', the sublimation curve of ice, represents the equilibrium between solid ice and vapour. The curve OB terminates at absolute Zero (-273°c) where there is no existence to vapour phase. The system is univariant and has only one degree of freedom.

The curve 'OC' the fusion curve of ice represents the equilibrium between ice and water. This curve shows the effect of pressure on the melting point of ice. The curve 'OC' is inclined towards the pressure axis indicates that the melting point of ice decreases with increase in pressure. The freezing point of water is lowered by 0.0075° by increase in pressure to one atmosphere.

Along the curves OA, OB and OC there are two phases in equilibrium.

$F = C - P + 2 = 1 - 2 + 2 = 1$

There fore, the system is univariant since it has one degree of freedom.

2) Areas AOC, AOB and BOC :

In water system, there are three areas namely AOC (water) ; AOB (water vapour) and BOC (ice). The areas between the curves show the conditions of temperature and pressure under which a single phase – ice, water or vapour, is capable of stable existence. In the area lying between the curves OA and OC, water alone is capable of stable existence, the area lying between OB and OC, ice alone and the area lying below the curves OB and OA, vapour alone is capable of stable existence.

In all the three areas AOC, AOB and BOC, there being one component and one phase. Thus on applying phase rule, each phase ice, water or vapour has two degrees of freedom and hence the system is bivariant.

The Triple Point 'O' :

The three curves OA, OB and OC meet at the point 'O' where all the three phases ice, water and water vapour coexist in equilibrium. Since all the three phases coexist at point 'O'. It has Zero degrees of freedom and the system becomes invariant or non-variant. At point 'O' known as triple point, the three phases can coexist at a definite temperature (0.0075°c) and vapour pressure (4.58mm Hg).

$F = C - P + 2 = 1 - 3 + 2 = 0$

Meta stable equilibrium :

It is possible that water can be super cooled below its freezing temperature with out the separation of ice. The vapour pressure of liquid water AO can be continued below the point 'O' as shown by the dotted curve 'OA'. The super cooled water vapour system is called as metastable equilibrium because on addition of a crystal of ice to the supercooled liquid, the entire liquid solidifies. In the phase diagram, the curve 'OA' lies above the curve OB, which indicates that the metastable system has a higher vapour pressure than the stable one at same temperature.

Different forms of ice :

In the explanation of water system, only one form of solid ice has been considered. By increasing pressure, seven different forms of ice can be isolated each of which can represent a separate phase. Inclusion of all the forms of ice in a single diagram makes it very much complicated and hence it is not represented.

Phase equilibria of two component system - condensed phase rule, solid – liquid equilibria - simple entectic – lead – silver system, desilverization of lead :

In a two component system, when there is a single phase, then the number of degrees of freedom is three, which means, all the three variables namely temperature, pressure and composition must be specified in order to describe the phase. Since it is not convenient to consider all the three variables simultaneously, only two variables are to be considered at a time, keeping the third variable as constant. In studying the solid liquid equilibria, in two component systems, the vapour phase is considered to be absent and the effect of pressure on the equilibrium is very small. Taking the remaining two variables i.e. temperature and composition, the phase diagrams are drawn. Such a two component system consisting of solid and liquid phases only, with the gas phase absent is called a condensed system and the number of degrees of freedom is reduced by one and the reduced phase rule takes the form

$$F = C - P + 1$$

where 'F' is the number of degrees of freedom.

3.1.5 Simple eutectic systems :

The components are completely miscible with one another in the liquid state. They do not form any compound and on solidification, they give rise to an entectic mixture (easy melting)

Example : Lead – Silver system :

It is a two component system and consists of four phases namely solid lead; Solid Silver; Solution of molten Silver and lead and vapour. The vapour phase is absent as the boiling point of lead and silver are very high. Hence it is a condensed system with three phases and pressure has no effect on the system.

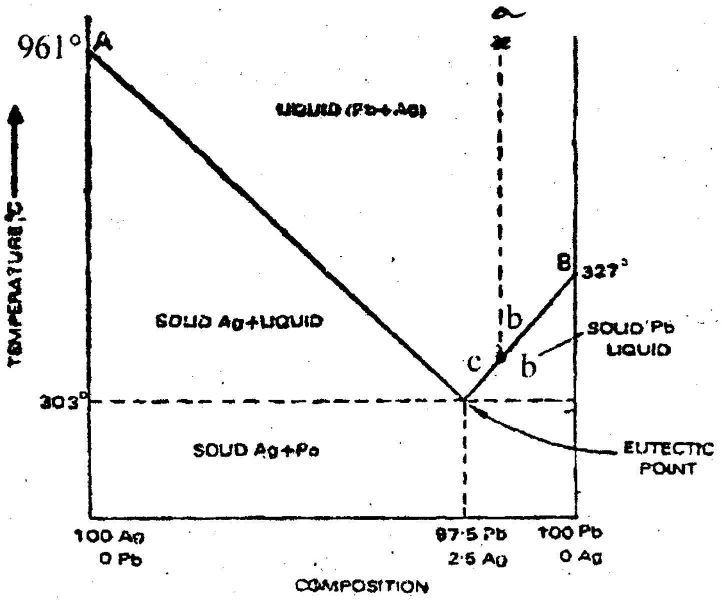


Fig : The Phase diagram of lead - Silver System

In the above phase diagram, there are two curves, AC and BC ; three areas - above ACB; below BC and below AC and one entectic point 'C'

Curve AC :

AC is the freezing point curve of silver. Pure silver melts at 961°c and the point 'A' represents the freezing point or melting point of pure silver and the addition of lead lowers its melting point along the curve AC. Pure silver and solution of silver and lead are the phases present in equilibrium along the curve 'AC'. On applying the reduced phase rule, it indicates the system pure silver and solution as univariant and has one degree of freedom.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

Curve BC :

The curve BC is the freezing point curve of lead. Pure lead melts at 327°c and the curve BC shows that the addition of silver lowers the melting point of lead. 'B' represents the melting point of pure lead. Along the curve 'BC' pure lead and solution phases are in equilibrium and the system is univariant with one degree of freedom.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

Areas :

The area above ACB represents the solution of molten lead and silver phase.

$$F = C - P + 1 = 2 - 1 + 1 = 2$$

The system is bivariant with two degrees of freedom. The area below AC represents the two phases pure silver and solution. In a similar manner, the area below BC represents, the phases, pure lead and solution. Below the temperature 303°c, the area represents pure, solid silver + Solid lead.

$F = C - P + 1 = 2 - 2 + 1 = 1$

In all these three areas, each has one degree of freedom and the system is univariant.

The entectic Point 'C' :

The curves AC and BC intersects a point C. the point 'C' is called the entectic point. The three phases solid silver, solid lead and solution are in equilibrium at c and the system is non – variount or invariant with zero degrees of freedom.

$F = C - P + 1 = 2 - 3 + 1 = 0$

At point 'C' both the variables i.e. temperature – 303°c and composition – 97.5% pb and 2.5% of Ag are fixed. The temperature at eutectic point is called as entectic temperature. At temperature above entectic temperature, the solid phases of silver and lead disappear but below the entectic temperature there exists the solid phases of silver and lead.

Desilverisation of lead by pattinson's process. :

The phase diagram of lead - silver system has importance in the desilverisation of lead by pattinson's process. The argentiferous lead containing a very small amount of silver i.e. less than 1% is melted above the melting point of lead. Let the point a represent the molten lead system on the diagram. On cooling the temperature of the melt falls along the dotted line 'ab'. As the temperature corresponding to 'b' on the curve 'BC' is reached, solid lead begins to separate out and the solution will contain relatively increasing amounts of silver. The lead separates along the curve BC until the entectic point 'C' is reached and the lead formed is continuously removed by means of ladles and the percentage of silver goes on increases in the melt. At point 'C' an alloy containing 2.6% of silver and 97.4% of lead is formed. The process of increasing the percentage of silver in the alloy is known as pattinson's process.

3.1.6 Solid solutions - compound with congruent melting point - Mg- Zn system :

There are a number of systems in metals, organic compounds and inorganic salts dissolved in water in which the two components combine to form compounds. Thus intermetallic compounds are formed when the two components are metals, salt hydrates are formed when the system contain a salt and water as two components.

These systems are of two types depending upon whether the compound formed has a congruent melting point or an incongruent melting point.

a) Formation of compounds with congruent melting points : Example – Mg – Zn system :

A compound which melts sharply at a constant temperature into a liquid of the same composition as the solid, is said to possess a congruent melting point. In Magnesium – Zinc system, there is a formation of an intermetallic compound $Mg(Zn)_2$. The system consists of four phases namely solid magnesium ; solid zinc ; solid $Mg(Zn)_2$ and the liquid solution of Mg and Zn. Zinc melts at 420% and magnesium at 650°c and the compound $Mg(Zn)_2$ melts at 590°c.

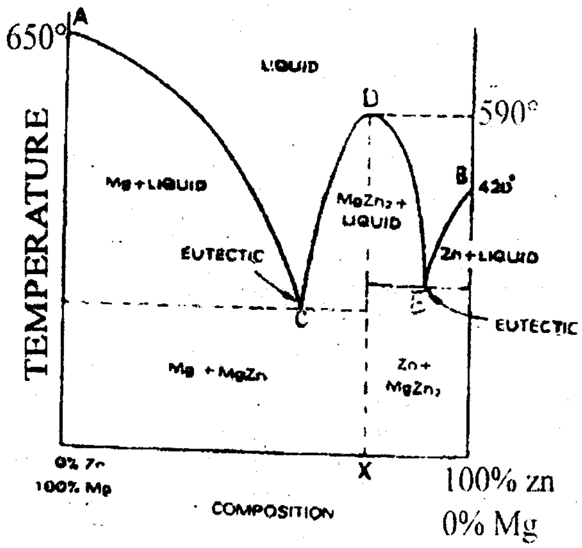
The Phase diagram of Mg- Zn system is made of two simple eutectic diagrams namely Mg-$Mg(Zn)_2$ and Zn – $Mg(Zn)_2$

Curve AC :Freezing point curve of magnesium.

The curve AC shows decrease in melting point of magnesium on the addition of zinc which continues until the point 'C' is reached where a new phase, solid $Mg(Zn)_2$ appears.

Cure CDE : Freezing point curve of the compound $Mg(Zn)_2$

The curve CD shows an increase in the concentration of zinc with increase in temperature. At point 'D' the composition of the melt and the solid compound $Mg(Zn)_2$ becomes the same. The point 'D' represent the melting point of Mg $(Zn)_2$ The curve DE shows the lowering of the melting point on the addition of zinc until the lowest point is reached where appears solid zinc.



Phase diagram of Magnesium-Zinc system

Curve BE : Freezing point curve of zinc:

The curve BE shows that the melting point of zinc is lowered on the addition of magnesium until the point 'E' is reached. Along the three curves AC, CDE and BE, there are two phases in equilibrium, one solid phase and another liquid phase. On applying the reduced phase rule equation

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

indicates that the systems Mg/ liquid ; Zn/liquid and Mg $(Zn)_2$/liquid are all univariant or monovariant.

The areas : At any point in the area, the system which indicates a single phase is bivariant.

Eutectic Points :

There are two entectic points C and E in the phase diagram and at each point, there are two components and three phases in equilibrium.

At point C, the phases present are solid magnesium, solid Mg (Zn)$_2$ and liquid. At point E, the phases present are solid Zn, solid Mg(Zn)$_2$ and liquid. On applying the reduced phase rule equation

$$F = C - P + 1 = 2 - 3 + 1 = 0$$

and hence the system at point C and E is non-variant.

Congruent melting Point ·

The composition of the solid compound Mg(Zn)$_2$ and the melt at 'D' is same and hence the corresponding temperature is called as the congruent melting point of the compound Mg(Zn)$_2$ Both the Phases, i.e. the solid Mg(Zn)$_2$ and the melt are represented by the same component Mg(Zn)$_2$ On applying the reduced phase rule equation.

$$F = C - P + 1 = 2 - 3 + 1 = 0$$

The system at Point 'D' is non-variant.

3.1.7 b) Formation of compounds with incongruent melting point – (NaCl – H_2O) system :

In a number of systems, the compounds formed by the combination of two components decompose when heated giving a new solid phase and a solution of the solid with a different composition from that of the solid. Such compounds are said to have an in congruent melting point. The decomposition of the compound at this temperature is known as transition reaction or meritectic or peritectic reaction and the in congruent melting point is known as transition temperature or meritectie or peritective temperature. Sodium chloride – water; sodium sulphate – H2O ; Gold – antimony ; Picric acid – benzene are some examples of two component systems which give rise to compounds with incongruent melting points.

Sodium Chloride – water (NaCl - H_2O) system :

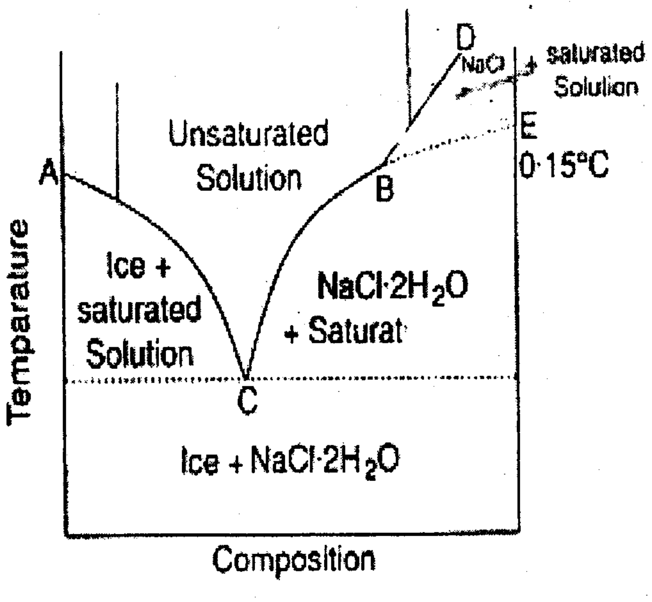


Fig : The Phase diagram of Nacl - H_20 System

Curve AC : Freezing point curve (Solution and ice) :

The curve AC shows the change in melting point of ice, which decrease, on the addition of sodium chloride to pure ice. The point 'A' indicates the freezing point of water or melting point of ice i.e. 0°c at one atmosphere pressure. Along this curve ice and salt solution are in equilibrium.

On applying the reduced phase rule equation

$F = C - P + 1 = 2 - 2 + 1 = 1$

indicates the system as monovariant. At point 'C' i.e. at 21°c, the solution gets saturated and thus ice and $NaCl\ 2H_2O$ crystals separate. At point 'C' there are three phases namely solution, ice, solid NaCl (in addition to vapour phase) and the point 'C' is known as entectic point or cryohydric point (entectic means easy melting). Thus addition of a salt to ice produces decrease in temperature. On addition of salt continuously in small amounts, a stage will reach and the salt, ice and solution exists in equilibrium which is stable at one particular temperature known as entectic point or cryohydric point. This is the lowest temperature that can be obtained with a salt water system.

Curve CB : Solubility curve of $NaCl\ 2H_2O$ hydrate :

The curve indicates that the solubility of NaCl in H_2O decreases slowly with rapid increase in temperature. At point 'B', the $NaCl\ 2H_2O$ hydrate crystals decompose to form anhydrous NaCl. Since $NaCl\ 2H_2O$ does not have a sharp melting point, it melts and decomposes to give a new phase. This is known as transition reaction and the temperature is known as incongruent melting point. At point 'B' the temperature is 0.15°c. The curve BD represents the solubility curve of anhydrous NaCl.

Thus, in NaCl H_2O system, there is one entectic point at 'C' and one incongruent melting point at 'B'.

3.1.8 Solid Solutions :

When a system consists of two metals as components, they combine and the metal melts on solidification gives rise to a solid mixture at the eutectic point. Such solid mixture or is called solid solutions.

For example, in lead – silver system at entectic point 2.6% Ag ; 97.4% Pb Solid solution forms.

2)In Mg – Zn system, Mg + Mg $(Zn)_2$ and Zn + Mg $(Zn)_2$ solid solutions are formed.

Freezing Mixtures :

When a salt is added to ice, in a salt water system, the melting point of ice falls. At 0°c, when salt is added to ice, there exist equilibrium between the three phases i.e. ice, salt and solution. It is stable at eutectic or cryohydric point. This is the lowest temperature known as cryohydric temperature that can be attained by a salt water system. Composition of the system at this temperature is called Freezing mixture. These freezing mixtures are used in the laboratory to bring down the reaction temperature to sub zero levels.

Examples :

Freezing Mixture	-	Lowest Temperature (Or) Cryohydric temperature
NaCl + Ice	-	-21°c
NH4Cl + Ice	-	-71°c
$CaCl_2$ + Ice	-	-55.9°c
KCl + Ice	-	- 11.4°c

3.1.9 Model Questions :

1) State phase rule and explain the terms involved. What is a phase diagram ? Explain.
2) Discuss the application of phase rule to a one component system.
3) Explain the following terms with suitable examples.

   i) Triple Point (ii) Univariant system (iii) Eutectic Point.

4) Apply the phase rule to silver – lead system and explain the importance of eutectic point.
5) What is congruent melting point ? Discuss the phase diagram of Mg – Zn system.
6) What is incongruent melting point ? Discuss the phase diagram of NaCl H_2O system.
7) Find the degrees of freedom and number of components in the following systems

   $CaCO_3 (s) \rightleftharpoons CaO(s) + CO_2 (g)$

8) Discuss the significance of triple point in water system.
9) Define Phase rule and explain the terms involved. Mention the degrees of freedom in the following systems.

   i) Pure gas (ii) Saturated solution of sodium chloride (iii) $I_2(s) \rightleftharpoons I_2(v)$

10) What is a component ? Give the number of components present in the following systems.

    i) Mixture of O_2 and N_2 (ii) Decomposition of Ca CO_3 (iii) water $\rightleftharpoons$ water vapour

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UNIT - III

Lesson - II

SOLUTIONS

3.2.1 A solutions is defined as a homogeneous mixture of two or more substances. The substance present in larger proportion is called as solvent while the substance present in smaller amounts is called as solute. A solution may exists in three states namely gaseous state; liquid state and solid state;. Depending upon the physical state of solute and solvent; nine types of solutions are possible, out of which, solid in liquid ; liquid in liquid and gas in liquid solutions are more significant.

Reasons for a substance to dissolve :

Every system exhibits two types of tendencies (i) the system always tends to move towards decrease in energy and (ii) to move towards increased disorderliness or randomness. Solution exhibits a state of greater randomness. Randomness favours solution. So, randomness always trying to increase the solubility while energy trying to decrease it. Temperature always increases randomness and hence solubility increases with rise in temperature.

3.2.2 Solubility of gases in liquids :

All gases are soluble in water as well as other solvents to a certain extent. The solubility of a gas is generally expressed in terms of absorption coefficient (α) introduced by Bunsen. The solubility of the gas in a liquid depends upon the pressure, temperature, the nature of the gas and the nature of the solvent. The absorption coefficient is defined as the volume of the gas reduced to N.T.P or S.T.P. dissolved by unit volume of the solvent at a given temperature and at a pressure of 1 atmosphere. The gases which are easily liquefied are more soluble in common solvents. eg: CO_2 ; NH_3 etc are more soluble in water. Gases which are highly ionized in water are more soluble in water. For example gases like HCl ; NH3 are highly ionized and hence they are more soluble in water. At a given pressure, the solubility of a gas decreases with rise in temperature.

The effect of pressure on the solubility of a gas in a given solvent was discovered by William Henry. He found a simple relation between the pressure and solubility of a gas. This relation is known as Henry's law and may be stated that at constant temperature, the mass of a gas dissolved per unit volume of a solvent is proportional to the pressure of the gas.

$m \alpha p$

$m = K.P$

Where

m = mass of a gas dissolved per unit volume of a solvent.

P = Pressure of the gas

K = Proportionality constant.

Gases obey Henry's law provided

(i) The temperature is not too low

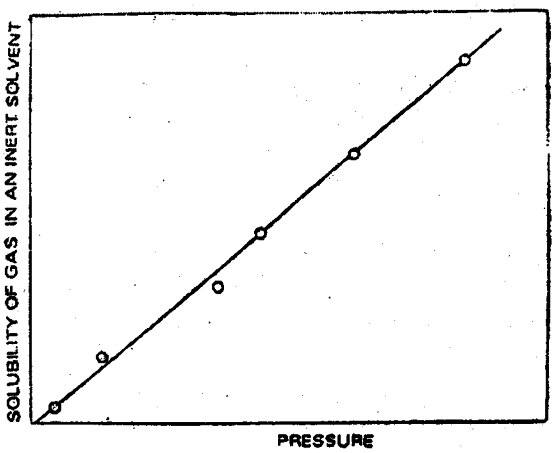
(ii) Pressure is not too high

(iii) The gas does not dissociate or enter into chemical combination with the solvent and the gas should not be highly soluble. For example the Henry's law is valid in case of solubility of ammonia in benzene since it is sparingly soluble but not in water since it enters into chemical combination with water.

$$NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Henry's law may be stated in another form, considering the volume of the gas dissolved instead of the mass. The volume of the gas dissolved will remain the same in spite of increase of pressure. Hence, Henry's law may be stated as that "The volume of the gas dissolved in a solvent at a given temperature is independent of the pressure" .

If Henry's law is valid, the graph obtained should be a straight line, when solubility of a gas is plotted against pressure at constant temperature.



Variation of solubility of agas with pressure.

3.2.3 Solutions of liquids in liquids :

Solutions containing only two liquids are known as binary liquid solutions. Depending upon their solubility in one another, the binary liquid solutions are classified into three types.

i) The two liquid are completely soluble in all proportions.

Example : Benzene and Toluene ; water and alcohol.

ii) Partially miscible liquids :

The two liquids are soluble in one another only to a limited extent.

Eg : Phenol and water; nicotine and water

iii) Immiscible liquids :

The two liquids do not mix with each other and hence form separate layers.

Eg : Carbon tetra chloride and water ; Carbon disulphide and water ; aniline and water,

Completely miscible liquids :-

Completaly miscible liquids are further classified into two types of solutions namely ideal and non - ideal solutions.

Ideal Solutions :

A solution in which the molecules attract one another with equal force irrespective of their nature is known as an ideal solution. For example in an ideal solution of two liquids A and B ; the force of attraction between A and A ; B and B and A and B molecules are same. Liquid mixtures Eg :- Benzene and toluene ; carbon tetrachloride and silicon tetrachloride; Ethylene chloride and ethylene bromide ; n – Hexane and n – Heptane are examples of ideal solutions.

In an ideal solution

i) Total volume of the solution = volume of one liquid + volume another liquid. i.e. no volume change occurs when the two liquids are mixed.

ii) No heat is evolved or absorbed on mixing the two liquids.

iii) Raoult's law is obeyed exactly at all concentrations and at all pressures. It is proved by a straight line graph obtained bye plotting vapour pressure versus mole fraction of components.

Raoult's law

According to Raoult's law the relative lowering of vapour pressure of a solution is equal to the mole fraction of the nonvolatile solute present in the solution.

Raoult law when applied to an ideal binary liquid mixture of two liquids A and B.

$$P_A = x_A.P^\circ_A$$

$$P_B = x_B P^\circ_B$$

Raoult's law may be stated as the partial vapour pressure of any volatile constituent of a solution at any temperature is equal to the vapour pressure of the constituent (P°) multiplied by the mole fraction of that constituent in the solution.

3.2.4 Non – Ideal Solutions :

The solution which does not obey Raoult's law are known as real or non ideal solutions. In non ideal solutions, the molecular interactions between the two components i.e A- B are either more or less than the molecular interactions between the individual components i.e A-A or B-B. In case of ideal solutions the graphs of vapour pressure versus composition (mole fraction) are straight lines while in the case of non - ideal solutions the graphs are curved lines. Depending upon these curves, the non ideal solutions are divided into three types namely

(i) solutions that show small positive deviations from Raoult's law

(ii) solutions that show large positive deviations and

(iii) Solutions that show large nagative deviations.

(i) Solutions that show small positive deviations from Raoult's law :-

The vapour pressure composition graphs of these solutions show small positive deviation. For any mole fraction the total vapour pressure of the solution as well as the partial vapour pressure of each component are very slightly more than that expected from Raoult's law for ideal solutions.

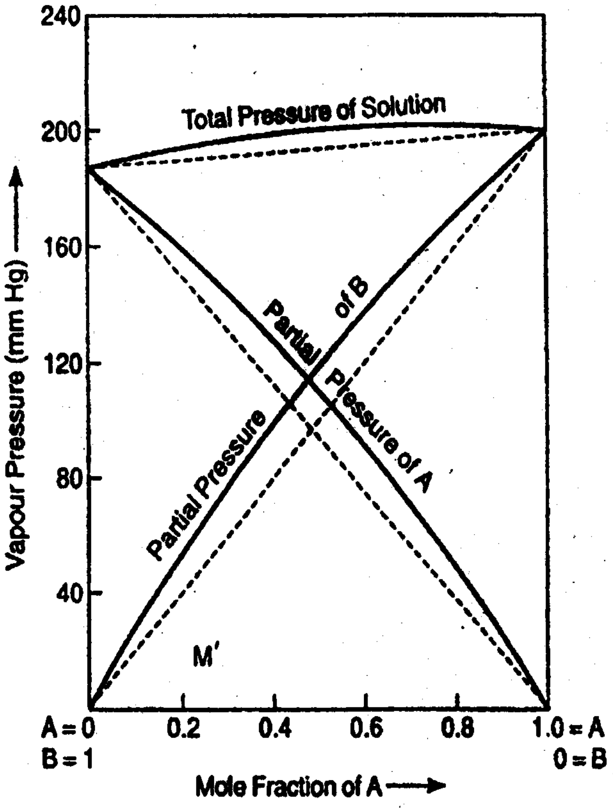


Fig : Vapour pressure - Composition plots for real Solution showing small positive deviation. The dotted lines represent ideal behaviour.

(ii) Solutions that show large positive deviations :-

In these solution salso, the total vapour pressure of the solution and, the partial vapour pressure of each component are greater or maximum than that calculated from the Raoult's law. The tendency for the molecules to escape from the solution is more than that from the pure liquids, In other words, the

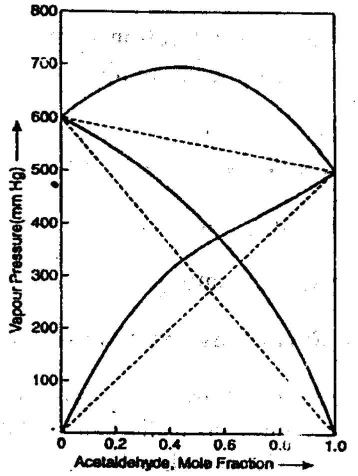


Fig : Vapour pressure composition plots for real Solution showing large positive deviation. The dotted lines represent ideal behaviour.

inter molecular attractions between A - B are weaker than A-A or B-B attractions, Formation of this type of solution is accompanied by an increase in volume and absorption of heat.

Examples : Water and ethanol ; acetaldehyde - carbon disulplide, Benzene and Cyclohexane etc.

iii) Solutions that show large negative deviations :

In these solutions the total vapour pressure of the solution is less than that calculated from the Raoult's law and hence show negative deviation. Here, the tendency for the molecules to escape from the solution is less than that from the pure components. It indicates that the intermolecular attractions between molecules of liquid pair A-B are stronger than either A-A or B-B attractions. Formation

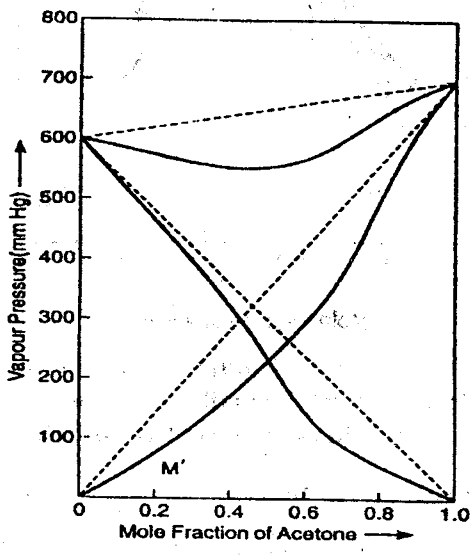


Fig : Vapour pressure composition plots for non - ideal Solution showing negative deviation. The dotted lines represent ideal behaviou

of this type of solutions is accompanied by decrease in volume and evolution of heat. Examples : Water and nitric acid ; Acetone and chloroform ; Pyridine and acetic acid etc.

3.2.5 Azeotropes mixtures :

Completely miscible liquids are divided into azeotropic mixtures (two types) and Zetropic mixtures, A mixture of two or more liquids which boils at a constant temperature with out change in composition is known as azeotropic mixture. But azeotropic mixtures can not be regarded as compounds because the boiling point and composition of an azeotrope change with the pressure while the composition of a compound remain unchanged with temperature and pressure.

Azeotropes – HCl-H2O; Ethanol- water systems, Fractional distillation:

The study of the vapour pressures of completely miscible liquids mixtures are of great help in the separation of liquids by fractional distillation. plotting the vapour pressures of these mixtures of completely miscible liquids against composition has revealed that the mixtures of completely miscible liquids are of three types –

i) Maximum boiling point azeotropic solutions

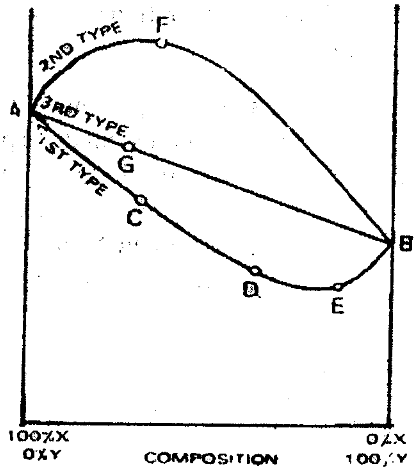
ii) Minimum boiling point azeotropic solutions and

iii) Zeotropic mixtures.

i) Maximum boiling point azeotropic solutions :

The vapour pressure curve of this first type of solutions exhibit minimum vapour pressure at a particular composition and thus a maximum boiling point. In a mixture of two liquids X and Y in which X is a more volatile component. On adding more and more of component 'Y', the vapour pressure of the mixture decreases and the point 'D' where the vapour pressure is minimum and thus boiling point is maximum. The mixture will boil at constant temperature and distil over completely without any change in its composition.

Complete separation of this type of solutions into its components is impossible. Such type of liquid mixtures which distil unchanged in composition at a constant temperature and show a maximum boiling point are called as maximum boiling point azeotropic solutions.



Vapour Pressure of Liquids

Example : HCl – H2O system.

Hydrochloric acid form a constant boiling mixture at 110°c containing 20.24% of hydrochloric acid.

ii) Minimum boiling point azeotropic solutions

The vapour pressure curve of this type of solutions of completely miscible liquid mixtures show maximum vapour pressure at point F and hence lowest boiling point. Such type of solutions show a constant boiling point until one of the component has been completely exhausted. After that the temperature rises and the other component will pass over. It is not possible to separate these solutions also into its components completely by fractional distillation. At the most, it is possible to separate it into a constant boiling mixture and one of the components in pure state.

Such liquid mixtures which distil without change in composition at a constant temperature are called minimum boiling point azeotropic solutions.

Example :

Ethanol or Ethyl alchol and water system. Ethanol – water mixture containing 95.59% alcohol boils at the minimum temperature of 78.13°c. Thus it is very difficult to get pure alcohol by distillation. How ever, by adding benzene, it is possible to convert it into low boiling benzene – water mixture and on distillation, pure alcohol may be left behind.

iii) Zeotropic mixtures.

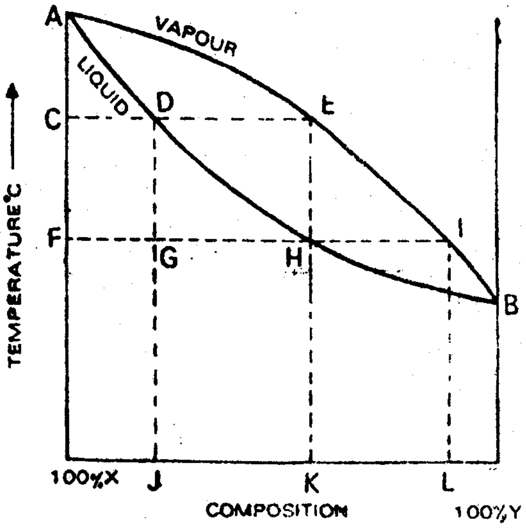
The liquid mixtures which distil with a change in composition are called zeotropic mixtures. The vapour pressure of this type of mixtures always lie between the vapour pressure of pure components and hence the vapour pressure composition curve is a straight line. This type of miscible liquid mixtures can be separated completely into its components by fractional distillation.

Examples : Methyl alcohol – water mixture.

3.2.6 Theory of fractional distillation :

The vapour pressure composition curves of completely miscible liquid mixtures are helpful in separation of the liquid mixtures by fractional distillation. Complete separation by fractional distillation is possible only in case of third type of solution i.e. in Zeotropic mixtures.

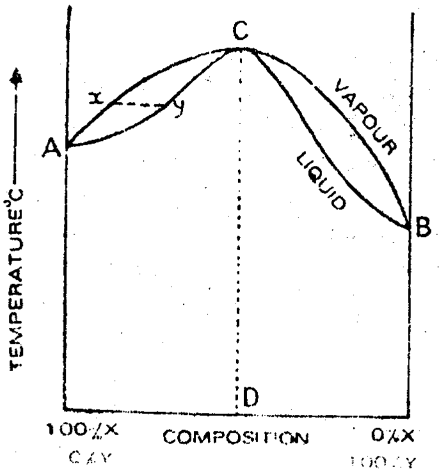
When a binary liquid mixture consisting of x and y components is heated, then the component having higher vapour pressure will boil at a lower temperature. To understand the process of fractional distillation it is necessary to have an idea of the composition of the vapour phase and that of liquid mixture at different boiling temperatures. For this purpose the temperature - composition curves are important. When we plot the boiling point of liquid mixture against its composition, and the composition of the vapour in contact with it, two separate curves for each type of solution are obtained. The curves obtained for third type of solutions are shown below.



Curves showing the composition of vapour and
liquid at various boiling temperatures.

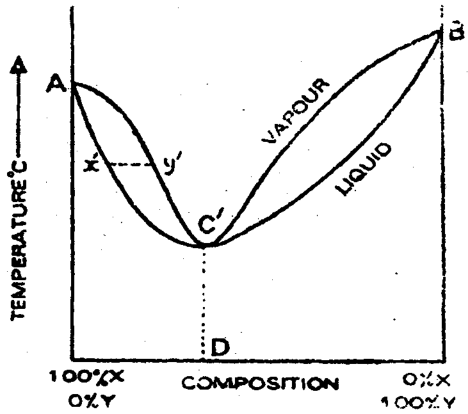
AEB and ADB are the temperature composition curves obtained for the vapour and liquid respectively. The composition of liquid mixture is represented by 'J' at temperature 'C' and that of vapour in equilibrium by K. The more volatile component 'Y' is present in greater proportion in the vapour than in the liquid mixture. Thus the distillate, richer in 'x' if it is subjected again to distillation, it will boil at 'F' and the fresh distillate will have the composition 'L'. Now the proportion of 'Y' in the second distillate is greater than in the first one. By repeating the process of distillation in this way, 'Y' can be obtained, almost in pure state.

In first type of solutions, (Maximum boiling pont azeeotropic Solutions) a boiling mixture indicated by 'Y' has its vapour, poor in 'Y' than the liquid mixture and there is gradual rise in boiling point till the maximum point 'C' is reached where the liquid mixture and vapour have the same composition. Here, the distillation proceeds without change of composition.



Boiling point curves
for Ist type of solutions.

In second type of solutions, (Minimum boiling point azeotropic solutions) a boiling mixture indicated by the point 'X'. In vapour the amount of 'Y' is in higher amount and there is gradual fall in boiling point till it reaches the minimum point 'C' Where the vapour and liquid mixtures have the same composition here, the mixture boils with out any change in composition.

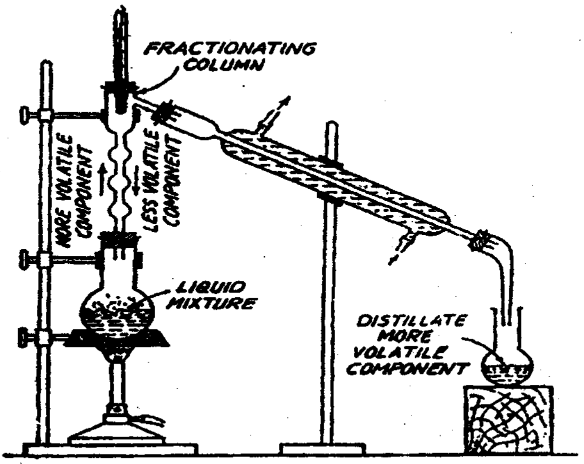


Boiling Point Curves
for 2nd type of solutions.

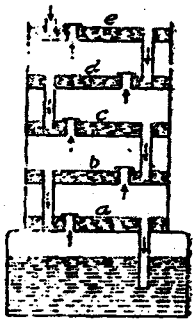
So, the above two types of solutions, can not be completely separated by fractional distillation.

Fractional distillation :

Fractionating columns are used in order to decrease the number of distillations and so increase the efficiency of the process of fractional distillation. It is a long tube provided with obstruction to the passage of vapour going upwards and that of the liquid coming downwards. The liquid mixture which is to be fractionated is taken in a distillation flask fitted with a fractionating column, a thermometer and a condenser.



-Fractional distillation.



-Bell and plate type fractionating column.

The flask is heated from below. The liquid vapourises and the vapours rise into the fractionating column where some of the vapours condense and start flowing down.

For industrial purposes a fractionating tower is employed which is divided into several compartments by means of trays that are set one above the other. At the centre of each tray, there is a hole which is covered by a bubble cap. Each tray has an over flow pipe which joins it with the tray present below it. The fractionating column is fitted in the neck of the distillation flask so that the vapours of the liquid being heated passes up through it. The temperature falls in the fractionating column as the vapours pass from bottom to the top. The hot vapours that enter the column get condensed in the lower part and when heating is continued more vapours travel upwards and boil the liquid already condensed. Thus the liquid condensed in the lowest part is distilled on to the upper part. A sort of condensation and distillation goes on along the height of the column which results in the increase of the proportion of the volatile component in the out going vapours. There exists an equilibrium between the liquid and vapour, at every point in the column vapours of the low boiling liquid escape at the top and are condensed while the high boiling liquid collects at the bottom.

3.2.7 Partially miscible liquids :

A large number of liquids which dissolve in one another, only to a limited extent are called as partially miscible liquids. Their solubility in one another is limited. For example, ether dissolves about 1.2% water and water dissolves about 6.5% ether. When equal volumes of ether and water are shaken, two separate layers are formed one of which is a saturated solution of ether in water and the other layer is a saturated solution of water in ether. These two solutions which are in equilibrium are known as conjugate liquids and the partially miscible liquids systems are divided into three types basing ont heir critical solution temperatures.

i) Partially miscible liquids having upper critical solution temperature **Eg** : Phenol – water system

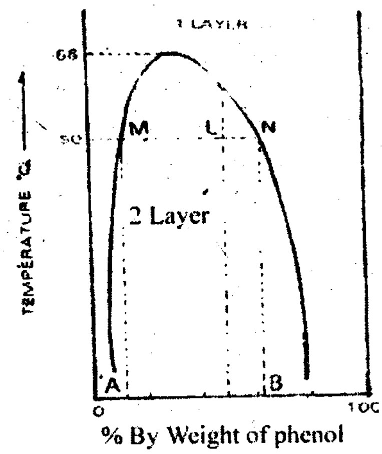
ii) Partially miscible liquids with lower CST, **Eg** : Triethyl amine – water system and

iii) Partially miscible liquids having upper as well as lower CST, **Eg** : Nicotine water system.

The temperature at which the two partially miscible liquids become completely miscible is called the critical solution temperature (CST) or consolute temperature of the system. Critical solution temperature is very much influenced by the presence of impurities. When the critical solution temperature is lower than the room temperature, it is known as lower critical solution temperature while if it is higher than the room temperature, it is known as upper critical solution temperature.

i) Phenol - water - system with upper CST :

Phenol and water are partially miscible at ordinary temperature. On shaking these two liquids, two saturated solutions of different compositions are formed i.e. one is phenol in water and the other is water in phenol. Such solutions of different composition coexisting with one another are called conjugate solutions. Their mutual solubility in one another increases with rise in temperature and hence the concentration of phenol in water and water in phenol goes on increases with rise of temperature and finally at a certain temperature, the two conjugate solutions merge into one another to form one layer of homogenous solutions. This temperature at which the two conjugate solutions merge into one another to form a single layer is called critical solution temperature (CST) or upper consolute temperature. This temperature for phenol water system.

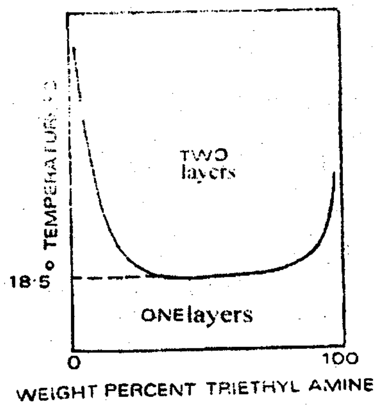


Phenol-Water System

Corresponds to 66°c and the composition of phenol as 33%. Above this critical solution temperature and outside the curve, the phenol and water are completely miscible and the system is homogeneous. But, below this curve, the complete miscibility depends upon the composition of the mixture. It is clear from the graph that at a temperature below 50°c, a mixtures of 90% phenol and 10% water (Point M) or 5% phenol and 95% water (Point N) will lie outside the curve and hence the above composition is completely miscible. At 50°c, a mixture of equal proportions (50%each) of phenol and water form two layers whose compositions are given by A and B. The critical solution temperature is very much influenced by the presence of impurities. Hence the critical solution temperature is used for testing the purity of phenol and other substances.

ii) Triethyl amine – water system - systems with lower CST :

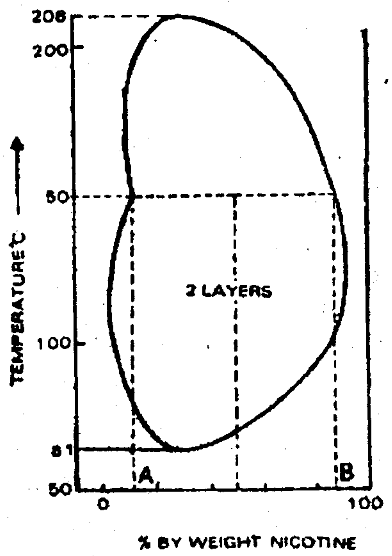
In triethyl amine – water system the mutual solubilities of the two components increases with decrease in temperature. The two liquids are completely miscible at 18.5°c. This temperature is called lower critical solution temperature or lower consolute temperature. Below 18.5°c temperature, the two liquids are completely miscible to form one layer but above this temperature the two liquids form two different layers.



Triethyl amine-water system.

iii) Nicotine water systems with upper as well as lower CST :

Some partially miscible liquid systems, for example Nicotine water system, appear to be as a combination of the above two types. These liquids are completely miscible above certain critical temperature and below certain critical temperature. They show both upper as well as lower consolute temperature. Thus the system has two critical solution temperatures or consolute temperatures upper 208°c and the lower 61°c . Above 208°c and below 61°c the two liquids are miscible in all proportions. In other wards, between these two limiting temperatures the two liquids are partially miscible. Increase of pressure on the system raises the value of lower critical solution temperature and decreases the values of the upper critical solution temperature and finally they become one at a particular pressure.



Niootine and water system.

3.2.8 Immiscible liquids :

Liquid pairs such as water ether ; water – benzene ; water – carbon tetrachloride and water – Cyclohexane do not mix with each other. Hence they are known as immiscible liquids or non- miscible liquids. In such liquid mixtures, each liquid exerts its own vapour pressure independent of the other. The total vapour pressure of the in the liquid mixture.

$$P = P_A + P_B$$

Where P_A and P_B are the individual vapour pressures of the liquids A and B respectively.

Any mixture of two immiscible liquids boil at a temperature lower than that at which any pure liquid of the mixture boils.

The relative proportion of the two liquids in the distillate can be calculated, considering the fact that the number of moles of each liquid present in the vapour phase is proportional to its vapour pressure. If n_A and n_B are the number of moles of the two liquids A and B

Then

$$\frac{P_A}{P_B} = \frac{n_A}{n_B}$$

$$= \frac{W_A/M_A}{W_B/M_B}$$

$$\frac{W_A}{W_B} = \frac{P_A}{P_B} \times \frac{M_A}{M_B}$$

W_A and W_B represent the actual weights and MA and MB are the molecular weights of the liquids A and B respectively.

Thus the weights of the liquids in the distillate are in the ratio of their vapour pressures and molecular weights.

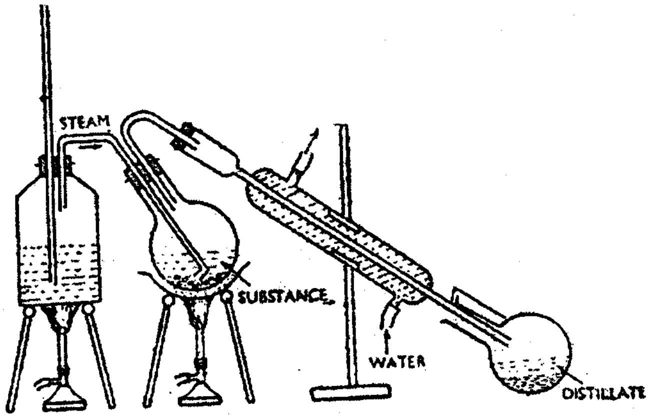
3.2.9 Steam distillation :

Steam distillation is a process of distillation carried out in a current of steam. It is used in the purification of organic compounds having high boiling points. These compounds should be immiscible in water. The process of steam distillation is done in preference to ordinary distillation

i) for the purification of organic liquids when it is difficult to remove impurities by other methods and

ii) when the given impure liquid decomposes at higher temperatures.

When a mixture of water and a high boiling liquid is heated in a current of steam, the mixture boils at a lower temperature than the boiling point of the organic liquid.



Steam distillation.

Steam distillation is used in the purification of organic compounds having high boiling points. The mixture to be distilled is placed in a round bottomed flask and steam is passed into it from a metallic can in which steam is produced by boiling water. The flask which is heated on a sand bath is connected to a water condenser which has a receiver placed below its lower end. Water and organic liquid collected in the receiver form two separate layers which can be separated by means of a separating funnel. The organic liquid is then dried and redistilled. The ratio of distilling liquids is given by the relation.

$$\frac{\text{Organic substance}}{\text{Water}} = \frac{P_O}{P_W} \times \frac{M_O}{18}$$

Where P_o and P_w are the vapour pressures of organic substance and water; M_o – molecular weight of organic substance and 18- molecular weight of water.

3.2.10 Problems :

1) A mixture of nitrobenzene and water boils at 99°c at one atmospheric pressure. The vapour pressure of water at that temperature is 733 m.m. calculate the proportion of water in nitrobenzene in the distillate at the boiling point.

Ans : Molecular weight of nitrobenzene = 123

Vapour Pressure of water (P_w) = 733m.m.

Vapour Pressure of nitrobenzene (PNB) = 760 – 733 = 27 mm

$$\frac{\text{Weight of } C_6H_5NO_2}{\text{Weight of } H_2O} = \frac{P_A \cdot M_A}{P_B \cdot M_B}$$

$$\frac{W_{C_6H_5NO_2}}{W_{H_2O}} = \frac{27 \times 123}{733 \times 18} = \frac{1}{3.97} \text{ or } 4:1$$

2) The vapour pressures of water and aniline at 98.5°c are 717m.m and 43m.m respectively. The molecular weights of water and aniline are 18 and 93. Calculate the relative weights of the two liquids in the distillate.

Ans : $$\frac{\text{Weight of aniline } (W_A)}{\text{Weight of water } (W_B)} = \frac{P_A \cdot M_A}{P_B \cdot M_B}$$

$$\frac{(W_A)}{(W_B)} = \frac{43 \times 93}{717 \times 18} = 0.3098$$

3) When a mixture of nitro benzene and water is distilled at a pressure of 732m.m at 98.2°c, the distillate contains 18.8 gm of nitrobenzene per 100 gm of water. Vapour pressure of water at 98.2°c is 712 m.m. Calculate the molecular weight of nitrobenzene.

Ans : Vapour pressure of nitrobenzene = 732 – 712 = 20m.m

Vapour Pressure of water = 712 m.m

$$\frac{(W_A)}{(W_B)} = \frac{P_A \cdot M_A}{P_B \cdot M_B}$$

$$\frac{W_{N.B}}{W_w}=\frac{P_A . M_A}{P_B . M_B}$$

$$\frac{18.8}{100}=\frac{20\times M_A}{712\times 18}$$

$$M_A=\frac{18.8\times 712\times 18}{2000}=120.5$$

Molecular weight of nitrobenzene = 120.5

3.2.11 Model Questions :

1) State and explain Henry's law. Show that the volume of a gas absorbed by a given volume of solvent is independent of pressure.
2) State and explain Raoult's law and Henry's law.
3) What are ideal and non- ideal solutions? Show that in an ideal solution, the volume of mixing and the enthalpy of mixing is zero.
4) what are azeotropic mixtures ? Explain with one example
5) Draw a labeled temperature composition diagram for the nicotine water system and discuss the variation of mutual solubility of nicotine and water with temperature.
6) Define the term critical solution temperature. Explain upper consolute temperature and lower consolute temperature with one example each.
7) What do you understand by positive and negative deviations from Raoult's law. Explain with suitable examples.
8) Explain the principle underlying the process of steam distillation.
9) Discuss the principle of fractional distillation of a miscible liquid pair.
10) Explain the terms consolute temperature and conjugate solution. Discuss the variation of mutual solubility of Phenol – water.
11) A mixture of chloro benzene and water which are immiscible boils at 90.30°c at an external pressure of 740m.m.The vapour pressure of pure water at 90.3°c is 630.1m.m. Calculate the weight composition of the distillate.
12) A mixture of Chlorobenzene and water distills at 90°c and at 734.4m.m pressure. At 90°c, the vapour pressure of water is 506m.m. Calculate the ratio of weight of chlorobenzene to water collected in the distillate.

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UNIT -III

Lesson - III

ELECTRO CHEMISTRY - I

3.3.1 Substances which allow electricity to pass through them are known as conductors while the substance which do not allow the electricity to pass through them are known as non-conductors or insulators.

Conductors can be divided into two types namely

i) metallic conductors and

ii) Electrolytic conductors or electrolytes.

Metallic conductors :

Conductors which conduct electricity without undergoing any chemical change are known as metallic conductors. In these conductors, the conductance is due to flow of electrons.

Examples : Metals and non metals like graphite.

Electrolytic conductors or Electrolytes :

Conductors which undergo chemical decomposition when electric current is passed through them are known as electrolytic conductors or electrolytes. In these conductors, the flow of electric current is due to the movement of ions.

Examples : Aqueous solutions of acids ; bases and salts and fused salts.

A substance which in the form of its molten state or solution conduct electricity and undergoes chemical decomposition is called an electrolyte and the phenomenon of decomposition by electricity is known as electrolysis. In a similar manner, the substance in the form of solution or in its molten state which do not conduct electricity is called a non electrolyte .

Example : Pure water and organic compounds.

Electrodes :

The medium through which electric current enters or leaves the electrolyte is known as electrode. It may be a metal rod, plate or a foil. There are two electrodes. i.e. a cathode or a negative electrode connected to the negative terminal of the battery. It allows the electric current to enter the electrolyte. An anode or positive electrode, connected to the positive terminal of the battery. It allows the electric current to leave the electrolyte.

Outside the electrolyte, the electric current flows from anode to cathode where as inside the electrolyte, the electric current flows from cathode to anode .

Molecules of electrolytes consist of two oppositely charged particles known as radicals or ions. Cations are positively charged ions. When electric current is passed through the solution of an electrolyte, these cations move towards the cathodes. The second type of ions known as anions are negatively charged ions move towards anode when an electric current is passed through the solution of an electrolyte.

Electrolysis :

The process of chemical decomposition of an electrolyte by passage of electric current through its aqueous solution or in the molten state is called electrolysis. The electrolytic cell is used for doing electrolysis. It is a glass vessel consist of electrolyte in the form of its solution or in molten state and two electrodes are dipped in the solution.

Mechanism of electrolysis :

Example :

Electrolysis of sodium chloride solution using platinum electrodes.

In the solution of sodium chloride : NaCl dissociates completely to give sodium and chloride ions while water dissociates to a small extent to form H^+ and OH ions. On passing electricity, hydrogen gas is liberated at the cathode while chlorine gas is liberated at the anode : and sodium hydroxide is formed in the solution.

At cathode :

H^+ ions have lower discharge potential than Na^+ ions and hence H^+ ions are liberated at the cathode.

Electrons enter the solution through the cathode and combine with H^+ ions to give neutral hydrogen atoms which then combine to form molecular hydrogen and escapes as gas

$H^+ + e^- \rightarrow H$ - Reduction

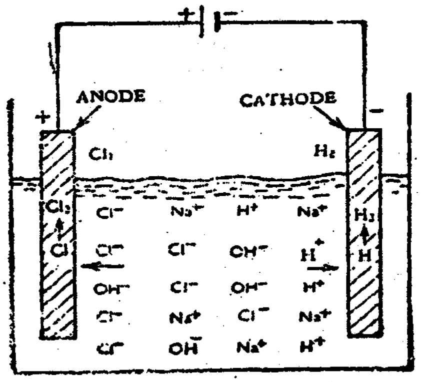
$H + H \rightarrow H_2$

At anode :

Chloride ions have lower discharge potential than $O\bar{H}$ ions and hence are liberated at the anode as chlorine gas.

$Cl^- \rightarrow Cl + e^-$ - oxidation

$Cl + Cl \rightarrow Cl_2$



Mechanism of electrolytic conduction.

The electrons furnished by the chloride ions flow through external circuit from the anode to the battery.

Thus, the phenomena of electrolysis involves oxidation at the anode and reduction at the cathode.

3.3.2 Faraday's laws of Electrolysis :

Michael Faraday, an English scientist studied the relation between the electricity and the amount of substance deposited on the electrode and discovered two important laws known as Faraday's laws of electrolysis.

I law :

The amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

Mathematically

$W \alpha Q$

W = Weight of the substance deposited (in grams)

Q = Quantity of electricity passed (in Coulomb)

$Q = c \times t$

Where

C = Current in amperes

t = time in seconds.

$W \alpha c \times t$

$W = Z \times C \times t$

Where Z is proportionality constant known as electro chemical equivalent of the substance.

When C = 1 ampere and t = 1 second i.e. a current of one ampere is passed through an electrolyte for one second

$W = Z \times 1 \times 1$

$W = Z$

Thus the electrochemical equivalent of a substance may be defined as the amount of the substance deposited by passing a current of one ampere for one second i.e. by passing one coulomb of electricity. One gram equivalent of an ion is always liberated by 96500 coulombs of electricity.

$$\text{Electro chemical equivalent } (Z) = \frac{\text{Equivalent weight}}{96500}$$

II law :

When the same quantity of electricity is passed through different electrolytes, then the weight of different substances produced are proportional to the equivalent weights of the substances.

$$\frac{W_1}{W_2}=\frac{E_1}{E_2}$$

Where W_1 and W_2 are the weights of two elements deposited by passing certain quantity of electricity through their salt solution and E_1 and E_2 are their equivalent weights.

According to I law

$$W = Z X C X t$$

$$\frac{Z_1 \times C \times t}{Z_2 \times C \times t}=\frac{E_1}{E_2}$$

$$\frac{Z_1}{Z_2}=\frac{E_1}{E_2}$$

Or

The electrochemical equivalent of an element is directly proportional to its equivalent weight.

$$E \alpha Z$$

$$E= F x Z$$

Where ' F ' is the proportionality constant called as Faraday which is equal to 96500 coulombs.

$$Z=\frac{E}{F}$$

$$\text{Electrochemical equivalent of the metal} = \frac{\text{Equivalent Weight of the metal}}{96500}$$

3.3.3 Conductance of electrolytes:

Every substance offers resistance to electricity to a small or large extent and its value is given by ohms law.

Mathematically

$$\text{Resistance} = \frac{Voltage}{Current}$$

$$R=\frac{E}{C}$$

$$ohms=\frac{Volts}{Amperes}$$

R = Resistance measured in ohms.

E = Voltage in volts.

C = Current strength in amperes.

Conductance(C) :

The conductance or conductivity is the ease with which the current flows through a conductor.The substance which offers lesser resistance will allow more current to flow through it.The reciprocal of electrical resistance is called as conductance or conductivity.It is expressed in

$$C = \frac{l}{R}$$

The unit called reciprocal ohm (ohm^{-1}) or mho.

Specific Conductance:

The resistance offered by a conductor to the passage of electricity through it is directly proportional to its length l and inversely proportional to the area of cross section 'a' ; i.e.

$$R \alpha \frac{l}{a}$$

$$R = \rho \frac{l}{a}$$

Where ρ (rho) is a constant and its value depends on the material of the conductor and is called as specific resistance.

When l =1 cm and a = 1cm^2 then R = ρ

Hence, the specific resistance or resistivity of an electrolyte is the resistance in ohms of a centimeter cube of material.

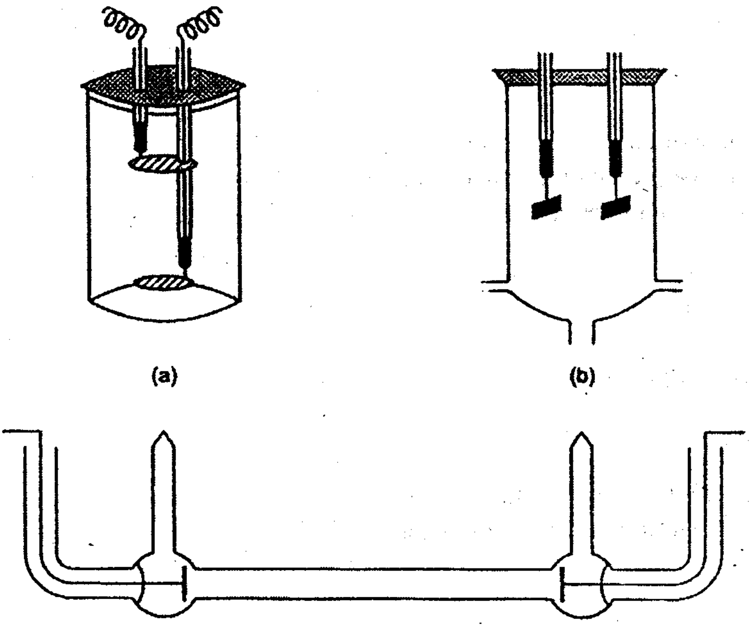
The reciprocal of specific resistance is known as specific conductance electrolytic conductivity and is denoted by the symbol K (Kappa)

$$K = \frac{1}{\rho} = \frac{l}{a} \times \frac{1}{R}$$

The electrolytic conductivity of a solution is defined as the conductance of a solution taken in a ce in which the electrodes are a unit distance and have a unit area.

Specific conductance is measured in units of ohm^{-1} cm^{-1}.

$$K = \frac{l}{a} \times \frac{1}{R} = \frac{cm \times 1}{(cm)^2 \times ohm} = \text{ohm}^{-1}\ \text{cm}^{-1}$$



(a) (b)

(c)

Some common typs of conductivity cells.
Cell of the type (a) are used for solution of low conductance, while cells of the types (b) and (c) are used for highly conducting solutions.

In measuring the specific conductivity of the aqueous solution of an electrolyte, the volume of the water in which a certain weight of the electrolyte is dissolved is always measured in cubic centimeters (C.C) and is known as the dilution.If the volume of the solution is 'V' c.c, the specific conductivity of such a solution at dilution 'V' is written as K_V.

Equivalent conductance :

If one gram equivalent weight of an electrolyte be dissolved in Vc.c. of the solution, the conductivity of all the ions produced from one gram equivalent is known as the equivalent conductance at the dilution 'v' and is written as λ_V. It is equal to the product of specific conductance K_V and the volume 'v' in ml containing one gram equivalent of the electrolyte.

$$\lambda_V = K_V \times V$$

The above relation is explained as follows -

9ml of a solution containing one gram equivalent of the electrolyte, when placed between two plates which are 1cm a part will consist of nine cubes each of which has a conductivity K_V. Then the total conductance of the solution is 9 X KV. In a similar way, Vml of solution will form V cubes and hence the total equivalent conductance λ_V will be K_V X V.

If C be the concentration of a solution in gram equivalents per litre, then the volume 'V' of the solution containing one gram equivalent will be 1000/c.

$$\therefore \lambda_v = K_v \times \frac{1000}{C}$$

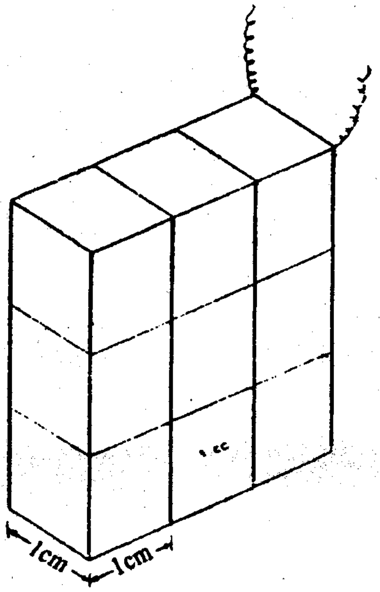
Units of equivalent conductance :

$$\lambda_v = K_v \times V$$

$$\text{But } K_v = \frac{l}{a} \times \frac{1}{R} \times V$$

$$= \frac{cm \times 1 \times (cm)^3}{(cm)^2 \times ohm \times equivalent}$$

$$= \text{ohm}^{-1}\ \text{cm}^2\ \text{Equi}^{-1}$$



Molecular conductance :

The conductance of all the ions produced, when one gram molecular weight of the solute be dissolved in Vml of the solution, is known as molecular conductance or molar conductance. It is represented as μ_v. It is obtained by multiplying the specific conductance by volume 'V' ml containing one gram molecular weight of the solute.

$$\mu_v = K_v \times V$$

Units of molecular conductance = ohm^{-1} cm^2 $mole^{-1}$.

Releation between equivalent conductance and molecular conductance :

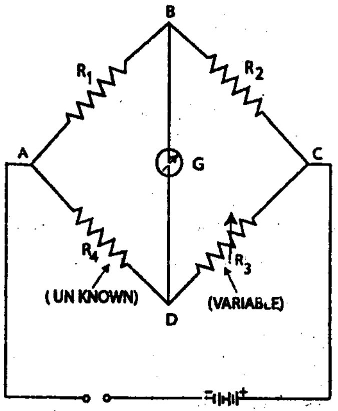
$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{\text{Number of charge on an ion}}$$

For Example in NaCl, the charge on each ion is 1

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{1}$$

3.3.4 Measurement of Conductance :

Conductance is the reciprocal of resistance and hence its value can be obtained by determining the electrical resistance of the solution using the principle of wheat stone bridge circuit. wheat stone bridge circuit consits four arms containing the resistance R_1, R_2, R_3 and unknown resistance R_4. The resistance R_1 and R_2 are fixed.R_3 is variable and R_4 is unknown.



A Simple Wheat Stone bridge

A small voltage is applied across points AC and the resistance R3 is varied until null point is obtained, i.e No deflection in the galvanometer 'G'. Connected across the points B and D i.e. then the solution whose conductance is to be determined is placed in a special type of cell known as conductivity cell.

Knowing the values R_1, R_2, and R_3, the value of R_4 can be calculated

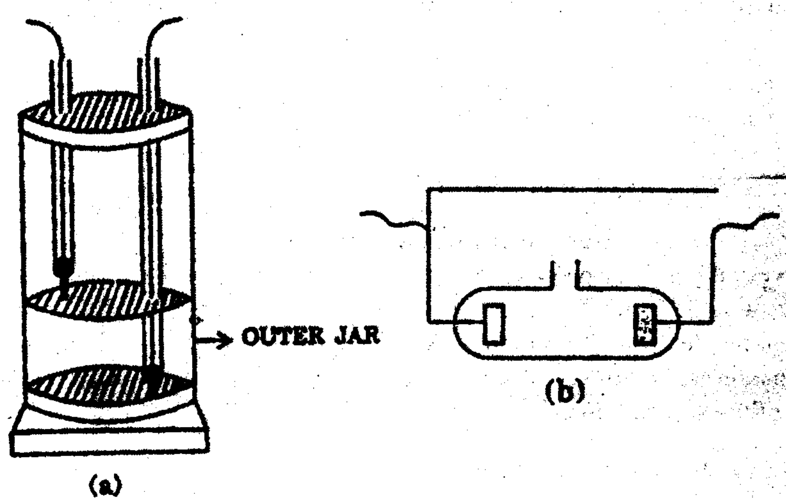
$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

The following types of conductivity cells are used.

Fig (a) type conductivity cell is used for solutions of low conductance and (b) type cell is used for solutions of high conductivity.

The conductivity cells are made of pyrex glass and fitted with two platinum electrodes. The electrodes consists of platinum discs coated with platinum black and welded to platinum wires fused in two glass tubes.

These glass tubes which contain mercury are firmly fixed in the ebonite cover of the cells so that the distance between the electrodes may not change during the experiment. The electrodes are connected to the circuit by dipping copper wires of the circuit in mercury placed in glass tubes. Conductance varies with temperature and hence the conductivity cell containing the solution is to be placed in a thermostat.



Conductivity Cell

The main difficulty in determining the resistance of the solution of an electrolyte by using direct current is it causes electrolysis of the solution in addition to conduction of current. The electrolysis of the solution produces the following effects -

1) The concentration of the electrolyte near the electrodes changes which results in polarisation effects. i.e. a back EMF is set up which opposes the current passed and hence causes the resistance to vary.

To avoid these difficulties, an alternating current is used. Since under these conditions, the galvanometer fails to detect the null point, it is replaced by a head telephone or magic eye.

The arrangement commonly used in class experiments is shown below.

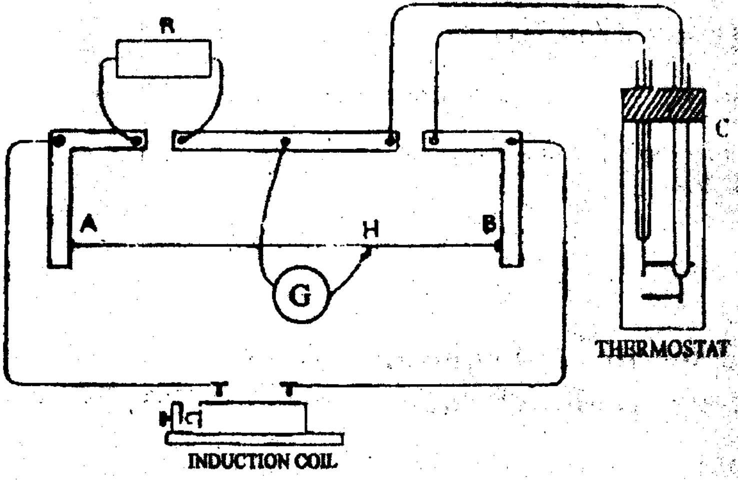


Fig . Apparatus for the measurement of the conductance of the solution of an electrolyte.

AB is a wire, mostly of platinum iridium alloy, tightly stretched over a metre scale graduated in millimetres. A sliding contact 'H' moves along this wire. R is a resistance box. 'C' is the conductivity cell containing the solution and is placed in the thermostat to maintain the temperature constant through out the experiment. 'I' is the induction coil and when the current is flowing, any resistance is unplugged in the resistance box R and the sliding contact 'H' is moved until the sound in the head telephone is minimum.

$$\frac{\text{Resistance of C}}{\text{Resistance of R}} = \frac{\text{Resistance of BH}}{\text{Resistance of AH}} = \frac{\text{Length BH}}{\text{Length AH}}$$

Cell constant :

The reciprocal value of cell resistance calculated as above does not give the exact specific conductance of the solution. It gives only a value proportional to it since the electrodes are not exactly 1cm apart and may not possess a surface area of 1cm². The exact value of specific conductance can be obtained by measuring the distance between the electrodes and their area of cross section. It is in convenient to measure the exact values of l and a ; an alternate method is used to calculate the specific conductance from the observed value of the conductance of the solution in cell 'C'.

When 'l' is the distance between the electrodes and 'a' is the area of cross section, the resistance R.

$$R = P \times \frac{l}{a}$$

$$R = P \times x$$

The ratio $\frac{l}{a}$ equal to x is called as the cell constant.

unit for cell constant = cm^{-1}.

$$\text{Cell constant, } x = \frac{R}{P}$$

$$= \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

Specific conductance = Cell constant x observed conductance.

According to the accurate measurements of Kohlrausch, the specific conductance of N/50Kcl solution at 25°c is 0.002765 mhos.

$$\text{Cell constant } x = \frac{0.002765}{\text{Observed conductance}}$$

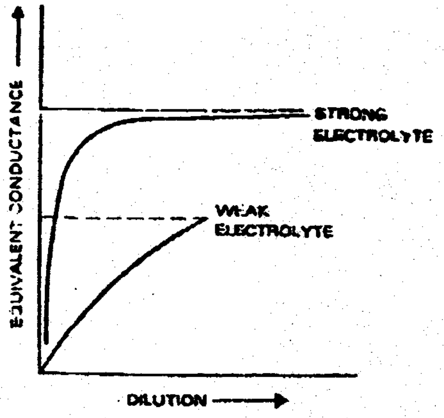
3.3.5 Variation of specific and equivalent conductance with dilution or Effect of dilution on specific and equivalent conductance :

Conductance of a solution is due to the presence of ions in the solution. Hence, greater the number of ions in a solution, greater will be its conductance. with dilution, the dissociation of the electrolyte increases and hence the conductance value should also increase. But the equivalent and molecular conductance valures of a solution increase with dilution where as the specific conductance of a solution decreases with dilution.

The specific conductance is the conductance of 1cm cube of the solution of an electrolyte. The specific conductance decreases with dilution because the number of ions present per centimeter cube of the solution decreases on dilution. Although the total number of ions increases with dilution, the number of ions per centimeter cube of the solution goes on decreases on dilution. The equivalent and molecular conductance values increase with dilution because these are the product of specific conductance and the volume of the solution. On dilution more and more of the electrolyte ionises and when the electrolyte has completely ionised, further addition of water produces no change in the value of equivalent and molecular conductances. Thus, the equivalent and molecular conductance values tends to aquire a maximum value with dilution. This maximum value of equivalent conductance at infinite dilution is represented as λ_{α} and that of molecular conductance as μ_{α}.

3.3.6 Classification of electrolytes :

Basing on their value of conductance, electrolytes are classified into two types namely strong electrolytes and weak electrolytes.



Effect of dilution on the equivalent conductance of weak and strong electrolytes

The electrolytes which posses a high value of equivalent conductance even at h concentrations and increases gradually with dilution and then reaches a maximum value are called ong electrolytes. Examples are HCl, HNO_3 ; H_2SO_4 ; NaOH ; KOH ; NaCl; KCl etc.

The electrolytes which posses a low value of equivalent conductance even at higher concentration and whose equivalent conductance increases rapidly with dilution but does not approach a constant value are called weak electrolytes.

Examples : CH_3COOH : NH_4OH etc.

3.3.7 Problems on specific conductance and equivalent conductance :

Example -1.

If the resistance of $\frac{N}{10}$ acid solution is 2.5 x 10^3 ohm when measured in a cell whose cell constant is 1.150, what will be the equivalent conductivity of the solution ?

Sol : Resistance of the solution , R = 2.5 x 10^3 ohm

Cell constant, x = 1.15

Strength of the solution = 0.1N

$$\text{Specific conductance, } K_V = \frac{x}{R} = \frac{1.15}{2.5\times10^3}$$

$$\text{Equivalent conductance} = \frac{K_V \times 1000}{C}$$

$$= \frac{1.15}{2.5\times10^3}\times\frac{1000}{0.1}$$

$$= 4.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}.$$

Example -2.

0.05N solution of a salt Occupying volume between two platinum electrodes 1.72cm apart and area 4.5cm^2 has a resistance of 250 ohms. Calculate the equivalent conductance of the solution

$$\textbf{Sol :} \text{ Cell constant, } x = \frac{\text{Length (l)}}{\text{area of cross section (a)}}$$

Length (l) = 1.72cm

area of cross Section (a) = 45cm^2

$$\text{Cell constant, } = \frac{1.72}{4.5} = 0.3822 \text{ cm}^{-1}$$

Strength of the solution = 0.05N

Resistance of the solution = 250 ohms

$$\text{Specific conductance, } K_V = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{x}{R}$$

$$= \frac{0.3822}{250} = 0.00153$$

Equivalent conductance $= K \times \frac{1000}{C}$

$= 0.00153 \times \frac{1000}{0.05}$

$= 30.6$ ohm cm^2.

Example -3.

The specific conductance of $\frac{N}{50}$ KCl solution at 25°c is 0.002765 ohm^{-1} cm^{-1} and the resistance of the cell contaning this solution is 100 ohms. Determine the cell constant.

Sol : Specific conductance = 0.002765 ohm^{-1} cm^{-1}

Resistance (R) of the solution = 100 ohms

Cell constant = Specific conductance x Resistance

= 0.002765 x 100

= 0.2765 cm^{-1}

Example -4.

The specific conductance of 0.1N Kcl solution is 0.0112 ohm^{-1}. The resistance of the cell contaning the above solution at the same temperature is 55ohms. Calculate the cell constant.

Sol : Specific conductance = 0.0112 ohm^{-1} cm^{-1}

Resistance = 55 ohms

Cell constant = Specific conductance x Resistance

= 0.0112 x 55

= 0.616 cm^{-1}

Example -5.

A conductance cell has two parallel electrodes of 1.25 cm^2 area and 10.5cm apart. when filled with 0.1N solution of an electrolyte at 298K, the resistance was found to be 2000 ohms. Calculate the cell constant and equivalent conductance of the solution of the electrolyte.

Sol : Cell constant $= \frac{\text{Length (l)}}{\text{area of cross section (a)}} = \frac{10.5}{1.25} = 8.4\text{cm}^{-1}$

Resistance = 2000ohms

Specific conductance $= \frac{l}{a} \times \frac{1}{R}$

$$= \frac{8.4}{2000} = 0.0042 \text{ ohm}^{-1}$$

Equivalent conductance $= K_v \times \frac{1000}{C}$

$$= 0.0042 \times \frac{1000}{0.1}$$

$$= 42 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

Example - 6 .

The cell constant of a cell is 0.5cm^{-1}. A solution of an electrolyte taken in the cell showed a resistance of 50ohms. Calculate the specific conductance of the solution.

Sol : Cell constant = 0.5 cm^{-1}

Resistance = 50 ohms

Specific conductance $= \frac{\text{Cell Constant}}{\text{Resistance}}$

$$= \frac{0.5}{50} = 0.01 \text{ ohm}^{-1}\text{cm}^{-1}$$

3.3.8 Model Questions :

1) State and explain Faraday's laws of electrolysis.
2) Write a short note on electrolytes and non electrolytes. What is electrolysis ? Compare metallic conductors and electrolytic conductors.
3) What do you understand by specific conductivity and equivalent conductivity ? What is the effect of dilution on them.
4) Define resistance, specific conductance and equivalent conductance. What are their units ?
5) What is cell constant ? What are its units ? How is it related to specific conductance ?
6) Define the term equivalent conductance and mention its units. Describe the effect of dilution on equivalent conductance.
7) Define equivalent conductance. Why does specific conductance decrease and equivalent conductance increase with dilution.

3.3.9 Problems :

1) The resistance of 0.1N solution of an electrolyte placed between two platinum electrodes 20cm a part and having an area of cross section of 4.0 sq.cm is 25 ohms. Calculate the equivalent conductivity of the solution.

(Ans : 200Ohm^{-1} cm^2 equiv^{-1})

2) The resistance of 0.5N solution of an electrolyte in a conductivity cell was found to be 45ohms. Calculate the equivalent conductivity of the solution, if the electrodes in the cell are 3.2cm apart and have an area of $3.8cm^{2}$.

(Ans : 25.74Ohm^{-1} cm^{2} $equiv^{-1}$)

3) The resistance of 0.2N solution of an electrolyte was found to be 250ohms at 25°c. Calculate the equivalent conductivity if the cell constant is $0.75cm^{-1}$

(Ans : 15 mho cm^{2} $equiv^{-1}$)

4) The resistance of 0.01N solution of an electrolyte was found to be 210ohms at 25°c. Calculate the equivalent conductance of the solution cell constant = 0.88

(Ans : 419 mho cm^{2} $equiv^{-1}$)

5) The resistance of a cell containing $\frac{N}{50}$ KCl solution was found to be 400 ohms. Calculate the equivalent conductance of KCl solution . cell constant = 1.10 cm^{-1}

(Ans : 137.5 Ohm^{-1} cm^{2} $equiv^{-1}$)

6) The resistance of an 0.1N solution of an electrolyte is 40ohms. If the distance between the electrodes is 1.2cm and area of cross section is $2.4cm^{2}$, calculate the equivalent conductance.

(Ans : 125 Ohm^{-1} cm^{2} $equiv^{-1}$)

7) The equivalent conductance of a 0.005N. NaOH solution is 240mhos cm^{2} $equi^{-1}$. what is the specific conductance and electrical resistance if the electrodes are 1cm a part and have a surface area of $1cm^{2}$.

(Ans : 0.0012mhos ; 833.33 Ohm)

8) The resistance of a deci normal solution of a salt occupying a volume between two platinum electrodes 1.80cm a part and $5.4cm^{2}$ in area was found to be 32ohms. Calculate the equivalent conductivity of the solution.

(Ans : 104.1 Ohm^{-1} cm^{2} $equiv^{-1}$)

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UNIT - III

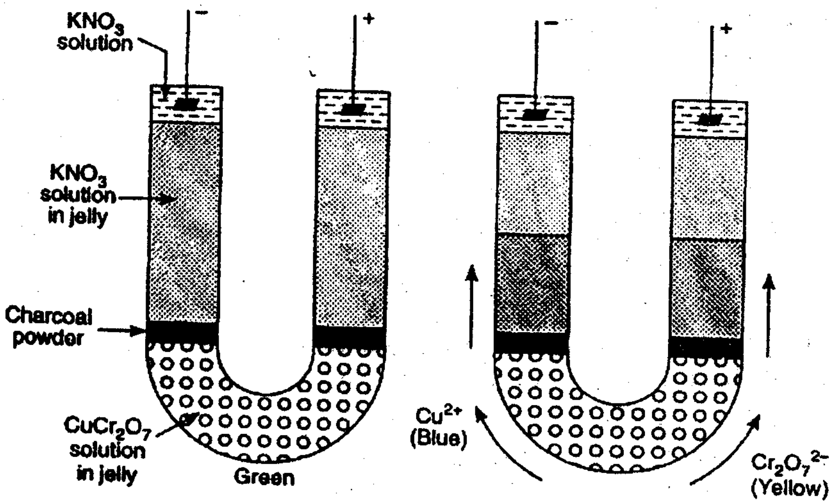
Lesson - IV

ELECTROCHEMISTRY – II

3.4.1 Migration of ions and Kohlrausch's law :

Ions exist independently in solution and they move towards the oppositely charged electrodes, on passing current through the solution. This movement of ions towards the oppositely charged electrodes is known as migration of ions. This can be demonstrated by the following experiment.

Movement of Coloured ions :



(a) Initial state (b) State after sometime

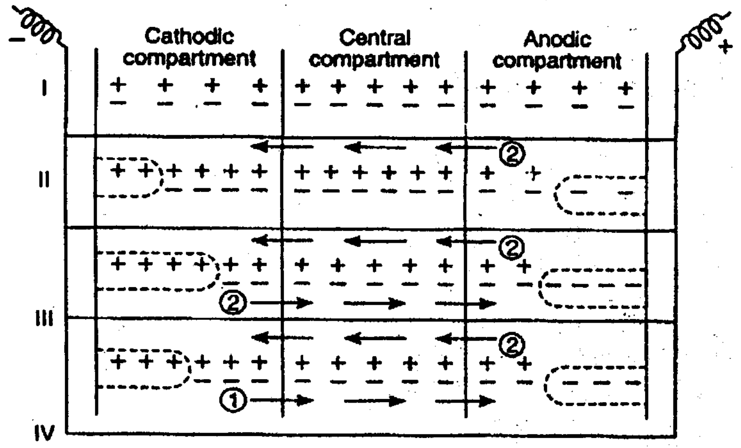
Demonstration of migration of ions.

The lower part of a 'U' tube is filled with a small amount of copper dichromate jelly which is dark green in colour prepared by mixing 5 percent of agar agar with a small amount of equimolar mixture of copper sulphate and potassium dichromate. A small amount of powdered charcoal is scattered on the surface of the jelly in both limbs. It indicates the initial position of the jelly in the limbs. Potassium nitrate solution in agar agar is placed over charcoal in both the limbs which is allowed to set. Over this layer, a solution of potassium nitrate in pure water is added in the two limbs and then platinum electrodes are inserted in it. When current is passed, the blue coloured copper ions rises into the jelly towards the negative electrode while the reddish yellow coloured dichromate ions move up towards anode. The migration of the ions will be indicated by the rise of blue colour in the negative electrode and reddish yellow colour in the anode of the tube. After some time the two types of ions are seen moving with well defined boundaries. The movement of the two coloured bands in the limbs is different indicating the difference in the speed of the two ions.

Relative speeds of ions during electrolysis :

According to Faraday's second law of electrolysis, when the same quantity of electricity is passed through solutions of different electrolytes, equal number of ions are always discharged at different electrolytes. It does not indicate that the ions move with the same speed. Hittorf explained by means of a theoretical device, that ions although move with different speeds yet they are liberated in equal number at respective electrodes.

Consider an electrolytic cell containing equal number of cations and anions of the same valency. The metal electrodes A and B represent the anode and cathode. The solution present between the two electrodes be devided into three compartments namely anodic, central and cathodic with the help of two imaginary partitions C and D which are permeable to ions and prevent the convection currents.



Hittorf's theoretical device showing the equivalence of discharge for any relative rate of migration of the two types of ions.

Before electrolysis, let there be 13 molecules in the vessel, four molecules being present in each anodic and cathodic compartments and five (5) in the central compartment.

On passing current, let us see what happens under the following conditions.

i) When either cations or anions move

ii) When cations and anions move

iii) When cations and anions move with different velocities.

i) When either cations or anions move :

In a unit time, suppose two cations from anodic compartment move to the middle compartment from there two cations will be pushed to the cathodic compartment. Now the number surplus anions of anodic compartment and cations of cathodic compartment is equal (position 11) although anions have not moved at all. The surplus ions are discharged at the respective electrode. As a result of this, the concentration of anodic compartment while that of the cathodic compartment has remain unaltered. Note that although only cations have moved, yet the number of anions and cations discharged at the two electrodes is equal. In a similar way, we can explain if there is movement of only anions.

ii) When cations and anions move with same velocities :

In a unit time, suppose two cations move towards the cathode and two anions move towards the anode (condition 111) The surplus cations and anions is same in the respective compartments i.e. 4 and will be discharged at the respective electrodes. The concentration in the two compartments has decreased to the same extent i.e. by two molecules.

iii) When cations and anions move with different velocities :

In a unit time, suppose two cations move towards the cathode and one anion move towards the anode showing that the speed of the cations is twice that of the anions (Condition IV) Hero also, the same number i.e. three surplus cations and three surplus anions will be discharged at the respective electrodes. In this case, the decrease in concentration in the anodic compartment is double the decrease in the cathodic compartment.

In all the above cases, the concentration of the central compartment has remained constant. This condition is realized, provided the current strength is small and no variation in the temperature.

From the above considerations, the following conclusions are drawn.

i) Irrespective of the relative speed of the two types of ions, they are always discharged in equal amounts

ii) Fall in concentration around any electrode is directly proportional to the speed of the ion moving away from it i.e.

Fall in concentration around anode α Speed of the cation.

Fall in concentration around cation α Speed of the anode.

Mathematically

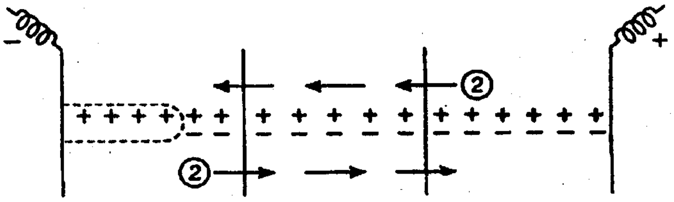
$$\frac{\text{Fall in conc. around anode}}{\text{Fall in conc. around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of cation}}$$

The relation given above, is valid, when the discharged ions do not react with the material of the electrode. But in some cases, where there ions react with the material of the electrode.

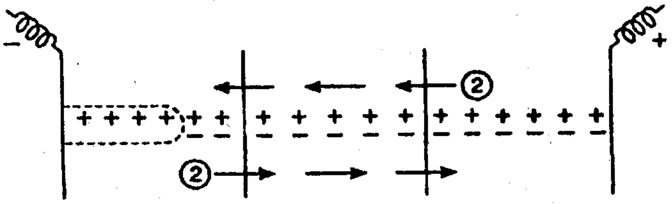
Example :

Electrolysis of silver nitrate solution using silver electrodes. In this, on electrolysis, there is increase in the concentration of silver nitrate around the anode. Every nitrate ion that reaches the anode dissolves one silver ion from it, to form silver nitrate which shows increase in concentration of silver nitrate in the anodic compartment.

Suppose the electrolysis is taking place between platinum electrodes, then condition (III) will occur. On the other hand if platinum electrodes are replaced by silver electrodes, it will be different from that of condition (III). In a unit time two anions move towards anode and two cations move towards cathode. In the cathodic compartment there will be four surplus cations, liberated at the cathode. Hence the concentration of cathodic compartment will fall from 4 to 2 molecules. The concentration of the anodic compartment has increased from 4 to 6 molecules. This is because, in the anodic compartment the two anions coming from the cathodic compartment will not be deposited on the anode but these together with two other anions unpaired due to migration of two cations, i.e. these four anions will react with anode liberating four silver cations in the anodic compartment.



Condition III of the above Hittorf's the oritical device



Schematic representation of the change of concentration when the electrodes are attacked. (The dark bold cations indicate the cations liberated from anode due to attack of four unpaired electrons in the anodic compartment).

So, in case of attack able electrodes –

i) Increase in concentration around an electrode is equal to decrease in concentration around the opposite electrode.

ii) The total ions deposited at cathode is equal to the sum of the ions lost from both of the electrodes.

3.4.2 Transport number :

An electrolyte solution conducts electricity due to migration of the ions. Each ion carries a definite fraction of the total current and the amount of current carried by each ion is proportional to its speed. The fraction of the total current carried by an ion is called as its transport number or Hittor number. Transport number of cations is represented by nc, tc or t+ while the transport number of anions is represented by na ; ta or t-.

Greater the speed of the ion, greater the amount of current carried by it and hence greater will be its transport number. If Uc and Ua are the speeds of the cation and anion, then

Current carried by the cation α Uc = KUc

Current carried by the anion αUa = KUa

Total current carried = current

Carried by anion + current

Carried by cation = KUa + KUc = K (Ua + Uc)

Transport number of anion $= \frac{K\,Ua}{K\left(Ua + Uc\right)}$

$$t_a = \frac{Ua}{\left(Ua + Uc\right)}$$

Transport number of cation $= \frac{K\,Uc}{K\left(Ua + Uc\right)}$

$$t_c = \frac{Uc}{\left(Ua + Uc\right)}$$

Important relation of transport number :

i) Sum of transport numbers of cations and anions of an electrolyte is always unity.

$$t_c + t_a = \frac{Uc}{\left(Ua + Uc\right)} + \frac{Ua}{\left(Ua + Uc\right)}$$

$$= \frac{Ua\ + Uc}{Ua\ + Uc} = 1$$

$$\text{ii) } t_c = \frac{Uc}{\left(Ua + Uc\right)}$$

$$= \frac{Uc/Ua}{Ua/Ua + Uc/Ua}$$

$$= \frac{r}{1+r}$$

Where $\frac{Uc}{Ua} = r$ (r = speed ratio of cation to anion)

$$= \frac{Ua}{(Ua + Uc)}$$

$$= \frac{Ua/Ua}{Ua/Ua + Uc/Ua}$$

$$= \frac{1+r}{r}$$

Determination of transport number by Hittorf method :

Hittorf method of determining transport number is based upon the principle, that fall in concentration around an electrode is proportional to the speed of the ion moving away from it.

$$\frac{\text{Fall in conc. around cathode}}{\text{Fall in conc. around anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{Uc}{Ua}$$

We know that

$$t_c = \frac{Uc}{(Ua + Uc)}$$

So,

$$t_c = \frac{\text{Fall in conc. around anode}}{\text{Fall in conc. around anode + Fall in conc. around cathode}}$$

$$= \frac{\text{Fall in conc. around anode}}{\text{Fall in conc. around both electrodes}}$$

When concentration is expressed in gram equivalents then

$$t_c = \frac{\text{Number of gram equivalents lost from the anodic compartment}}{\text{Total no of gm equiv. lost from both the compartments}}$$

According to Hittorf's theoritical device, the total number of gm equiv lost from both the compartmetns is equal to the number of gm equiv deposited on each electrode which can be obtained by placing a silver or copper voltameter in series.

$$t_c = \frac{\text{Number of gram equivalents lost from the anodic compartment}}{\text{Number of gm equiv. deposited in the voltameter}}$$

Since $t_c + t_a = 1$

$t_a = 1 - t_c$.

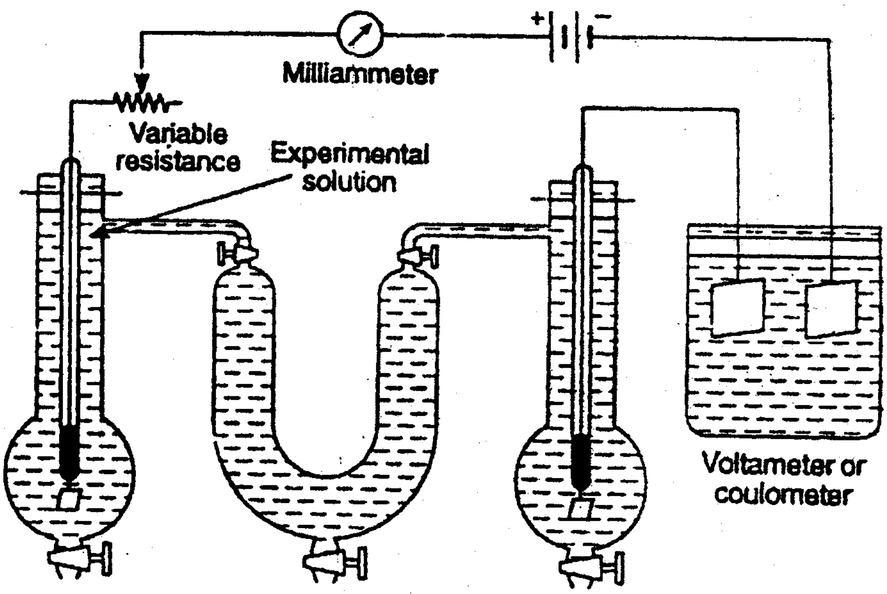


Fig. Hittorf apparatus for determining transport number.

Hittorf apparatus consists of two vertical glass tubes joined together through a 'U' tube in the middle and all the three provided with stop cocks at the bottom. The glass tubes contain anode and cathode and acts as anodic and cathodic compartments. The 'U' tube constitutes the middle compartment. A silver or copper voltameter is connected in series with the apparatus through a battery, a milliammeter and a variable resistance.

All the three compartments are filled with the electrolyte solution in which the transport number of ions is to be determined. Concentration of the electrolyte solution is determined by titrations. A current of 10 to 20 milliamperes is passed for 2 to 3 hours. The passage of current should be for a short time only, so that a large change in concentration does not take place. After electrolysis, the solution from the anodic compartment is removed and weighed and titrated as above to know the amount of electrolyte present in it. The solution from the central compartment and its concentration is also determined. The concentration of the central compartment should be same as before electrolysis. The weight of silver deposited in the silver voltameter or that of copper in case of copper voltameter is determined. If copper voltameter is used, the weight of copper deposited is converted into silver equivalent by multiplying the weight of copper deposited by 108/31.8.

Calculations :

When the electrodes are attackable i.e. when electrodes are of silver and the anode is attacked by nitrate ions.

a) Concentration of anodic solution after electroysis :

Let the weight of anodic solution taken out = a gms

Weight of $AgNO_3$ in 'a' gms of anodic solution = b gms

Weight of water = (a-b) gms

(a-b) gms of water contain b gms of $AgNo_3$ = x gms of Ag NO_3.

b) Concentration of anodic solution before electrolysis :

Let the weight of anodic solution = c gms

Weight of $AgNO_3$ in c gms of anodic solution = d gms

Weight of water = (c-d) gms

If (c-d) gms of water contain d gms of $AgNO_3$

(a-b) gms of water contain = $\frac{d}{c-d}$ X a-b gms of $AgNO_3$

= y gms of $AgNO_3$.

c) Increase in concentration around anode due to reaction of anion with anode :

Since the electrodes are of silver which are attackable, the nitrate ions reaching the anode attack the electrode forming silver nitrate and thus increases the concentration of silver ions in the anodic solution.

Hence the weight x is grater than y

$x > y$

Increase in concentration around anode = $\frac{(x-y)}{1/0}$ X 108 gm eq.of Ag.

d) Weight of silver deposited in the silver voitameter :

Let the weight of silver deposited in the silver voltameter = w gms

$= \frac{w}{108}$ gm. eq.of Ag

= Z gm. eq.of Ag

e) Fall in concentration around anode due to migration of silver ions towards cathode :

The increase in concentration of silver ions around anode is inspite of the ususal migration of silver ions from anodic compartment to the cathodic compartment. Suppose, if there is no migration of silver ions from the anodic compartment, the increase in concentration of silver ions in the anodic compartment would be much more higher and equal to the amount of silver deposited in the silver voltameter i.e. Z gm.equi of Ag.

Fall in concentration in the anodic compartment due to migration of silver ions

= Z- (x-y) gm.eqof Ag

f) Transport number of Ag+ and NO_3^- ions :

$$t_{Ag^+} = \frac{\text{Fall in conc. of Ag (gm.eq) around anode}}{\text{Amount of Ag deposited (in gm eq) in silver voltameter}}$$

$$t_{Ag^+} = \frac{Z-(x-y)}{Z}$$

$$tNO_3^- = 1-t_{Ag^+}$$

3.4.3 Problems :

Example :1

A solution of silver nitrate containing 0.00739 gm of $AgNO_3$ per gm of water was electrolysed between silver electrodes. During the experiment 0.078 gm of silver was deposited in the silver voltameter in series. At the end of the experiment the anodic solution contained 23.14gm of water and 0.236 gm of $AgNO_3$. Calculate the transport number of silver and nitrate ions.

After Electrolysis :

23.14 gms of water contained 0.236 gm of $AgNO_3$

$$= \frac{0.236}{170} \text{ X } 108$$

= 0.1499 gm.eq of Ag

Before Electrolysis :

1 gm of water contain 0.00739 gm of $AgNO_3$

23.14gms of water contain 0.00739 X 23.14 gm of $AgNO_3$

=0.1710 gm of $AgNO_3$

$$= \frac{0.1710}{170} \text{ X } 108$$

= 0.1086 gm.eq of Ag

Increase in conc around anode = 0.4199-0.1086

= 0.0413 gm.eq of Ag

Weight of Ag deposited in silver voltameter = 0.078 gm.eq of Ag

Fall in conc in the anodic compartment due to migration of silver ions = Z- (x-y)

= 0.078 - 0413

= 0.0367 gm.eqof Ag

$$\text{Transport number of } Ag^+ = \frac{\text{Fall in conc. around anode}}{\text{Amount of Ag deposited in Ag voltameter}}$$

$$= \frac{0.0367}{0.078}$$

= 0.4705

Transport number of NO_3^- = 1 - 0.4705

= 0.5295

Example : 2

Calculate the transport number of silver ion if the transport number of nitrate ion is 0.5797.

$t_a + t_c = 1$

$t_{NO_3^-} = 0.5797$

$t_{Ag^+} = 1 - 0.5797 = 0.4203$

Example : 3

During electrolysis of silver nitrate solution the speed ratio of silver and nitrate ions between silver electrodes is found to be 0.916. Determine the transport number of the two ions.

$$\frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{Uc}{Ua} = r = 0.916$$

$$t_{NO_3^-} = \frac{1}{1+r} = \frac{1}{1+0.916} = 0.521$$

$t_{Ag^+} = 1 - 50.521$

= 0.429

Example : 4

A solution containing 0.0074 gm of Ag NO_3 per gram of water was electrolysed between silver electrodes. During the experiment 0.0785 gm eq of silver was deposited in the voltameter placed in series.

After the electrolysis 25 gm of anode solution contained 0.2553 gm of Ag NO_3. Calculate the transport number of Ag+ and NO_3^-

After Electrolysis :

Weight of $AgNO_3$ solution = 25 gms

Weight of $AgNO_3$ = 0.2553 gms

Weight of water = 25.000 - 0.2553

= 24.7447 gm

Before Electrolysis :

1 gm of water contain 0.0074 gm of $AgNO_3$

24.7447 gms of water contain 0.0074 X 24.7447 gm of $AgNO_3$

= 0.1831 gm of $AgNO_3$

Increase in conc around anode = 0.2553 - 0.1831

= 0.0722 gm. of $AgNO_3$

$$= \frac{0.0722 \times 108}{170}$$

= 0.0459 gm.eq of Ag

Weight of Ag deposited in voltameter = 0.0785 gm.eq of Ag

Fall in conc around anode = 0.0785 - 0.0459

= 0.0326 gm.eqof Ag

$$\text{Transport number of } Ag^+ = \frac{0.0326}{0.0785}$$

= 0.4153

Transport number of NO_3^- = 1 - 0.4153

= 0.5847

Example : 5

An aqueous solution of copper sulphate was electrolysed between copper electrodes. on the cathode 0.3 gm of copper was deposited. The solution in the anode compartment contained 1.43 gm of copper after electrolysis and the same weight of water contained 1.214 gm of copper before electrolysis. Calculate the transport number of copper

Sol :

Weight of copper in the anodic compartment after electrolysis = 1.43 gms

Weight of copper in the anodic compartment before electrolysis = 1.214 gm

Increase in concentration around anode = 1.43 - 1.214

= 0.216gm

Fall in concentration around anode due to migration of copper ions = 0.300-0.216

= 0.084 gm

$$\text{Transport number of copper ion } t_{Cu^{2+}} = \frac{\text{Fall in conc. around anode}}{\text{Amount of Copper deposited at cathode}}$$

$$= \frac{0.084}{0.30}$$

$$= 0.28$$

3.4.4 Kohlrausch's law :

Kohlrausch studied the equivalent conductivities at infinite dilution for a number of pairs of strong electrolytes with common cation or anion and calculated the difference of λ_α values for each pair. He obtained a constant difference in λ_α values of an ion pair irrespective of the nature of the other ion.

Table 1 . Equivalent conductivities at infinite dilution λ_∞ (in ohm^{-1} cm^2 at 25°C of some pairs of electrolytes having a common ion.

Electrolyte	λ_∞	Difference	Electrolyte	λ_∞	Difference
NaCl	126.45	2.06	NaCl	126.45	23.41
NaBr	128.51		KCl	149.86	
KCl	149.86	2.06	NaBr	128.51	23.41
KBr	151.92		KBr	151.91	
LiCl	115.03	2.06	NaOH	248.11	23.41
LiBr	117.09		KOH	271.52	
NH_4Cl	149.74	2.06	$NaNO_3$	121.55	23.41
NH_4Br	151.80		KNO_3	144.96	

When the bromide is replaced by the chloride, a constant difference of 2.06 is produced in the value of the conductivity at infinite dilution. In a similar manner, the replacement of potassium by Sodium causes a difference of 23.41 when the anion remains the same. Each ion makees a certain definite contribution to the total equivalent conductivity of an electrolyte at infinite dilution, irrespective of the nature of the other ion of the electrolyte. This individual contribution of an ion towards the total equivalent conductance is called as ionic conductance of that ion. Kohlrausch, in 1875 put forward a generalization, known as Kohlrausch's law of independent migration of ions, stated follows :

" The equivalent conductance of an electrolyte at infinite dilution is the sum of two values, one depending upon the cation andthe other upon the anion ".

Mathematically

$$\lambda_{\alpha} = \lambda_c + \lambda_a$$

Where λ_a and λ_c are the equivalent conductances or ionic conductances of the anion and cation respectively.

The ionic conductance of an ion is fixed at a given temperature. The ionic mobility of an ion is defined as its absolute velocity under a potential gradient of one volt per cm. Ionic conductance is directly proportional to the ionic mobility of the ion.

$$\lambda_c \; \alpha \; Uc$$

$$\lambda_c = KUc$$

$$\lambda_a \; \alpha \; Ua$$

$$\lambda_a = KUa$$

Where λ_a and λ_c are ionic conductances and Ua and Uc are the ionic mobilities of anion and cation. K is proportionality constant and its value is equal to 96500 coulombs or one Faraday of electricity.

$$\therefore \text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

Relation between ionic conductance and transport number :

$$\lambda_c = KUc$$

$$\lambda_a = KUa$$

$$\frac{\lambda_c}{\lambda_a} = \frac{KU_C}{KU_a} = \frac{U_c}{U_a}$$

$$\frac{\lambda_c}{\lambda_a} + 1 = \frac{U_c}{U_a} + 1$$

$$\frac{\lambda_c + \lambda_a}{\lambda_a} = \frac{U_c + U_a}{U_a}$$

Taking reciprocal of both sides

$$\frac{\lambda_a}{\lambda_c + \lambda_a} = \frac{U_a}{U_c + U_a}$$

$$\frac{\lambda_a}{\lambda_\alpha} = \frac{U_a}{U_c + U_a}$$

Where $\lambda_\alpha = \lambda_c + \lambda_a$

$$\frac{\lambda_a}{\lambda_\alpha} = t_a \qquad \left(\because \frac{U_a}{U_c + U_a} = t_a \right)$$

$$\lambda_a = \lambda_\alpha \text{ X } t_a$$

$$\lambda_c = \lambda_\alpha \text{ X } t_c$$

Ionic conductance of an ion = Equivalent conductance at infinite dilution of a strong electrolyte containing that ion X Transport number of that ion.

3.4.5 Applications of Kohlrausch's law :(conductivity measurements)

1) Calculation of equivalent conductance at the infinite dilution (λ_α) for weak electrolytes :

The value of λ_α a weak electrolyte can not be determined experimentally since these electrolytes do not ionise completely even at great dilution. In such case, λ_α can be calculated using Kohlrausch's law.

Method - 1

using acetic acid as an example, at infinite dilution.

$$\lambda\alpha(\text{CH3COOH}) = \lambda_{(\text{CH3CO}\bar{\text{O}})} + \lambda_{(\text{H}^+)} \qquad \text{-(i)}$$

Knowing the equivalent conductivities at infinite dilution for the strong electrolytes CH3COOK : KCl and HCl and by applying Kohlrausch's law

λ_α of CH_3COOH can be calculated.

$$\lambda\alpha(\text{CH3COOK}) = \lambda_{(\text{CH3CO}\bar{\text{O}})} + \lambda_{(\text{K}+)} \qquad \text{- (ii)}$$

$$\lambda_\alpha(\text{KCl}) = \lambda_{\left(\text{C}\bar{\text{l}}\right)} + \lambda_{(\text{K}+)} \qquad \text{-(iii)}$$

$$\lambda_{\alpha}(^{+}\mathrm{HCl}) = \lambda_{\left(\bar{\mathrm{Cl}}\right)} + \lambda_{\left(H^{+}\right)} \qquad \text{-(iv)}$$

Subtracting (iii) from the sum of (ii) and (iv) we get

$$\lambda_{(\mathrm{CH3CO\bar{O}})} + \lambda_{\left(\mathrm{K^{+}}\right)} + \lambda_{\left(\mathrm{H^{+}}\right)} + \lambda_{\left(\bar{\mathrm{Cl}}\right)} - \left[\lambda_{(\mathrm{K}^{+})} + \lambda_{\left(\bar{\mathrm{Cl}}\right)}\right] = \lambda_{(\mathrm{CH3CO\bar{O}})} + \lambda_{\left(\mathrm{H^{+}}\right)}$$

Or

$$\lambda_{\alpha}(\mathrm{CH_3COOK}) + \lambda_{\alpha}(\overset{+}{H}\mathrm{Cl}) - \lambda_{\alpha}(\mathrm{KCl}) = \lambda_{\alpha}(\mathrm{CH_3COOH})$$

Method - 2

Example - Acetic acid

According to Kohlrausch's law

$$\lambda_{\alpha}(\mathrm{CH_3COOH}) = \lambda_{(\mathrm{CH_3CO\bar{O}})} + \lambda_{\left(\mathrm{H^{+}}\right)}$$ 216

By knowing the ionic conductances of $\mathrm{CH3CO\bar{O}}$ and H^+ ions. We can determine the λ_{α} for CH_3COOH by adding these values.

$$\lambda_{(\mathrm{CH_3CO\bar{O}})} + \lambda_{\left(\mathrm{H^{+}}\right)} = \lambda_{\alpha}(\mathrm{CH_3COOH})$$

Ionic conductances of H^+ and $\mathrm{CH3CO\bar{O}}$ ions can be calculated by using transport numbers of these ions and λ_{α} of any strong electrolyte that contains these ions.

Using HCl

$$\lambda_{\left(\mathrm{H^{+}}\right)} = t_{\mathrm{H^{+}}} \times \lambda_{\alpha}(H\mathrm{Cl})$$

Using CH_3COONa

$$\lambda_{(\mathrm{CH3CO\bar{O}})} = t_{\mathrm{CH3CO\bar{O}}} \times \lambda_{(\mathrm{CH3COONa})}$$

2) Calculation of ionic mobility or absolute velocity of Ions :

Knowing the value of ionic conductance using Kohlrausch's law ionic mobility can be calculated.

$$\text{Ionic mobility (U)} = \frac{\text{Ionic conductance } (\lambda)}{96500}$$

3) Calculatin of degree of dissociation and dissociation constant of a weak electrolyte :

Examples : CH_3COOH ; NH_4OH etc.

The degree of dissociation of a weak electrolyte at dilution V can be calculated by dividing the equivalent conductivity of the electrolyte at any given dilution , λ_V by the equivalent conductivity of the electrolyte at infinite dilution.

$$\alpha = \frac{\lambda_V}{\lambda_\alpha}$$

The ratio of equivalent conductance at any dilution (λ_V) to that at infinite dilution (λ_α) is called conductance ratio. In case of strong electrolytes the value of conductance ratio is close to unity at any concentration but for weak electrolytes, this ratio is very small and hence it is a quantity called degree of dissociation. The degree of dissociation is the fraction of molecules dissociated out of unit concentration of the electrolyte.

$$CH_3COOH \rightleftharpoons CH3CO\bar{O} + H^+$$

Initial conc.	1	0	0
Equilibrium conc.	1- α	α	α
When C moles are taken initially	(1- α)C	α C	α C

Dissociation constant Ka of acid $$Ka = \frac{\left[CH3COO\bar{O}\right]\left[H^+\right]}{CH3COOH} = \frac{(\alpha C)\times(\alpha C)}{(1-\alpha)C}$$

Ka of uni univalent acid = $\frac{\alpha^2 c}{(1-\alpha)}$ Where $\alpha = \frac{\lambda_V}{\lambda_\alpha}$

4) Determination of solubility product of a sparingly soluble salt :

Salt like AgCl ; $BaSO_4$; $PbSO_4$ etc. are ordinary considered as insoluble in water but they do posses a definite value of solubility. Hence, these salts are called as sparingly soluble salts. The solubility of such salts can be determined using Kohlrausch's law and conductivity measurements. Specific conductivity of the saturated solution of sparingly soluble salt, for example, AgCl is determined as follows -

K (for AgCl) = K (for saturated solution of

(AgCl in H_2O) - K (for H_2O)

Equivalent conductivity of this salt at this dilution = λ_V (for AgCl) = K (for AgCl) X V

Where 'V' is the volume in C.C Containing 1 gm equivalent of the salt.

Since the solution is very dilute, λ_V, calculated may be considered as equal to λ_α i.e. equivalent conductivity at infinite dilution.

$$\lambda_V = K \times V = \lambda_\alpha$$

$$V = \frac{\lambda_\alpha}{K}$$

The value of λ_α can be calculated using Kohlransch's law

$$\lambda_\alpha(AgCl) = \lambda_{(Ag^{\cdot})} + \lambda_{(Cl^{\prime})}$$

V ml of solution contain 1 gm equi of(143.5gms) of AgCl

1000ml of solution contain = $\frac{143.5}{V} \times 1000$

Solubility of the sparingly soluble salt, AgCl = $\frac{143.5 \times 1000}{V}$ gml^{-1}

3.4.6 Problems :

Example : 1

The equivalent conductances at infinite dilution of sodium acetate, hydrochloric acid and sodium chloride at 25°c are 91.0 ; 426.16 and 126.45 ohm⁻ cm² equiv⁻¹ respectively. Calculate the equivalent conductance at infinite dilution for acetic acid.

Solution :

i) $\lambda_{\alpha(CH_3COOH)} = \lambda(CH_3CO\bar{O}) + \lambda_{(H^{\cdot})}$

ii) $\lambda_{\alpha(CH_3COONa)} = \lambda(CH_3CO\bar{O}) + \lambda_{(Na^{\cdot})} = 91.0\ ohm^{-}\ cm^{2}\ equiv^{-1}$

iii) $\lambda_{\alpha(HCl)} = \lambda_{(Cl^{\prime})} + \lambda_{(H^{\cdot})} = 426.16\ ohm^{-}\ cm^{2}\ equiv^{-1}$

iii) $\lambda_{\alpha(NaCl)} = \lambda_{(Cl^{\prime})} + \lambda_{(Na^{\cdot})} = 426.16\ ohm^{-}\ cm^{2}\ equiv^{-1}$

By adding equations (ii) and (iii) and subtracting equation (iv) from it

$$\lambda(CH_3CO\bar{O}) + \lambda_{(Na^{\cdot})} + \lambda_{(H^{\cdot})} + \lambda_{(Cl^{\prime})} - (\lambda_{(Na^{\cdot})} + \lambda_{(Cl^{\prime})}) = \lambda(CH_3CO\bar{O}) + \lambda_{(H^{+})}$$

$$\lambda_{\alpha(CH_3COONa)} + \lambda_{\alpha(HCl)} - \lambda_{\alpha(NaCl)} = \lambda_{\alpha(CH_3COOH)}$$

$$91.0 + 426.16 - 1236.45 = 390.71$$

$\lambda_{\alpha\,(CH_3COOH)} = 390.71\,\text{ohm}^{-}\ \text{cm}^{2}\ \text{equiv}^{-1}$

Example 2 :

The equivalent conductivities at infinite dilution for HCl and CH_3COONa are 383.5 and 78.4 respectively. If the transport numbers of hydrogen and acetate ions are 0.841 and 0.46 respectively, calculate the ionic conductances of the acetate and hydrogen ions as well as the equivalent conductivity of acetic acid at infinite dilution.

Solution :

$\lambda_{\alpha\,(H^+)} = \lambda_{\alpha\,(HCl)} \times t_{H^+}$

$= 383.5 \times 0.841$

$= 322.52$ mhos

$\lambda\,(CH_3CO\bar{O}) = \lambda_{\alpha\,(CH_3COONa)} \times t_{(CH_3CO\bar{O})}$

$= 383.5 \times 0.841$

$= 322.52$ mhos

Equivalent conductivity of acetic acid at infinite dilution, $\lambda_{\alpha} =$

$\lambda_{\alpha\,(CH_3COOH)} = \lambda\,(CH_3CO\bar{O}) + \lambda_{H^+}$

$= 36.06 + 322.52$

$= 358.58\,\text{ohm}^{-}\ \text{cm}^{2}\ \text{equiv}^{-1}$

'Example : 3

The molecular conductivity at infinite dilution of KCl is 130.1 ohm^{-} cm^{2} equiv^{-1}. The transport number of chloride ions is 0.505 at 25°c. Calculate the ionic mobilities of potassium and chloride ions.

Solution :

Since equivalent and molecular weights of KCl are same ; the equivalent and molecular conductivites are also same.

Ionic conductance of chloride ion

$\lambda_{(Cl^-)} = \lambda_{\alpha\,(KCl)} \times t_{Cl^-}$

$= 130.1 \times 0.505$

$= 67.7005$

Ionic conductance of potassium ion

$\lambda_{(K^+)} = \lambda_{\alpha(KCl)} \times t_{K^+}$ $\quad (t_{K^+} = 1-0.505 = 0.495)$

$= 130.1 \times 0.495$

$= 64.3995$

Ionic mobility of K^+ ion =

$$U_{K^+} = \frac{\lambda_{K^+}}{96500}$$

$$= \frac{64.3995}{96500}$$

$= 0.000667$ cm sec^{-1}

$$U_{Cl^-} = \frac{\lambda_{Cl^-}}{96500}$$

$$= \frac{67.7005}{96500}$$

$= 0.000681$ cm sec^{-1}

Example : 4

Absolute velocity of silver ions is 5.7×10^{-4} cm sec^{-1} and that of nitrate ions is 6.3×10^{-4} cm sec^{-1} at 18°c. Calculate the equivalent conductivity of silver nitrate at infinite dilution.

Sol :

Ionic mobility or absolute velocity of silver ions = 5.7×10^{-4} cm sec^{-1}

$$U_{Ag^+} = \frac{\lambda_{Ag^+}}{96500}$$

Ionic conductance of silver ions λ_{Ag^+}

$\lambda_{Ag^+} = U_{Ag^+} \times 96500$

$= 5.7 \times 10^{-4} \times 96500$

$= 55.005$ ohm^{-1}

Ionic mobility of nitrateions = 6.3×10^{-4} cm sec^{-1}

$$U_{NO_3^-} = \frac{\lambda_{NO_3^-}}{96500}$$

Ionic conductance of silver ions λ_{Ag^+}

$$\lambda_{NO_3^-} = U_{NO_3^-} \times 96500$$

$$= 6.3 \times 10^{-4} \times 96500$$

$$= 60.795 \text{ ohm}^{-1}$$

According to Kohlrausch's law

$$\lambda_{\alpha\,(AgNO_3)} = \lambda_{Ag^+} + \lambda_{NO_3^-}$$

$$= 55.005 + 60.795$$

$$= 115.8 \text{ ohm}^{-} \text{ cm}^2 \text{ equiv}^{-1}$$

Example : 5

The equivalent conductance at 18°c of a normal solution of KCl is 98.2 and for infinite dilution at the same temperature is 131. Calculate the degree of ionisation of KCl at this dilution.

Sol :

$$\lambda_{V\,(KCl)} = 98.2 \text{ ohm- cm2 equiv}^{-1}$$

$$\lambda_{\alpha\,(KCl)} = 131 \text{ohm- cm2 equiv}^{-1}$$

$$\alpha = \frac{\lambda_V}{\lambda_\alpha}$$

$$= \frac{98.2}{131}$$

$$= 0.75$$

Example : 6

At 25°c the equivalent conductance of 0.1N benzoic acid is 8.9ohm⁻ cm² equiv⁻¹ the ionic conductances at infinite dilution of the hydrogen ion and benzoate ion are 349.8 and 32.3ohm⁻¹ calculate the degree of dissociation of benzoic acid.

Sol :

$$\lambda_{\alpha\,(C_6H_5COOH)} = \lambda_{(C_6H_5CO\bar{O})} + \lambda_{H^+}$$

$$= 32.3 + 349.8$$

$$= 382.1 \text{ ohm}^{-} \text{ cm}^2 \text{ equiv}^{-1}$$

$$\lambda_{\alpha\,(C_6H_5COOH)} = 8.9 \text{ ohm}^{-} \text{ cm}^2 \text{ equiv}^{-1}$$

Degree of dissociation of benzoic acid ; α

$$\alpha = \frac{\lambda^{v}_{(C_6H_5COO^-)}}{\lambda^{\alpha}_{(C_6H_5COO^-)}}$$

$$= \frac{8.9}{382.1}$$

$$= 0.023$$

3.4.7 Conductometric titrations :

Conductometric titrations are those in which the end point of acid - alkali reactions, some displacement reactions and precipitation reactions is detected using conductivity measurements. Conductometric titrations are based on the fact that the conductance of a solution at a constant temperature depends upon the number and mobility of ions present.

The titrant is added from a burette into a known volume of the solution to be titrated, taken in a conductivity cell and the conductivity readings are noted after the addition of certain amount of the titrant each time. These conductivity readings are then plotted against the volume of titrant added. Two linear curves are obtained which intersect at one point, known as the end point.

Examples :

1) Titration of a strong acid with a strong base ·

Example : (HCl + NaOH)

NaOH solution (alkali) is taken int he burette. 20ml of hydrochloric acid solution taken in a conductivity cell is placed in a thermostat and the conductance of the solution which is due to H^+ and Cl^- ions is noted. The acid contains the fastest moving H^+ions hence the conductivity value is very high initially. 1ml of NaOH solution is added at a time to the acid solution and after the addition of each ml, the conductance of the solution is measured.

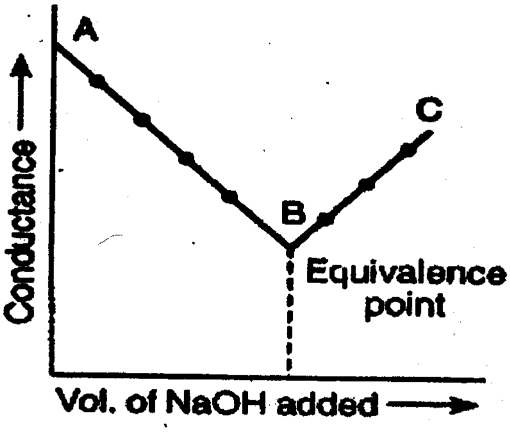
$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

The addition of NaOH solution to the HCl solution. some of H^+ ion are replaced by slow moving Na^+ ions due to which the conductance of this solution decreases and it is lesser than that of pure HCl.

When all the H^+ ions are replaced by Na^+ ions i.e. when the end point is reached, further addition of NaOH introduces the OH- ions which are fast moving among the ions present in the solution ($Na^+ + Cl^-$ and OH^-) After the end point, the further addition of NaOH solution results in increase of conductance values.

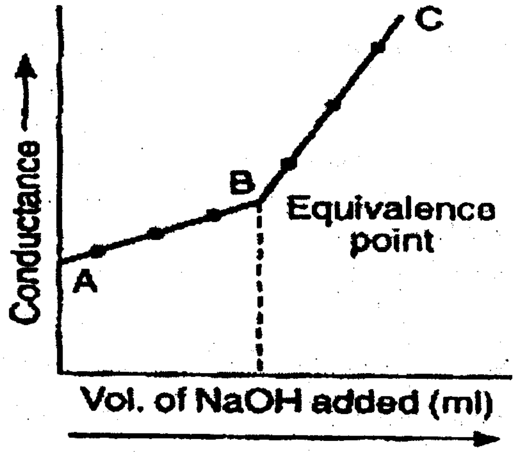
$$Na^+ + Cl^- + H_2O \rightarrow Na^+ + OH^-$$

When the conductance values are plotted against the volume alkali added the points will be on two straight lines AB and BC. The point of intersection 'B' of the two lines gives the end point.



Conductometric titration of a strong acid against a strong base.

2) Titration of a weak acid against a strong alkali (Example : CH_3 COOH ; NaOH)



Conductometric titration of a weak acid against a strong base.

When acetic acid is titrated against sodium hydroxide, the inital conductance of the solution is low due to the poor dissociation of acetic acid. On adding NaOH, highly ionised sodium acetate is formed.

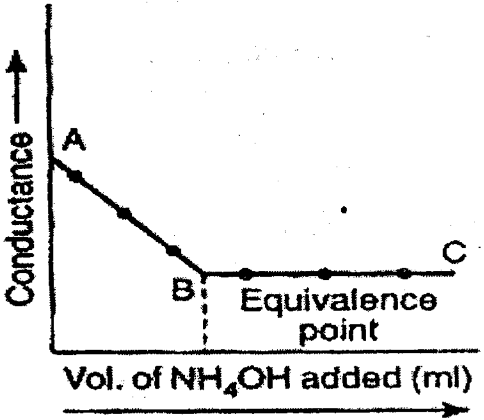
$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$$

The acetate ions at first tend to suppress the ionisation of acetic acid still further due to common ion effect but some time after, the conductivity begins to increase because the conducting power of highly ionised salt exceeds that of the weak acid.

After the end point, further addition of NaOH increases the conductance sharply because further addition of NaOH introduces the fast moving OH^- ions. 'B' the point of intersection of the two curves, gives the end point.

3) Titration of a strong acid against a weak base : (Ex : $HCl + NH_4OH$)

The conductance of HCl solution is initially high. When NH_4OH is added to HCl solution, the conductance of the solution decreases due to the replacement of fast moving H^+ ions by the slow moving NH_4^+ ions. After the end point has reached the addition of NH_4OH will not cause any appreciable change in conductance value because it is a weak electrolyte.

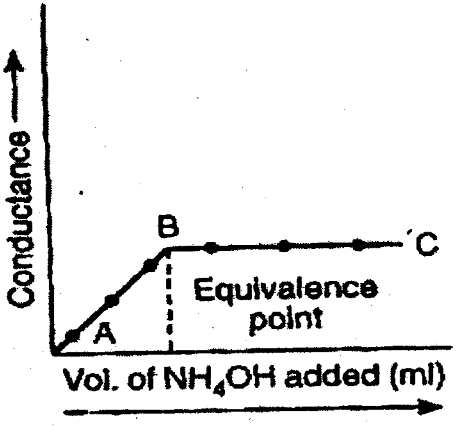


Conductometric titration of a strong acid against a weak base

$$H^+ + Cl^- + NH_4OH \rightarrow NH_4^+ + Cl^- + H_2O$$

4) Titration of a weak acid against a weak base : (Ex : $CH_3COOH + NH_4OH$)

Conductometric method is suitable for such titrations because they do not give a sharp end point with indicators. The initial conductance of CH_3COOH solution is low due to its poor dissociation. The conductance starts increasing on the addition of NH_4OH which is due to the formation ammonium salt. After the end point which is sharp, the conductance remains almost constant because the free base NH_4OH is a weak electrolyte.

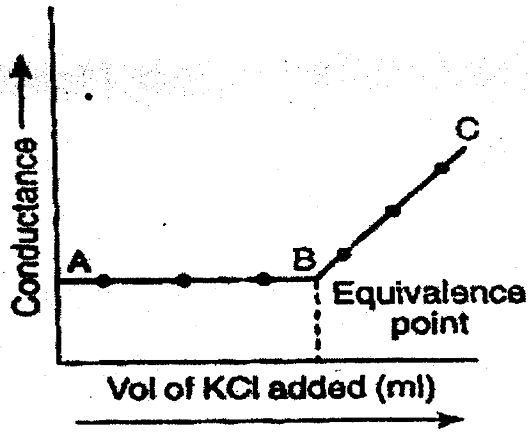


Conductometric titration of a weak acid against a weak base.

5) Titration involving precipitation reactions : (Ex : AgNO$_3$ + KCl)

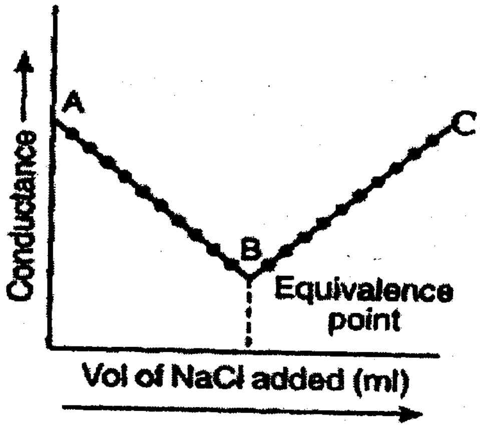
$$Ag^+ + NO_3^- + K^+ + Cl^- \rightarrow AgCl + K^+ + NO_3^-$$

Since the mobility of potassium and silver ions is nearly similar, replacement of Ag$^+$ ion by K$^+$ ion will not effect the conductance of the solution. Hence the conductatnce value will remain as almost constant till the end point is reached. After the end point, there is a sharp increase in conductance because the addition of KCl introduces the free K$^+$ and Cl$^-$ ions.



Conductometric titration of AgNO3 solution against KCl solution

The curves are different when NaCl is used in place of KCl. Which is due to the difference in the ionic mobility of Na^+ and K^+ ions. The ionic mobility of Na^+ ions is less than Ag^+ ions, addition of NaCl to $AgNO_3$ solution will replace the fast moving Ag+ by the slow moving Na^+ ions. Hence the conductance goes on decreases till all the Ag^+ ions are replaced by Na^+ ions. After the end point the conductance value increases because of the introduction of free Na^+ and Cl^- ions by the further addition of NaCl.



Conductometric titration of $AgNO_3$ solution against NaCl solution.

Advamtages of conductometric titrations :

1. The method is very usefül for the titration of weak acids against weak bases which do not give a sharp colour change with indicators.
2. The method is useful in case of titration of coloured solutions where no indicator can work properly.

3.4.8 Theories of Ionisation :

1) Arrhenius theory of electrolytic dissociation :

In order to explain the behaviour of electrolytes, Arrhenius in 1887 put forward his theory of electrolytic dissociation . The main postulates of the theory are -

i) The molecules of an electrolyte in aqueous solution undergo dissociation spontaneously to form positive and negative ions.

$$NaOH \rightarrow Na^+ + OH^-$$

$$KCl \rightarrow K^+ + Cl^-$$

ii) The degree of dissociation (The fraction of the total amount of electrolyte which dissociates) increases with dilution and at infinite dilution it approaches unity.

iii) At moderate concentration, exists an equilibrium between the ions and undissociated molecules.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

According to Arrhenius, electrolytes are of two types namely strong electrolytes and weak electrolytes. At moderation concentration, the degree of dissociation is high in case of strong electrolytes while it is very low in case of weak electrolytes.

iv) Each ion formed produces the same effect on osmotic pressure and other colligative properties. Each ion behaves osmotically as a molecule.

Limitations of Arrhenius theory :

1) According to Arrhenius, electrolytes remain unionised in the solid state and undergo ionisation only when dissolved in water. But X – ray studies have shown that electrolytes are in ionised form in the solid state.

2) Arrhenius could not explain the function of water. Strong electrolytes are good conductors of electricity even in molten state.

3) Arrhenius theory assumes that ionic mobilities do not vary with concentration of solution which is found to be incorrect.

4) It is utter failure when applied to strong electrolytes.

5) The ostwalds dilution law which is based on Arrhenius theory fails completely when applied to strong electrolytes.

6) The degree of dissociation (α) of strong electrolytes calculated from conductance measurements was found to be different from that calculated from colligative properties.

3.4.9 Ostwald's dilution law :

Arrhenius theory of electrolytic dissociation assumes a dynamic equilibrium between the ions and the undissociated molecules.

$$AB \rightleftharpoons A^+ + B^-$$

Ostwald, applied the law of chemical equilibrium to such systems.

Consider an electrolytes AB 'C' moles of AB is dissolved in per litre of an aqueous solution and let α be its degree of dissociation.

$$AB \rightleftharpoons A^+ + B^-$$

Initial conc.	C	0	0
Equilibrium conc.(moles per litre)	$C(1-\alpha)$	$C\alpha$	$C\alpha$ mole litre^{-1}

According to the law of mass action, the equilibrium constant of the above reaction -

$$K = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K = \frac{C\alpha^2}{(1-\alpha)} \text{ moles litre}^{-1}$$

If one gram mole of an electrolyte be dissolved in 'V' litres of the solution, then

$$C = \frac{1}{V}$$

Where 'V' is known as the dilution for the solution and the above expression becomes

$$K = \frac{\alpha^2}{(1-\alpha)V}$$

The above mathematical expression representing the variation of degree of dissociation with dilution is known as Ostwald's dilution law. The equilibrium constant, K is called as dissociation constant or ionisation constant of the electrolyte.

Uses of Ostwald's dilution law :

i) It is useful in the calculation of dissociation constants of weak electrolytes, by determining the degree of dissociation from conductance measurements ($\frac{\lambda_V}{\lambda_\alpha}$) at any concentration

ii) Knowing the value of K which is constant for a particular weak acid or weak base at a given temperature the degree of dissociation of that weak acid and weak base can be calculated at any concentration.

iii) Used in the determinations of degree of hydrolysis of a salt.

Limitations of Ostwald's dilution law :

1) The value of K comes out constant only for weak electrolytes when the solutions are very dilute.

2) The value of K does not become constant for strong electrolytes.

So, Ostwald's dilution law is valid only for weak electrolytes in dilute solutions and it does not hold good for strong electrolytes.

3.4.10 Debye – Huckel – onsagar's equation for strong electrolytes :

According to Arrhenius, the degree of dissociation increases with dilution which is true in case of weak electrolytes. But the increase in conductance of strong electrolytes with dilution depends on some other factors. In 1923, Debye and Huckel and in 1926 Onsagar put forward the theory of strong electrolytes and the salient features of the theory are given below –

i) Strong electrolytes are completely ionised at all dilutions.

ii) Every ion is surrounded by oppositely charged ions known as ionic atmosphere in a spherically symmetrical manner. These ions are continuously replaced by other similar ions present in the solution.

iii) Under the influence of electric field the central ion and ionic atmosphere move in opposite direction. Thus the ionic atmosphere effects the speed of the central ion in an electric field.

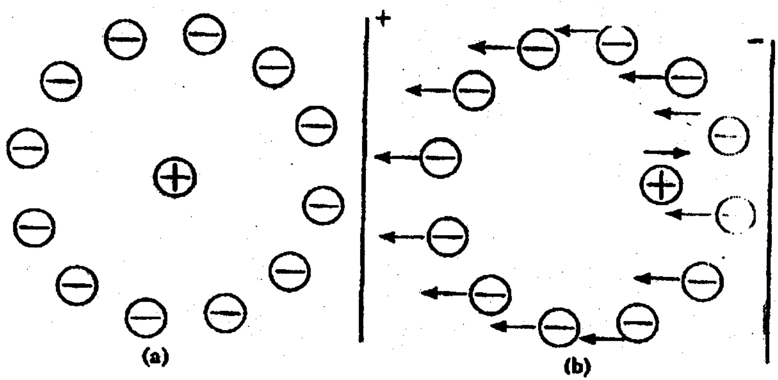
iv) The increase in conductance on dilution is due to increase in the mobility of ions but not due to increase in the number of ions. Electrical force and viscous drag are responsible for the mobility of ions.

v) $\frac{\lambda_V}{\lambda_\alpha}$ is only a ration but not α degree of dissociation.

According to Debye – Huckel theory the speed of an ion in electrical field is slowed down or decreased by the electrical attraction between the oppositely charged ions. Such effects are known as interionic effects and out of which, relaxation effect or asymmetry effect and electrophoretic effect are very important.

Relaxation or asymmetry effect :

Each ion in a solution is surrounded by ionic atmosphere. The central positively charged ion is surrounded by an atmosphere of negatively charged ions and vice versa when no electric field is applied the ionic atmosphere remains symmetrical around the central ion. The force of attraction of the ionic atmosphere is uniform in all directions on the central ion and hence will be cancelled. But when an electric field is applied, the central ion and ionic atmosphere move in opposite direction i.e. the cations move toward cathode while the anions move toward anode. The ionic sphere about the central ion becomes asymmetric. Now there is a large negative charge behind the cation than in front of it which results in a net attractive force in the back ward direction. Because of it, the cation experiences a retarding force which tends to drag it backward. In turn the movement of the ion is slowed down. In the same way, it happens when anion is surrounded by cationic atmosphere.



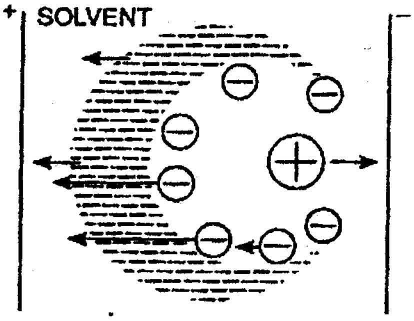
(a) Symmetrical ionic atmosphere in absence of an electric field.

(b) Asymmetric ionic atomosphere in presence of an electric field.

The slowing down of the speed of the ions is due to asymmetry of the ionic atmosphere and hence the effect is known as asymmetric effect.

A similar ionic atmosphere is rebuilt around the central ion, when it is moving out of the ionic atmosphere. Destruction of the old ionic atmosphere and the formation of the new ionic atmosphere, both of them takes some time known as relaxation time during which the old ionic atmosphere pulls the moving ion back ward and hence retards the motion. Hence the asymmetric effect is also called as relaxation effect.

Electrophoretic effect. :



Movement of central ion in a direction opposite to that of the ionic atmosphere and the

The association of solvent molecules as water of hydration with the ionic atmosphere is another factor which tends to retard the movement of an ion in solution. When EMF is applied ionic atmosphere along with solvent molecules associated with it move in opposite direction to the central ion and causes a retarding force on the movement of the central ion. This relarding effect is equal to the viscous resistance of the solvent on the central ion. By analogy to the resistance acting on the movement of a colloidal particle under the influence of electric field, this effect is called as electrophoretic effect.

When an electrolyte solution is diluted, the number of ions per unit volume decreases and the ions will be at larger distance and hence the influence of the asymmetric and electrophoretic effects on the speed of ions will be less and hence the ions will move very fast. Hence the equivalent conductance of the solution increases. On further dilution a stage will be reached i.e. the oppositely charged ions are at a greater distance and hence the solution exhibits maximum equivalent conductance which is known as equivalent conductance at infinite dilution. Thus the increase in equivalent conductance of a strong electrolyte on dilution is due to an increase in the speed of the ions but not due to an increase in the degree of ionisation.

Considering the inter ionic effects Debye and Huckel derived a mathematical expression for the variation of equivalent conductance with concentration. The equation was further improved by Onsager and hence the equation is known as Debye – Huckel – Onsager equation or onsager equation. For a particular solvent, at a given temperature the equations for a uni – univalent electrolyte is as given below.

$$\lambda_V = \lambda_\alpha - \left(A + B\lambda_\alpha\right)\sqrt{C}$$

Where

C = Concentration in gram equivalents per litre

A = Constant represent electrophoretic effect

B = Constant represent asymmetric effect

The values of A and B depend on the temperature and nature of the solvent,

$$A = \frac{82.4}{(D.T)^{1/2}\,\eta}$$

$$B = \frac{82.4 \times 10^5}{(D.T)^{3/2}}$$

Where

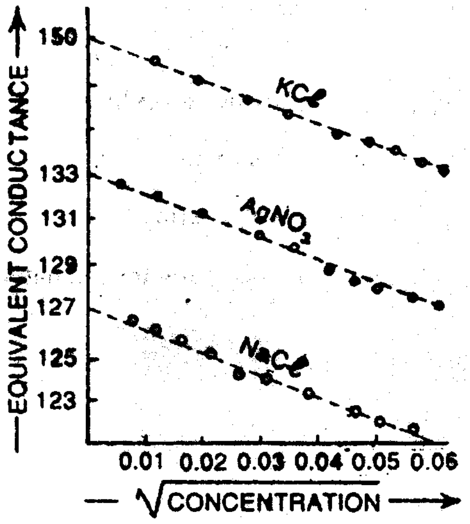
D = Dielectric constant

η = Viscosity of the medium

T = Temperature on absolute scale.

As the concentration decreases, the magnitude of $\left(A + B\lambda_\alpha\right)\sqrt{C}$ term decreases and hence the equivalent conductance, λ_V increases. Further, when concentration approaches Zero, the solution is at infinite dilution and hence the equivalent conductance becomes equal to λ_α.

Onsager equation can be tested in two ways. (1) The Plot of λ_V versus the the square root of the concentration ($\sqrt{C}$) should be linear. The slope of the line should be equal to $A + B\lambda_\alpha$, calculated by substituting the values of various constants directly. But in some cases λ_V versus $\sqrt{C}$ curves are straight times, but the on sagers slope is not equal to the slope obtained experimentally.



3.4.11 Model Questions :

1) What do you understand by the term transport number ? How is the transport nun determined experimentally.

2) Define transport number. How is transport number of an ion related to

i) speed of the ion and

ii) Ionic conductance of an ion.

3) Define Kohlransch's law of independent migration of ions and discuss its applications.

4) How does Kohlransch's law help in determining the equivalent conductivity of a weak electrolyte like acetic acid at infinite dilution ?

5) Write a short note on applications of conductivity measurements.

6) What are conductometric titrations ? Write an account of acid base conductometric titrations.

7) What is the principle underlying conductometric titrations ? During conductometric titration of a strong acid against strong base, the conductivity decreases upto the neutralisation point and then increases sharply. Explain why this happens ?

8) Deduce an equation for Ostwald's dilution law and discuss its uses and limitations.

9) Explain the terms relaxation effect and electrophoretic effect.

10) Discuss the Debye – Huckel theory of strong electrolytes. Give Onsagar equation

Numerical Problems :

1) A solution of $AgNO_3$ is electrolysed between silver electrodes. 50 gms of anodic solution before and after electrolysis contain 0.0901 gm and 0.1563 gm of $AgNO_3$ respectively. If 0.0792gm of silver is deposited in the silver coulometer connected in series, calculate the transport numbers of Ag^+ and NO_3^- ions.

(Ans : $t_{Ag^+} = 0.473$; $t_{NO_3^-} = 0.527$)

2) In a Hittorf experiment involving CuSO4 electrolysis between copper electrodes, 0.1836 gm of copper was deposited at the anode. The electrolyte in the anodic compartment before and after electrolysis contain 0.948 gm and 0.987 gm of copper respectively. Calculate the transport number of copper and sulphate ions.

(Ans : $t_{Cu^{2+}} = 0.212$; $t_{SO_4^{2-}} = 0.788$)

3) A solution of $AgNO_3$ having the composition 0.2096 gm of $AgNO_3$ in 25.5238 gms of water was electrolysed between silver electrodes. The current passed deposited 0.000799 gm equivalent of silver. After electrolysis the anodic solution was found to have 0.2877 gm of $AgNO_3$ in 25.5238 gms of water. Calculate the transport numbers of Ag^+ and NO_3^- ions.

(Ans : $t_{Ag^+} = 0.424$; $t_{NO_3^-} = 0.576$)

4) The speed ratio of the silver and nitrate ions in a solution of $AgNO_3$ electrolysed between silver electrodes is 0.916. Calculate the transport number of the two ions.

(Ans : $t_{NO_3^-} = 0.521$; $t_{Ag^+} = 0.479$)

5) A solution of silver nitrate having the composition 28.435 gms of H_2O ; 0.099 gm of $AgNO_3$ was electrolysed using silver electrodes. The current passed deposited 0.00792 gm. Equivalent of silver. At the end of electrolysis the solution around the anode was found to have the composition 28.435 gms of H_2O; o.2874 gm of $AgNO_3$ .Calculate the transport number of nitrate ion.

(Ans : 0.859)

6) Calculate the equivalent conductivity at infinite dilution for ammonium hydroxide, given that the equivalent conductivities at infinite dilution for $Ba(OH)_2$; $BaCl_2$ and NH_4Cl are 228.8 ; 120.3 and 129.8 $ohm^- cm^2 equiv^{-1}$ respectively.

(Ans : 238.3 $ohm^- cm^2 equiv^{-1}$)

7) The equivalent conductivity of 0.05N solution of propionic acid at 25°c is 6.32 $ohm^- cm^2 equiv^{-1}$ and the value increases to 385.6 $ohm^- cm^2 equiv^{-1}$ at infinite dilution. Calculate the degree of dissociation of the acid at that temperature.

(Ans : 0.0164)

8) **At 18°c the equivalent conductivities at infinite dilution of NH_4Cl ; NaOH and NH_4Cl are 129.8; 217.4 and 108.9 ohm$^-$ cm^2 equiv^{-1} respectively if the equivalent conductivity of $\frac{N}{100}$ solution of NH_4OH is 9.33 ohm$^-$ cm^2 equiv^{-1} Calculate the degree of dissociation of NH_4OH.**

(Ans : 0.039)

9) **The ionic conductance at infinite dilution of silver ions is 61.92 ohm^{-1} at 25°c. Calculate the ionic mobility of silver ions at 25°c.**

(Ans : 6.416 x 10^{-4} cm sec^{-1})

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UNIT - III

LESSON - V

ELECTROCHEMISTRY – III

3.5.1 An electrochemical cell is an arrangement of two electrodes and an electrolyte, used for producing an electric current due to chemical reaction in the cell or for producing chemical reaction due to passage of electricity. Electrochemical cells are of two types namely Galvanic or Voltaic cells and Electrolytic cells. Electrolytic cells are those in which electrical energy is used in bringing about a chemical reaction.

Eg : electrolysis or aqueous solution of hydrochloric acid into hydrogen and chlorine. Galvanic or Voltaic cells are those in which chemical energy is converted into electrical energy i.e electrical energy is produced by any physical or chemical process within the cell. The chemical reactions taking place at the electrodes of the electro chemical cells are oxidation and reduction

Electronic concept of oxidation - reduction reactions :

Oxidation is a process which involves the loss of electrons by a substance where as reduction involves gain of electrons by a substance. The substance that loses electrons is said to be oxidized while the substance that gains the electrons is said to be reduced. The two reactions oxidation and reduction always take place simultaneously.

Electrode reactions :

When ever two electrodes of a galvanic cell are connected by a conducting wire, certain chemical reaction take place in the cell. Such reactions which involve transfer of electrons from or to the electrode, are called as electrode reactions. At one electrode, the electrode material goes into the solution as positive ions leaving the electrode with a net negative charge or as negative ions leaving a net positive charge on the electrode. The excess electrons are continuously taken up by the other electrode. This flow of electrons results into oxidation at one electrode called anode and reduction at the other electrode called cathode. The combination of electrode and the solution in which it is immersed, called Half Cell.

Oxidation – Reduction in electrochemical cells :Example : Reaction of zinc and copper sulphate

Take copper rod dipped in a dilute solution of copper sulphate in one beaker and zinc rod dipped in a dilute solution of zinc sulphate in another beaker and the two electrodes are connected (metal rods) to an ammeter through a variable resistance. Then connect the two solution with each other through a glass tube containing potassium sulphate solution known as salt bridge. The current starts flowing as indicated by the reading on the ammeter and then the following reaction takes place.

$$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu^{0}$$

The reaction stops and no current flows when the metal rods are disconnected or the salt bridge is taken out.

The flow of current is due to flow of electrons, which is from zinc to copper rod. After the completion of the reaction it is found that there is loss in weight of zinc rod and gain in weight of copper rod.

The loss in weight of zinc rod is due to release of zinc into solution as zinc ions.

$$Zn_{(s)} \rightarrow Zn^{2+} + 2e^{-}$$

The reaction is called as oxidation half reaction.

The gain in weight of copper rod is due to the deposition of copper ions in the form of metal on the copper rod.

$Cu^{2+} + 2e^- \rightarrow Cu$

This reaction is known as reduction half reaction.

The over all redox reaction taking place in the cell is obtained by adding the two half reactions.

$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$

Hence, an electro chemical cell is a device in which oxidation reduction or redox reaction take place indirectly and the decrease in potential energy of the reactants appears in the form of electrical energy. The voltage or potential difference between the two electrodes of an electrochemical cell is known as electromotive force; EMF of the cell.

3.5.2 Reversible and irreversible cells :

Irreversible cells are those in which the electrode reactions take place even when no current is drawn from it. Example : The cell consisting of zinc and copper electrodes immersed in dilute H_2SO_4. Zinc reacts with dilute H_2SO_4 spontaneously even if no current is drawn from it.

Reversible cells are those cells in which there is no reaction until the electrodes are joined together by a conductor and current is drawn from it. The conditions for the thermodynamic reversibility are –

i) The driving and opposing forces be only infinitesimally different from each other.

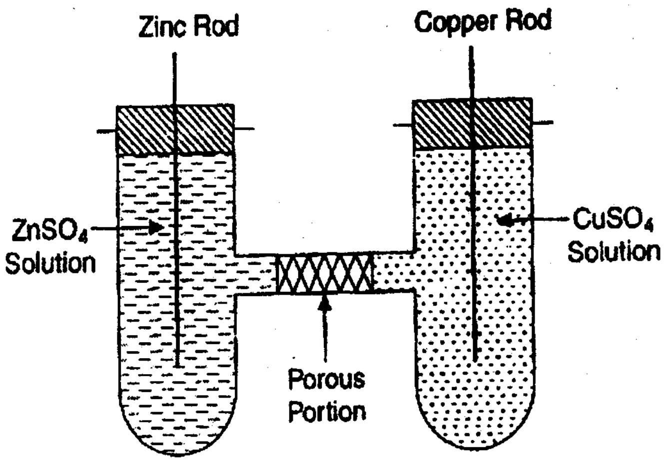
ii) It should be possible to reverse any change taking place by applying a force infinitesimally greater than the force acting. How ever, a reversible cell must satisfy the following conditions –

1) If an external EMF equal to that of the cell is applied in opposite direction, no current is given out by the cell and no chemical reaction takes place in the cell

2) If the opposing EMF is infinitesimally smaller current is given out by the cell and chemical reaction takes place to a small extent in the cell.

3) If the opposing EMF is infinitesimally greater than that of the cell, small current flows through the cell in the opposite direction and a small amount of chemical reaction takes place in reverse direction.

Example : Daniel Cell.



Daniel cell

The Daniel cell consists of a zinc electrode dipped in zinc sulphate solution and a copper rod dipped in copper sulphate solution. The two solutions are separated with the help of a porous diaphragm. There is no salt bridge but the ions of the two solutions can pass through the porous portion.

3.5.3 Types of reversible electrodes :

Each reversible cell consists of two reversible electrodes. The reversible electrodes are classified into four types –

1) Metal – Metal ion electrodes :

This type of electrodes consist of a metal rod in contact with ions of its own.

Eg : Zinc rod dipped in $ZnSO_4$ solution or a copper rod dipped in Cu SO_4 solution. If the metal is univalent, the electrode reaction may be represented as

$$M \rightleftharpoons M^+ + e^-$$

If the metal rod behaves as negative electrode (oxidation), the concentration of metal ions (M^+) in solution will increase. When the metal rod behaves as positive electrodes (reduction) the concentration of metal ions (M^+) in solution will decrease. Thus the electrodes is reversible with respect to M^+ ions.

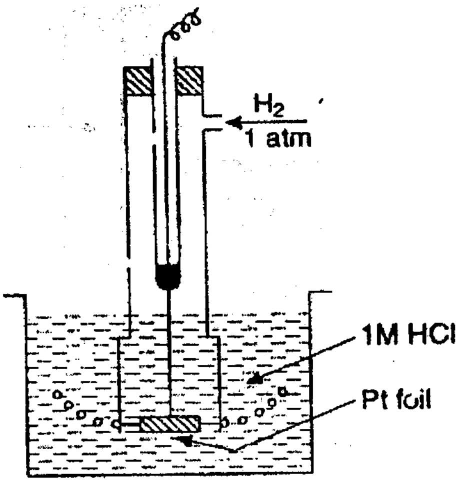
In general if the valency of the metal is Z, the equilibrium is represented as

$$M \rightleftharpoons M^{Z+} + Ze^-$$

2) Gas electrodes :

i) Hydrogen electrode

Hydrogen gas bubbling in a solution of an acid (HCl)



The hydrogen electorde

By bubbling hydrogen gas on platinum foil dipping in a solution containing H^+, an electrode reversible to H^+ ions is obtained.

P_t ; $H_{2(g)} \rightleftharpoons H^+$

ii) Chlorine electrodes :

In chlorine electrode ; chlorine gas is bubbled into a solution of hydrochoric acid at a given pressure.

P_t ; Cl_2 ; Cl^-

The equilibrium is represented as

$\frac{1}{2} Cl_{2(g)} + e^- \rightleftharpoons Cl^-$

This electrode is reversible with respect to chloride ion.

iii) Oxygen electrode :

In this electrode, oxygen gas is bubbled through a solution containing hydroxyl ions (OH-) at a given pressure.

$O_{2(g)} + 2H_2O + 2e^- \rightleftharpoons 4OH^-$

Due to some side reactions oxygen electrode does not behave as a true reversible electrode.

3. Metal – metal salt ion electrodes*:

This type of electrode consist of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion.

Example : Calomel electrode consists of mercury, solid mercurous chloride and potassium chloride solution.

Mercury of high degree of purity is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of mercurous chloride. A saturated, normal or decinormal potassium chloride solution is introduced through the side tube. A platinum wire sealed into a glass tube serves to make electrical contact of the electrode with the circuit.

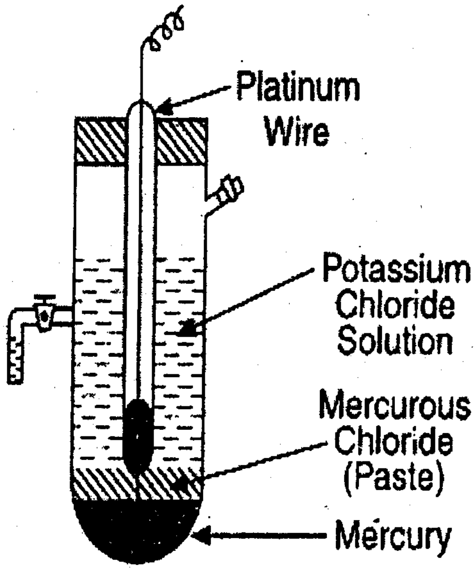
If the electrode acts as anode, electrode reaction involves oxidation, liberate electrons and releases mercurous ions into solution. These (Hg_2^{2+}) ions combine with chloride ions given by KCl, forming sparingly soluble Hg_2Cl_2 which results in fall in concentration of the chloride ions in solution.

$$2Hg(l) \rightleftharpoons Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_{2(s)}$$

$$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_{2(s)} + 2e^-$$

On the other hand, if the electrode acts as cathode, the reaction involves reduction,



Calomel electrode

The ions given by Hg_2Cl_2would be discharged at the electrode. Hence more and more of calomel (mercurous Chloride) passes into solution which results in an increase in the concentration of chloride ions.

$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$$

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

Hence the calomel electrode is reversible with respect to chloride ions.

4) Oxidation – Reduction Electrodes :

The electrodes in which the potential is developed from the presence of ions of the same substance in two different valency or oxidation states.

Such electrodes are set up by inserting an unattackable metal (eg:pt) in the solution. Thus when a platinum wire is inserted into a solution containing Fe^{2+} and Fe^{3+} ions, it is found that the wire acquires a potential

$$Fe^{2+} \rightleftharpoons Fe^{3+} + 2e^-$$

$$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$$

3.5.4 Single electrode Potential :

Single electrode potential or the potential of any electrode or a half cell is the potential difference between it and the electrolyte surrounding the electrode. The electrode potential depends upon the nature of the metal, concentration of the metallic ions in solution. The potential of an electrode can not be determined experimentally but the potential difference between the two electrodes can be measured accurately. By arbitrarily fixing potential of one electrode as zero it is possible to assign numerical values to various other electrodes. So, the potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit activity has been fixed as zero. This electrode is known as standard hydrogen electrode(SHE) or normal hydrogen electrode (NHE).

The standard electrode potential of a metal may be defined as the potential difference in volts at 25°c developed in a cell consisting of two electrodes, the normal hydrogen electrode and the other electrode i.e. the pure metal in contact with a molar solution of one of its ions.

Table : 1 Standard Reduction Electrode Potentials (E°) In Volts at 25°c (Electrochemical Series)

Electrode	Half Cell Reduction Reactions		E°
	Oxidising agent	**Reducing agent**	
	(Weakest)	**(Strongest)**	
$Li^+ ; Li$	$Li^{2+} + e \rightleftharpoons$	Li	−3.045
$K^+ ; K$	$K^{2+} + e \rightleftharpoons$	K	−2.925
$Ca^{++} ; Ca$	$Ca^{++} + 2e \rightleftharpoons$	Ca	−2.866
$Na^+ ; Na$	$Na^+ + 2e \rightleftharpoons$	Ca	−2.714
$Mg^{++} ; Mg$	$Mg^{++} + 2e \rightleftharpoons$	Mg	−2.363
$Al^{+++} ; Al$	$Al^{+++} + 3e \rightleftharpoons$	Al	−1.662
$Zn^{++} ; Zn$	$Zn^{++} + 2e \rightleftharpoons$	Zn	−0.763
$Fe^{++} ; Fe$	$Fe^{++} + 2e \rightleftharpoons$	Fe	−0.440
$Sn^{++} ; Sn$	$Sn^{++} + 2e \rightleftharpoons$	Sn	−0.136
$Pb^{++} : Pb$	$Pb^{++} + 2e \rightleftharpoons$	Pb	−0.126
$H^+ : H_2 , Pt$	$2H^+ + 2e \rightleftharpoons$	H_2	0.000
$CU^{++} ; Cu$	$Cu^{++} + 2e \rightleftharpoons$	Cu	+0.340
$Ag^+ : A$	$Ag^+ + e \rightleftharpoons$	Ag	+0.800
$Cl : Cl_2$	$Cl_2 + 2e \rightleftharpoons$	$2Cl^-$	+1.36
$Au^{+++} : Au$	$Au^{+++} + 3e \rightleftharpoons$	Au	+1.50
$F^- ; F_2 , Pt$	$F_2 + 2e \rightleftharpoons$	$2F^-$	+2.87
	(Strongest)	**(Weakest)**	

The electrode potential is given a positive sign, if the electrode reactions involves reduction when connected to the standard hydrogen electrode and a negative sign if the electrode reaction involves oxidation when connected to the standard hydrogen electrode.

Eg :

i) When copper electrode dipped in a solution of copper sulphate is connected with the standard hydrogen electrode, reduction takes place at the copper electrode and hence the potential of copper electrode is taken as positive E (Cu^{2+} : Cu) is positive.

Electrode reactions are

N.H.E : $H_{2(g)} \rightleftharpoons 2H^+ + 2e^-$ (Oxidation)

Copper electrode : $Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$ (Reduction)

ii) When zinc electrode is connected with the normal hydrogen electrode, oxidation occurs at the zinc electrode.

Zinc electrode : $Zn_{(s)} \rightleftharpoons Zn^{2+} + 2e^-$ (Oxidation)

Copper electrode : $2H^+ + 2e^- \rightleftharpoons H_{2(g)}$ (Reduction)

The potential of zinc electrode is taken as negative. E (Zn, Zn^{2+}) is negative.

3.5.5 Nernst equation – effect of electrolyte concentration on electrode potential:

The variation of electrode potential with concentration of metallic ions in solution is given by Nernst equation.

The reduction reaction for an electrode in general.

$M^{n+} + ne^- \rightleftharpoons M$

According to Nernst equation

$$E = E^\circ - \frac{2.303.\ RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

Where

E = Electrode potential of the metal.

E° = Standard electrode potential

T = Temperature on Kelvin scale

R = Gas constant = 8.314 Joules per moles per degree abs

n = Number of electrons involved in the half cell reaction.

F = One Faraday or 96500 coulombs.

[Mn+] = Activity of the metal ions in solution.

[M] = Activity of metal taken as unity.

At 298K, $\frac{2.303.\ RT}{nF} = 0.059$

$$E = E^\circ - \frac{0.059}{n}\log\frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \frac{0.059}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

3.5.6 Electrochemical series and its significance :

Arrangement of metals in the increasing order of their standard reduction potentials is known as **electrochemical series. The same** is the arrangement of metals when arranged in the order of their standard **electrode reduction potentials.** The values of oxidation potentials are obtained just by changing the sign of **the reduction potential value.**

Table 28.1 page 794

The lower the metal is in the series the greater is its tendency to be reduced. Thus the metals high up, in the series are strong reducing agents and their ions are stable where as those near the bottom of the series are stable metals and their ions are easily reduced to the metals.

Weakly electronegative metals in the upper part can displace more electronegative metals below them from their salts. Eg : Displacement copper of from copper sulphate by iron.

Any metal above hydrogen will displace hydrogen from a dilute acid solution and hydrogen will reduce the oxidized form of any metal lying below it in the series.

Hydroxides of metals in the upper part of the series are strongly basic and their salts do not undergo hydrolysis where as hydroxides of metals in the lower part of the series are weakly basic and their salts undergo hydrolysis. More weakly electronegative metals like K, Na, Ca etc. displace hydrogen from water.

Applications of electrochemical series :

1) Calculate the standard EMF of a galvanic cell formed by combining any two half cells and determine the cell reaction using the standard electrode potentials.
2) Predicting spontaneity or feasibility of the cell reaction. If the standard EMF of the cell is positive, the cell reaction is spontaneous, i.e. feasible. For a reaction to be spontaneous, the free energy change must be negative.
3) The standard electrode potentials are used for determining free energy change and equilibrium constant of a reaction.
4) With the help of standard electrode potentials, we can predict whether a given metal would react with acid to liberate hydrogen or not.

3.5.7 Cell potentials or E.M.F. from electrode potentials :

Each cell is made up of two half cells namely the oxidation half cell acts as anode or negative electrode and reduction half cell acts as cathode or positive electrode. Due to the difference in the electrode potentials of the two half cells, current flows from the electrode at higher potential to the electrode of lower potential. The potential difference of the two half cells of a cell is known as electromotive force or E.M.F. of the cell or cell potential. The cell potential is expressed in volts and measured directly with a Volta meter cell potential or E.M.F. of the cell can be determined from electrode potentials in the following way.

1) cell potential (E cell) = Reduction potential of cathode – Reduction potential of anode.

E cell = E cathode – E anode.

Or E cell = Reduction potential of right hand electrode – Reduction potential of the left hand electrode.

$E\ cell = E_{Right} - E_{Left}$.

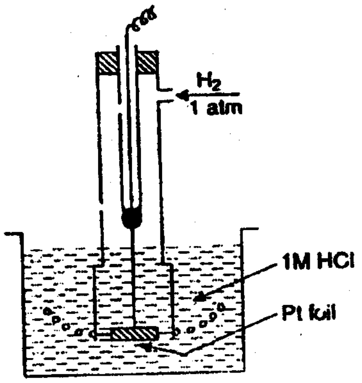
2) E cell = Oxidation potential of anode – oxidation potential of cathode.

Or E cell – E anode – E cathode

If cell potential (E cell) is positive, the reaction is spontaneous. On the other hand, if the cell potential is negative, the reaction will occur but it will not take place spontaneously.

Standard hydrogen electrode or Normal hydrogen electrode :

It is a primary standard electrode. It consists of a small platinum foil coated with platinum black to absorb hydrogen gas. A platinum wire welded to the electrode and sealed through a glass tube makes contact with the other circuit.



The hydrogen electorde

The platinum foil is surrounded by an other glass tube which has an inlet for hydrogen at the top and a number of holes at the base for the escape of excess of gas. The electrodes is placed in 1M hydrochloric acid solution and then pure hydrogen gas is then passed into it at one atmosphere pressure. A certain amount of hydrogen gas is absorbed by the platinised electrode while the remaining escapes through the lower holes.

When the hydrogen electrodes acts as anode, in the cell, the following reaction i.e. oxidation takes place.

$H_2 \rightleftharpoons 2H^- + 2e^-$

Some hydrogen gas changes into H^+ ions and goes into the solution.

If the electrode acts as cathode the following reaction i.e. reduction takes place.

$2H^+ + 2e^- \rightleftharpoons H_2$

Some H^+ ions from the solution changes into H_2 gas.

The hydrogen electrode is reversible with respect to H^+ ions. The potential of the standard or normal hydrogen electrode is arbitrarily fixed as zero.

Reference electrodes :

Since it is not always easy to set up the normal hydrogen electrode which is used as primary reference electrode because of the difficulties in maintaining the activity of H^+ ions at unity and pressure of the gas uniformly at one atmosphere, some other electrodes known as secondary reference electrodes have been employed.

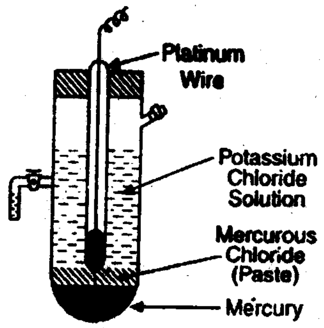
Examples :

i) Calomel electrode (Metal – metal salt ion electrode) :

Calomel electrode consists of mercury, solid mercurous chloride and potassium chloride solution.

$Hg_{(l)}$; $Hg_2Cl_{2(s)}$; KCl (solution)

Mercury of high degree of purity is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of mercurous chloride. A saturated, normal or decinormal potassium chloride solution is introduced through the side tube. A platinum wire sealed into a glass tube serves to make electrical contact of the electrode with the circuit.



Calomel electrode

If the electrode acts as anode, electrode reaction involves oxidation, liberate electrons and releases mercurous ions (Hg_2^{2+}) into solution. These mercurous ions combine with chloride ions given by KCl, forming sparingly soluble Hg_2Cl_2 which results in fall in concentration of the chloride ions.

$2Hg(l) \rightleftharpoons Hg_2^{2+} + 2e^-$

$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_{2(s)}$

$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_{2(s)} + 2e^-$

On the other hand when the electrode acts as cathode, the reaction **involves reduction**. the ions given by Hg_2Cl_2 would be discharged at the electrode. Hence more and more of mercurous chloride (calomel) passes into solution which results in an increase in the concentration of chloride ions.

$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+} + 2Cl^-$

$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$

$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$

Hence, the calomel electrode is reversible with respect to chloride ions.

The potential of the **calomel electrode** depends upon the concentration of potassium chloride solution. The potential of the **calomel electrode** has been measured, by connecting it to a standard hydrogen electrode and the **reduction potentials** obtained for the various concentrations at 25°c are

For

0.1N KCl solution	= +0.3335volt
1.0N KCl solution	= +0.2810volt
Saturated KCl solution	= +0.2422volt

ii) Silver – Silver chloride electrode :

This electrode consists of a silver wire coated with a layer of silver chloride which is inserted in the solution of a chloride (eg : KCl or HCl) of unit activity.

$Ag ; AgCl(s) ; Cl^- (a = 1)$

The reduction potential of the electrode on the hydrogen scale at 25°c is + 0.2225volt.

3.5.8 Representation of electrochemical cells :

An electro chemical cell is represented with the help of following convention –

1) The half cell in which oxidation occurs is represented on the left hand and thus the left hand electrode acts as anode. The half cell in which reduction occurs is represented on the right and this right hand electrode acts as cathode.
2) The left hand electrode is represented by writing the symbol of the metal (or the gas) first followed by the symbol of the ion with its concentration in bracket. The electrode on the right

hand side is written by first writing the ion along with its concentration in the bracket followed by the symbol of the metal or the gas.

3) The phase boundaries of each electrode is separated by single vertical line.

4) The two electrodes are separated by double vertical lines which represent the salt bridge.

5) In case of gases at equilibrium it is necessary to represent the pressure of the gas.

For Example. :

i) Daniel cell, having zinc electrode in $ZnSO_4$ solution of C_1 concentration and copper electrode in $CuSO_4$ solution of C_2 concentration will be represented as

$Zn \mid Zn^{2+} (C=1) \mid\mid Cu^{2+} (C=2) \mid Cu$

ii) $Pt \mid H_2(1\ atm) \mid H^+ (C_1) \mid\mid Cu^{2+} (C=2) \mid Cu$

3.5.9 Writing the cell reaction from conventions of electrochemical cells :

Left hand electrode represents oxidation half cell and the right hand electrode represents the reduction half cell and the two half cells are separated by double vertical lines.

Example :

i) Zn – Cu cell

$Zn \mid Zn^{2+} (C=1) \mid\mid Cu^{2+} (C=2) \mid Cu$

L.H.E. R.H.E.

Oxidation half cell reaction $Zn \rightarrow Zn^{2+} + 2e^-$

Reduction half cell reaction $Cu^{2+} + 2e^- \rightarrow Cu$

Complete cell reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

iii) ii) $Pb \mid Pb^{2+} \mid\mid Cd^{2+} \mid Cd$

L.H.E. R.H.E.

Oxidation half cell reaction $Pb \rightarrow Pb^{2+} + 2e^-$

Reduction half cell reaction $Cd^{2+} + 2e^- \rightarrow Cd$

Complete cell reaction $Pb + Cd^{2+} \rightarrow Pb^{2+} + Cd$

3.5.10 E.M.F of a cell and its measurement :

Due to the difference in the electrode potentials of the two half cells, the current flows from the electrode at higher potential to the electrode of lower potential. This potential difference of the two half cells of cell is known electromotive force or E.M.F. of the cell or cell potential expressed in volts.

Measurement of cell potential :

The E.M.F. of a cell can be measured by connecting the two electrodes to the two terminals of a voltameter. But, this method is not accurate because the current drawn by the voltameter for the measurement disturbs the electrochemical equilibrium of the cell, there by causes change in E.M.F. of the cell. The E.M.F. of a cell can be measured accurately using a method based on poggendorff's compensation principle. In this method, the E.M.F. of a cell under examination is balanced by an equal and opposite E.M.F. of another cell. The electrical assembly used is known as potentiometer which consists of a uniform wire AB of high resistance. A storage battery of constant E.M.F. which should be larger than the E.M.F. of the cell to be measured is connected at the ends of A and B of the wire. The cell 'X', the E.M.F. of which is to be determined is connected through a Galvanometer G to a sliding contact 'D', such that it opposes the E.M.F. of the storage battery. The sliding contact 'D' is moved along the wire AB till no current flows through the Galvanometer. The position of D is then noted. Now the E.M.F. of the cell E_X is proportional to the distance AD.

$$E_X \alpha AD$$

Now the cell 'X' is replaced by a standard cell, the E.M.F. of which say Es is known. Again the sliding contact 'D' is moved along the wire AB till no current flows through the Galvanometer i.e. the null point is reached at 'D^1'

$$E_X \alpha AD^1$$

$$\frac{E_X(\text{EMF of X})}{E_S(\text{EMF of S})} = \frac{AD}{AD^1}$$

$$\therefore E_X = \frac{AD}{AD^1} \times E_S$$

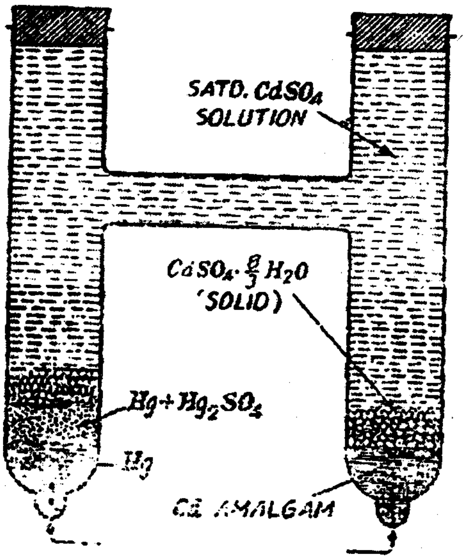
Thus, by knowing Es ; Ex can be calculated.

Weston standard cell :

A standard cell is one whose potential is highly reproducible and accurate upto a fraction of millivolt such a cell should be reversible and should not be damaged by the passage of current through it. Its EMF should not vary with temperature.

Eg : Weston cell

It is a 'H' shaped glass tube. The positive electrode (anode) consists of mercury covered



The Weston Standard Cell.

with solid mercurous sulphate and the negative electrode (cathode) consists of 12.5% cadmium amalgam, covered with $3CdSO_4 . 8H_2O$ crystals over its top. 'H' tube is filled with a saturated solution of cadmium sulphate. The ends of the tube are then sealed. The cell may be represented as.

$$Cd\ (Hg)\ |\ Cd^{2+}\ (satd)\ ||\ Hg_2SO_{4(S)}\ |\ Hg$$

The EMF of the cell lies with in the range 1.0188 to 1.0198volt, depending on the exact activities of amalgam. The cell is used to calibrate the slide wire of the potentiometer.

Cell reaction :

$Cd_{(s)} \rightleftharpoons Ca^{2+} + 2e^-$ (Oxidation half cell)

$Hg_2SO_{4(S)} \rightleftharpoons 2Hg_{(l)} + SO_4^{2-}$ (Reduction half cell)

$Cd_{(s)} + Hg_2SO_{4(S)} \rightleftharpoons Cd^{2+} + 2Hg_{(l)} + SO_4^{2-}$

3.5.11 Relation between free energy change and electrical energy :

Earlier, it was believed that the electrical energy of a reversible cell was equal to the heat of cell reaction at constant pressure. It is equal to the decrease in enthalpy ($-\Delta H$) of the reaction. Gibb's – Helmholtz equation shows that the electrical energy of a reversible cell is measured by the decrease in the free energy of ($-\Delta G$) of the cell reaction.

Suppose in a particular cell reaction, n is the number of electrons liberated or taken at one electrode, then nF Faradays of electricity will be generated in the reaction. If E is the EMF of the cell, then electrical energy supplied by the cell= nFE

Decrease in free energy of the system $-\Delta G = nFE$

According to Gibb's – Helmholtz equation, decrease in free energy of a system at constant pressure

is $-\Delta G = -\Delta H - T\left(\frac{\int(\Delta G)}{\int T}\right)_P$

Where $-\Delta H$ is the decrease in enthalpy or heat content. of the reaction at constant pressure.

$\because -\Delta G = nFE$

$$nFE = -\Delta H - T\left(\frac{\int(-nFE)}{\int T}\right)_P$$

$$= -\Delta H + TnF\left(\frac{\int E}{\int T}\right)_P$$

Calculation of K :

For reactions in which the reactants and products are in their standard states.

$-\Delta G^\circ = nFE^\circ$ cell

The standard free energy change for a reaction is related to the equilibrium constant as follows.

$-\Delta G^\circ = RT\ln K = nFE^\circ$

Where K is the equilibrium constant

Conditions of spontaneity of the reaction under standard conditions

ΔG°	K	E°cell	Reaction under standard conditions
Negative	>1	Positive	Spontaneous
0	=1	0	At equilibrium
Positive	<1	Negative	Non.- spontaneous

3.5.12 Calculation of EMF of the cell :

Example : 1

Calculate the standard EMF of the cell Cd |Cd^{2+}|| Cu^{2+}| Cu and determine the cell reaction given that

E° Cd^{2+};Cd = 0.40 volt

E° Cu^{2+};Cu = 0.34 volt

Solution :

Oxidation half cell reaction	$Cd \rightarrow Cd^{2+} + 2e^-$
Reduction half cell reaction	$Cu^{2+} + 2e^- \rightarrow Cu$
Complete cell reaction	$Cd + Cu^{2+} \rightarrow Cd^{2+} + Cu$

$E°\ cell = E°_R - E°_L$

Standard reduction potential of the right hand electrode - standard reduction potenctial of left hand electrode.

$E°_R$ (Cu^{2+}, Cu) = 0.34volt

$E°_L$ (Cd^{2+} , Cd) = -0.40volt

$E°cell = 0.34 - (-0.40)$

$= 0.74$ volt

Example : 2

Write the cell reaction and calculate the standard E° of the cell Zn | Zn^{2+}(C= 1) | | Cd^{2+}(C= 1)| Cd standard reduction potentials of zinc and cadmium electrodes are 0.763volt and 0.403 volt respectively

Solution :

$E°\ cell = E°_R - E°_L$

$E°_R$ (Cu^{2+}, Cd) = 0.403volt

$E°_L$ (Zn^{2+} , Zn) = 0.763volt

$E°cell = 0.403 - (0.763)$

$= -0.36$ volt.

Cell reaction :

Oxidation half cell reaction	$Zn \rightarrow Zn^{2+} + 2e^-$
Reduction half cell reaction	$Cu^{2+} + 2e^- \rightarrow Cu$

Complete cell reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Example : 3

Calculate the standard EMF of the following cell $Cd | Cd^{2+} || Ag^{2+} | Ag$. Write the cell reaction given that

$E^\circ (Cu^{2+}, Cd) = -0.40$volt

$E^\circ (Ag^{-}, Ag) = 0.80$volt

$E^\circ \text{cell} = E^\circ R - E^\circ L$

$E^\circ \text{cell} = 0.80 - (- 0.40)$

$= 1.20$ volt.

Cell reaction :

Oxidation half cell reaction $Cd \rightarrow Cd^{2+} + 2e^-$

Reduction half cell reaction $2Ag^{2+} + 2e^- \rightarrow 2Ag$

Complete cell reaction $Cd + 2Ag^{2+} \rightarrow Cd^{2+} + 2Ag$

3.5.13 Model Questions :

1. what is a reversible electrode ? Mention the various types of reversible electrodes. Explain the electrode reaction in each type.
2. What is meant by E.M.F. of a cell ? what are its units ? How is it determined.
3. What do you understand by single electrode potential ? How would you measure single electrode potential?
4. What is meant by a reference electrode ? Describe the construction and working of a calomel electrode.
5. Write short notes on
   i) Nernst equation
   ii) Standard hydrogen electrode.

6) Distinguish between single electrode potential and standard electrode potential. Draw a neat sketch of calomel electrode and discuss.

7) What is a cell potential ? How it can be determined from the electrode potentials ? How is spontaneity of a reaction related to E.M.F ?

8) What is electrochemical series ? Give its applications.

3.5.14 Problems :

1) Calculate the EMF of the cell $Zn \mid Zn^{2+} (1M) \mid\mid Ag^{2+} (1M) \mid Ag$

Given

$E° Zn \rightarrow Zn^{2+} = + 0.762$ volt (oxidation potential)

$E° Ag^{+} \rightarrow Ag = 0.80$volt (Reduction potential)

(Ans : 1.562 volts)

2) Consider the cell $Zn \mid Zn^{2+} (1M) \mid\mid Cu^{2+} (1M) \mid Cu$

The standard reduction potentials are

Cu^{2+} ; Cu) = 0.35volt

Zn^{2+} ; Zn = -0.763 volt

Write down the cell reaction and calculate the EMF of the cell. Is the cell reaction spontaneous or not ?

(Ans : 1.113 volts)

3) Calculate the EMF of the cell $Zn \mid Zn^{2+} (1M) \mid\mid H^{+} (1M) \mid\mid H_2 (1atm) \mid (Pt)$

Given that the oxidation potential of Zn^{2+} ; Zn is 0.7618 volt

(Ans : 0.7618 volts)

4) Calculate the EMF of the following cell

$Zn \mid Zn^{2+} (0.1M) \mid\mid Cu^{2+} (0.01M) \mid Cu$

Given that standard reduction potential for zinc and copper electrodes are 0.7623 volt and 0.33 volt respectively.

(Ans : 0.4323 volts)

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UNIT - IV

Lesson - I

MOLECULAR SYMMETRY

4.1.1. Symmetry elements and symmetry operations in molecules, definition of plane of symmetry centre of symmetry and Axis of symmetry (simple axis Cn) and alternating axis (Sn). Examples.

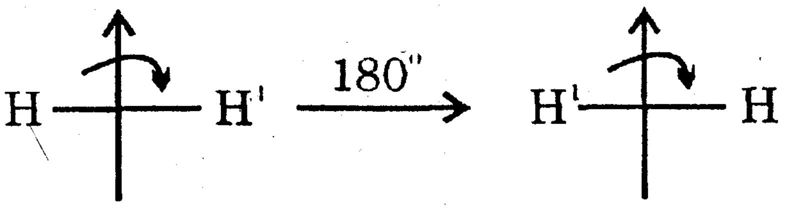
4.1.2. Symmetry :

Symmetry is a geometrical property. An object is said to be symmetrical if it can take up more than one equivalent orientations.

Explanation:

When there is no change in the initial state and final state of the molecule it is called equivalent orientation. They are indistinguishable.

Example: Hydrogen molecule



Orientation I Orientation II

The Hydrogen molecule with orientation I on rotation by 180° along the axis shown gives orientation II. Orientation II can not be distinguished from orientation I. Hence they are equivalent orientations.

4.1.3. Symmetry operation and symmetry element:

1. Symmetry operation :

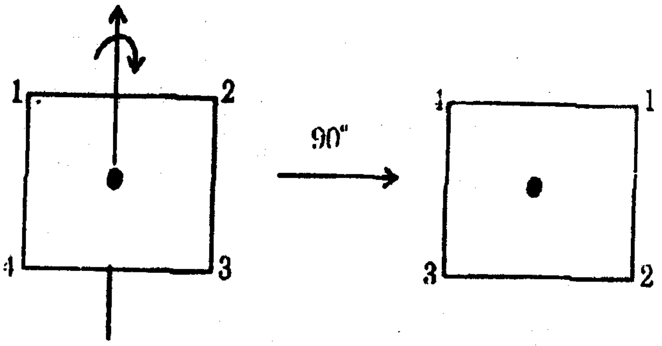
Symmetry operation is the process carried out on a molecule, which brings the molecule from original orientation to an equivalent orientation.

During symmetry operation the point of centre of gravity of the molecule should not be changed.

Symmetry element :

Symmetry elements are geometrical entities such as an axis, plane or point over which a symmetry operation can be carried out.

2. Symmetry operations are intimately connected with the symmetry elements possessed by the body. A given rotation must be carried out about it's symmetry axis. Any reflection must be carried out with respect to a specified plane.



3. Symmetry operations are the movements of an objects which carry the object into an equivalent orientation. All symmetry operations can be expressed in terms of rotations and reflections.

The axes and planes constitute symmetry elements. They define rotations and reflections that are symmetry operations.

S.No.	Symmetry element	Symmetry operation
1.	Symmetry Point	It involves inversion through centre.
2.	Symmetry axis	It involves rotation about axis
3.	Symmetry plane	It involves reflection through plane
4.	Improper Symmetry axis	It involves successive rotation about the axis and reflection through the plane perpendicular to the axis.
5.	Rotatory inversion axis	It involves successive rotation about the axis and inversion through the centre lying on the axis.

4.1.4. Symmetry Elements :

Symmetry elements are geometrical entities such as an axis, plane or point over which a symmetry operation can be carried out. They are four types.

1) Axis of symmetry (Rotation)

2) Plane of symmetry (Reflection)

3) Centre of symmetry(Inversion)

4) Alternating axis of symmetry (Rotation - Reflection)

4.1.4.1. Axis of symmetry (Cn) :

It is an imaginary axis about which a molecule is rotated through 360° such that it gives more than one equivalent orientations.

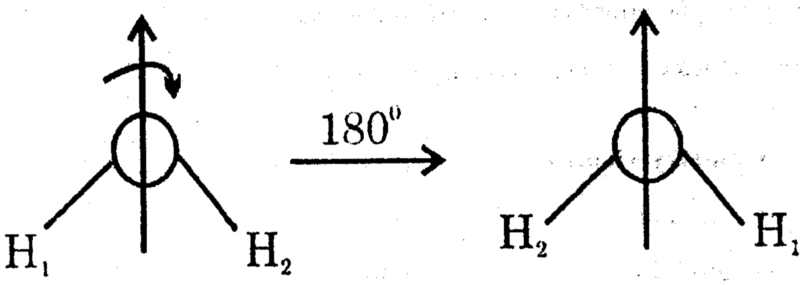
Rotational axis is represented by *Cn*, where $n = \frac{360}{\theta}$

Here θ is the angle of rotation.

When $\theta = 360°$, $n = \frac{360}{360} = 1$

It is called C_1 axis. It is also called Identity element.

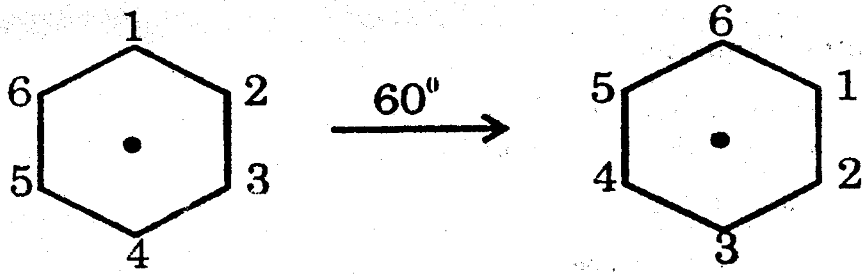
Examples : 1. Water molecule :



These are equivalent orientations.

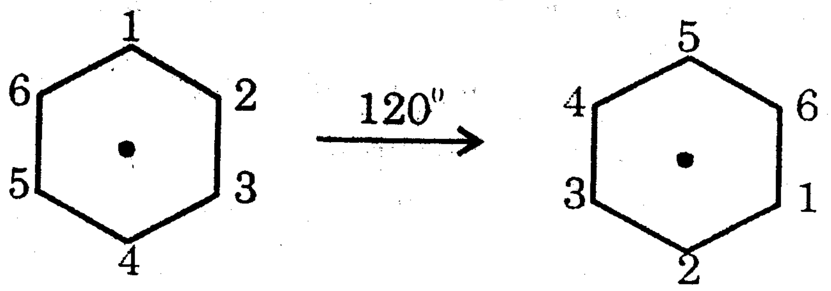
Here n = $\frac{360}{180} = 2$ It is C_2 axis.

2. Benzene molecule :



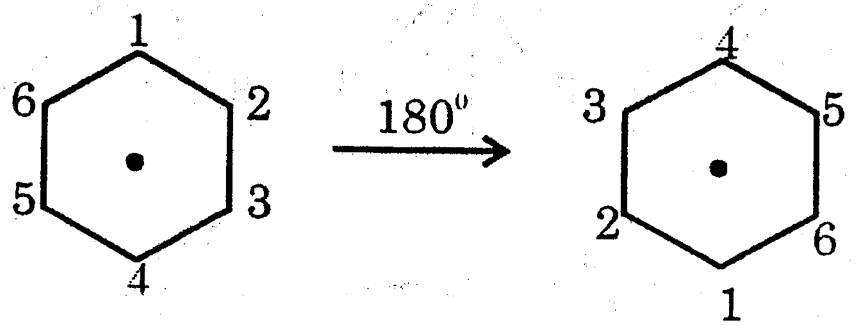
These are equivalent orientations.

Here $\theta = 60°$ $n = \frac{360}{60} = 6$ It is C_6 axis.



These are equivalent orientations.

Here n = $\frac{360}{120} = 3$ It is C_3 axis.



These are equivalent orientations.

Here $\theta = 60°$. $n = \frac{360}{180} = 2$ It is C_2 axis.

Principal rotational axis :

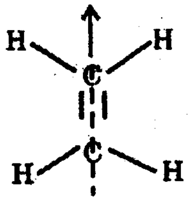
1. When a molecule has only one rotational axis, it is the principal rotational axis.

   Ex : For NH_3 principal rotational axis is C_3 because it has only C_3 axis.

2. When a molecule has several rotational axes of different order, then the axis of highest order is the principal rotational axis.

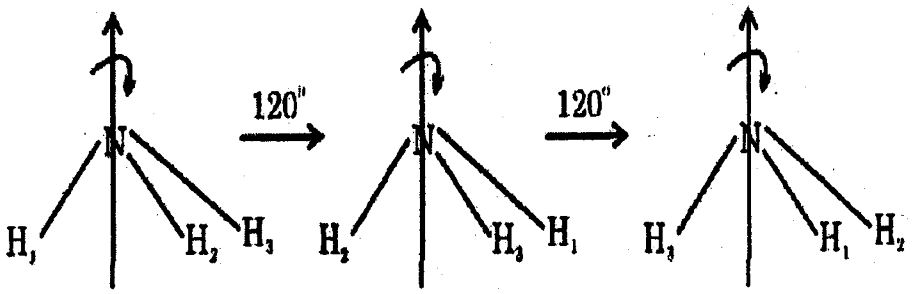
   Ex : Benzene has C_6, C_3 and C_2 rotational axes. Here C_6 axis with highest order 6 is the principal axis.

3. When a molecule has several rotational axes of same order, the axis passing through the minimum number of atoms is the principal axis. Ex : Ethylene.



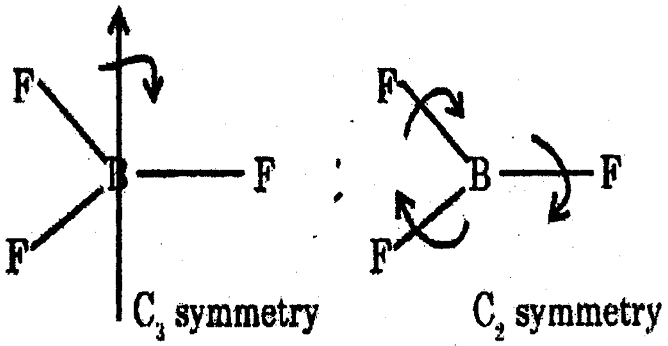
4. Always principal rotational axis is made as Z-axis.

Ammonia (NH_3) :



The order of the axis $n = \frac{360}{120} = 3$. It has three fold axis C_3 symmetry.

Boron trifluoride:



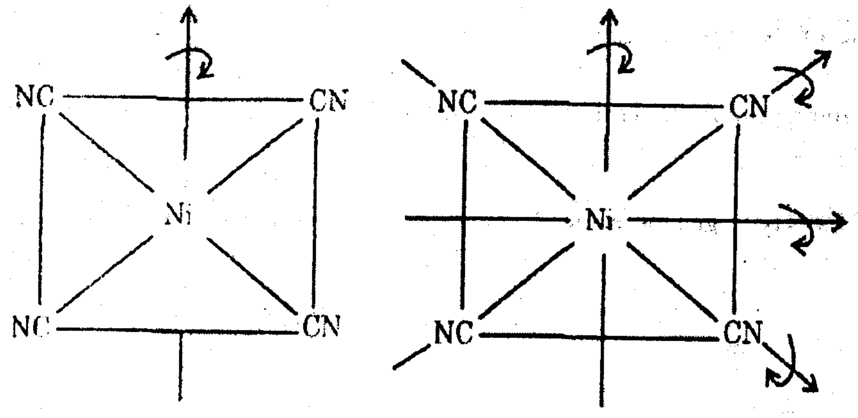
BF_3 is a trigonal planar molecule. The axis passing through Boron and perpendicular to the triangle containing three fluorine atoms is a three fold axis C_3 The angle of rotation is 120°.

Order of the axis $n = \frac{360}{120} = 3$

It has two fold axis C_2 symmetry also. The angle of rotation is 180°.

Order of the axis $n = \frac{360}{180} = 2$.There are three C_2 axes of symmetry.

$[Ni(CN)_4]^{-2}$:



C_4 symmetry C_2 symmetry

It is a square planar molecule. The axis passing through Nickel atom and perpendicular to the square containing four cyanide ions is a four fold axis C_4. The angle of rotation is 90°

Order of the axis $n = \frac{360}{90} = 4$

It has four two fold axis C_2 symmetry also.

Linear molecules : All linear molecules have an infinite fold axis C α

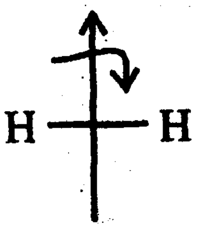
Ex : $— H —— Cl \longrightarrow$ $— H —— H \longrightarrow$

Hydrogen chloride Hydrogen

Heterodiatomic molecule Homodiatomic molecule

Rotation by any fraction of angle along the axis gives an equivalent orientation.

Homodiatomic molecules like Hydrogen have two fold axis C_2 symmetry also.

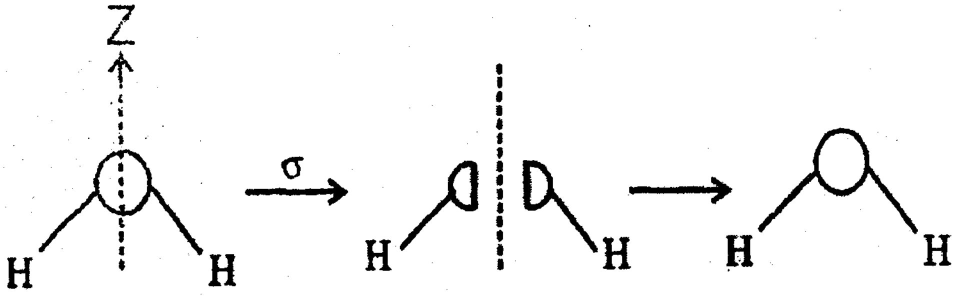


C_2 symmetry

4.1.4.2. Plane of Symmetry (σ):

It is an imaginary plane that divides the molecule into two halves such that one is the mirror image of the other.

Ex : Hydrogen molecule



mirror images

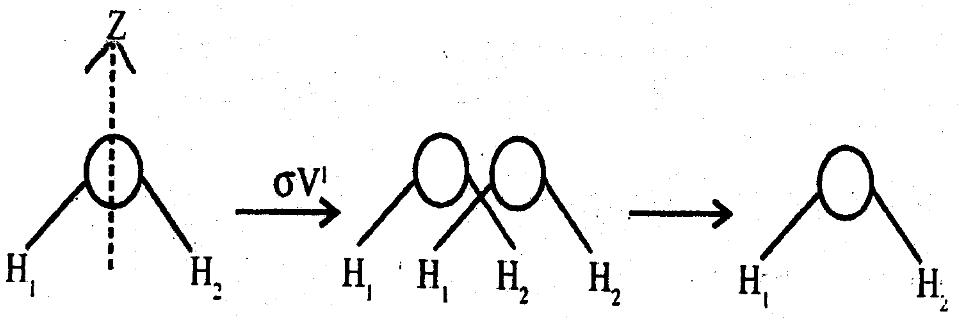
They are three types:

1) Vertical plane of symmetry
2) Horizontal plane of symmetry.
3) Dihedral plane of symmetry.

1) vertical plane of symmetry:

This is a plane passing through [illegible] principal axis and through one of the two subsidiary axes. It is represented by σV. (V vertical) because the molecule is drawn with the principal axis set vertically by convention.

Ex : Water molecule



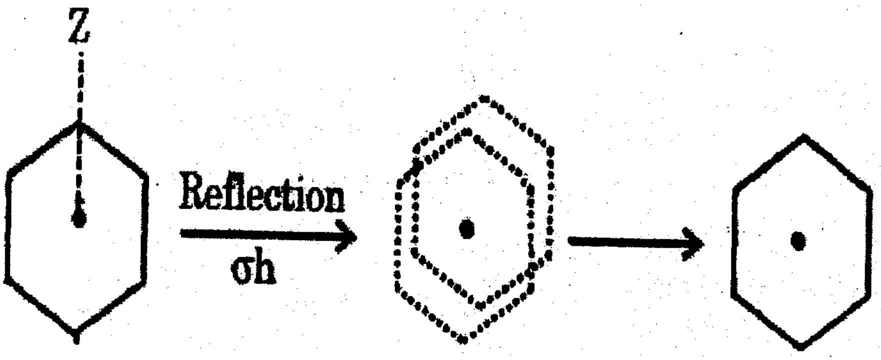
The vertical plane of symmetry of water molecule.

This plane σYZ contains the principal axis and lies in the plane of the molecule. It is the vertical plane σV¹.

2. Horizontal plane :

This is a plane perpendicular to the principal axis. It is represented as *σh* Here '*h*' stands for horizontal.

Ex : Benzene molecule



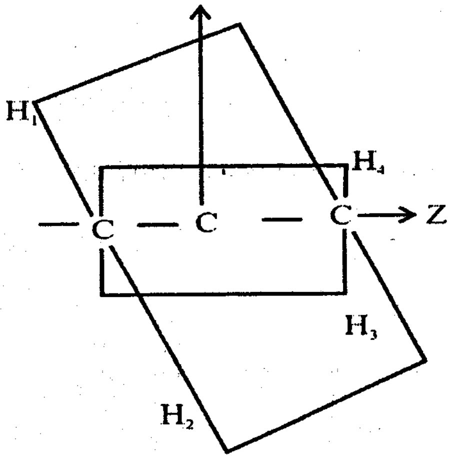
The horizontal plane of symmetry of Benzene molecule.

The plane σxy is passing through the six carbon atoms and is perpendicular to the principal axis C_6 It is the horizontal plane σ h.

3. Dihedral plane:

This is a plane passing through the principal axis and passes between the two subsidiary axes. This plane bisects the angle between the vertical planes. It is represented by σ*d*. (d = dihedral) some authors called it as "diagonal"

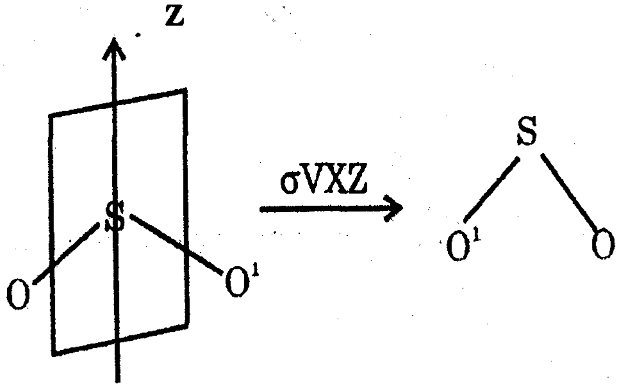
Ex : Allene ($CH_2 = C = CH_2$



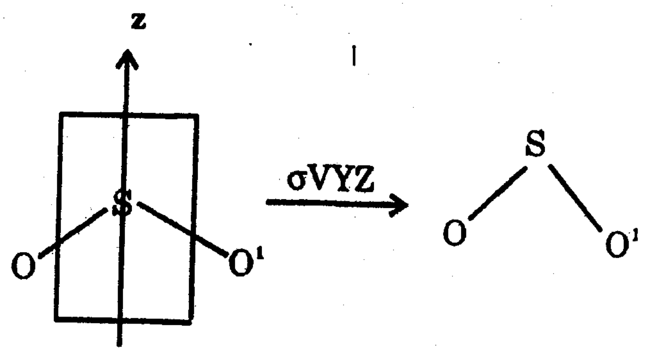
The dihedral plane of symmetry of Allene molecule . The plane is passing through the molecular axis and through H_1 H_2 or H_3 H_4. It is the dihedral plane because H_1 H_2 or H_3 H_4 are between the subsidiary axes.

Sulphur dioxide (SO_2) :

In Sulphur dioxide there are two vertical planes σVXZ and σVYZ.

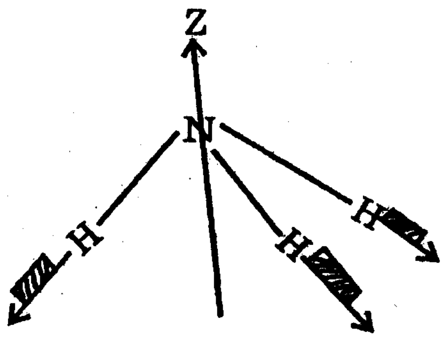


The plane σVXZ is passing through the sulphur atom and in between two oxygen atoms. In σVXZ the oxygen atoms are shifted.



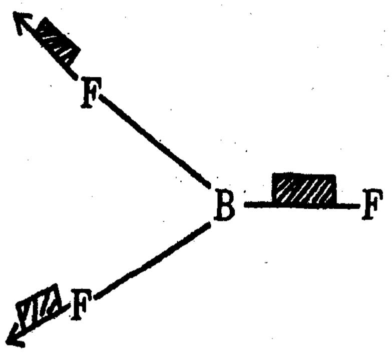
The plane σVYZ is passing through the sulphur atom and also through the two oxygen atoms. In σVYZ all atoms remain unshifted.

Ammonia (NH_3) :



In Ammonia molecule there are three vertical planes of symmetry each passing through the Nitrogen atom and one of the three Hydrogen atoms. They are represented as σV^{I} σV^{II} and σV^{III}.

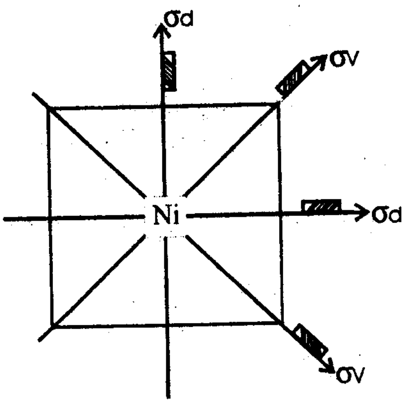
Boron trifluoride (BF_3) :



It has three vertical planes of symmetry σV each passing through the Boron atom and one of the three Fluorine atoms.

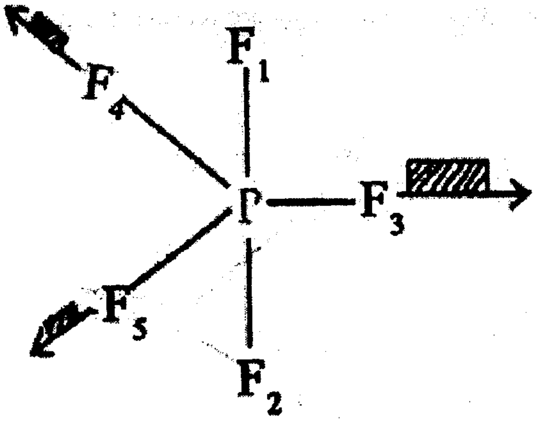
It is trigonal planar molecule. The plane of the molecule (passing through the Boron and three Fluorides) is a plane of symmetry. It is perpendicular to the Principal axis. So, it has Horizontal plane of symmetry σh.

$[Ni(CN)_4]^{-2}$: In $[Ni(CN)_4]^{-2}$ there are four σV planes each passing through the central Ni (II). Two σV planes pass through the cyanides at opposite corners. They are denoted as σV. The other two σV planes pass through the centres of opposite edges. They are denoted as σd. But they are not really dihedral planes because they are passing through the subsidiary axis.



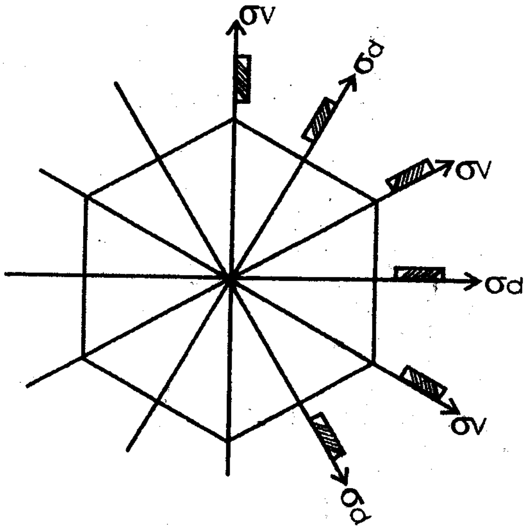
It is a square planar molecule. The plane of the molecule passing through the Nickel (II) and four cyanides is plane of symmetry. It is perpendicular to the principal axis. It is the horizontal plane σh.,

Phosphorus pentafluoride (PF_5) : **In PF_5** there are three σV each passing through the phosphorus atom and three Fluorine atoms. They are $F_1\ F_2\ F_3$ $F_1\ F_2\ F_4$ and $F_1\ F_2\ F_5$.



It is a trigonal bipyramidal molecule. The plane passing through the phosphorus and F_3 F_4F_5. is a horizontal plane σh. It is a plane of symmetry perpendicular to the principal axis.

Benzene (C_6H_6) :

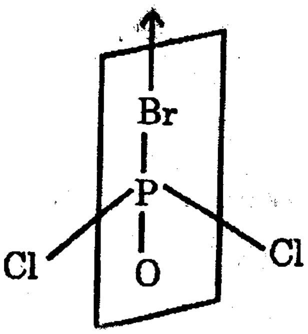


In Benzene molecule there are six σV planes each passing through C_6 and one of the C_2 axes. Three ventical planes pass through the carbon atoms on opposite corners. They are denoted as σV. The other three ventical planes pass through the centres of opposite edges. They arc denoted as σd. But they are not really dihedral planes because they are passing through the subsidary axis also.

Benzene is a hexagonal planar molecule. The molecular plane passing through the six carbon atoms is perpendicular to the C_6. axis. It is horizontal plane of symmetry *σh.*

$POBrCl_2$:

Molecules like $POBrCl_2$., have no axis of symmetry. But they have plane of symmetry. It is denoted by σ. Such molecules can not have vertical or horizontal plane of symmetry.

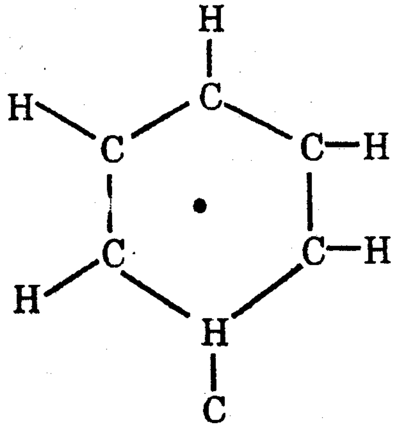


The plane containing POBr is a plane of symmetry.

4.1.4.3. CENTRE OF SYMMETRY (i) :

It is a point at the centre of the molecule through which reflection of each atom can be carried out to result in an equivalent atom. Benzene molecule has centre of symmetry.

Ex : Benzene molecule.



4.1.4.4. ALTERNATING AXIS OF SYMMETRY : (S_n) (Rotation - Reflection) :

It is an imaginary axis about which a molecule is rotated through $\frac{360^\circ}{n}$ and then reflected across a plane at right angle such that equivalent orientation is obtained.

$Sn = \sigma Cn$

Where, n = order of the improper axis.

One fold rotation - reflection (S_1) :

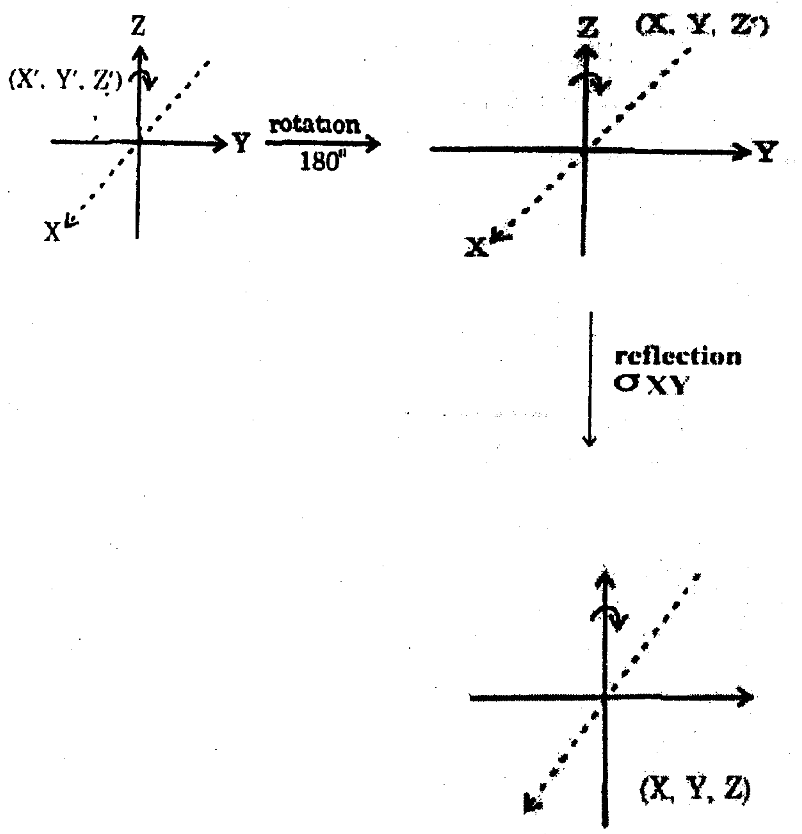
S_1 is simply a reflection

$S_1 = \sigma$

Two fold rotation - reflection (S_2) :

S_2 is equivalent to inversion at centre. It is centre of symmetry. $S_2 = i$

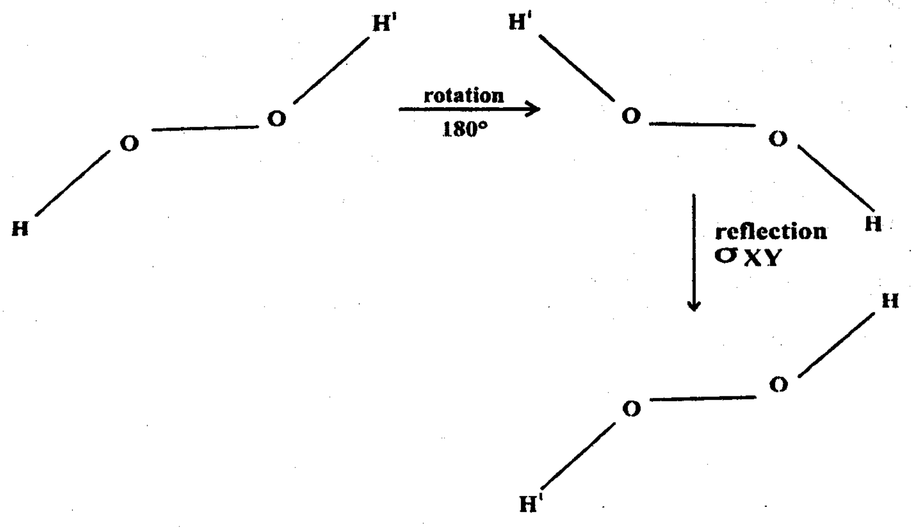
This is illustrated by the point $(X^1.Y^1.Z^1)$



If rotation takes place about Z-axis, then rotation by 180° converts $(X', Y', Z') \rightarrow (X, Y, Z')$.

Reflection in a plane perpendicular to the Z-axis takes place in XY plane. It converts $(X, Y, Z') \rightarrow (X, Y, Z)$. Thus inversion operation S_2 = Centre of symmetry (i)

Ex : Trans form of Hydrogen peroxide

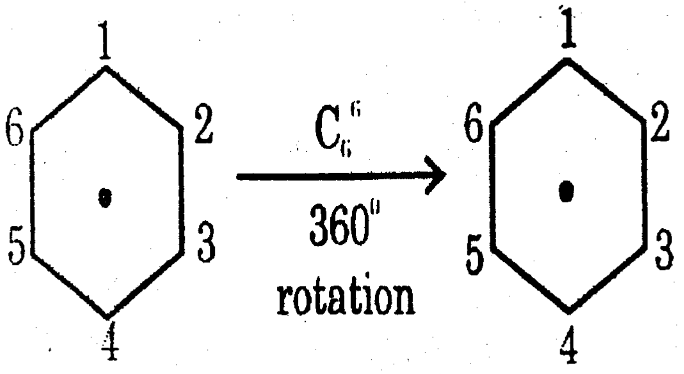


4.1.5 IDENTITY (E) :

Identity is a symmetry operation which brings back the molecule to original orientation.

It is represented by E (E = Einhert). In German Einhert means unity.

Ex : Benzene molecule.



Here $C_6^6 = C1 = E$. It is identity element. When $\theta = 360°$

$n = \frac{360}{360} = 1$. It is called C_1 axis or identity element. Every molecule has identity element E.

Importance : Identity operation means doing nothing on the molecule. Hence it does not have much consequence. But its importance lies in considering the molecule as a group and to apply group theory to molecules.

4.1.6. Model Question :

1. Write a note on Elements of Symmetry.
2. What is identity element ?
3. Explain symmetry element and symmetry operation.
4. Write symmetry elements for the following.
   a) H_2O
   b) NH_3
   c) C_6H_6
5. List the elements of symmetry for molecules and explain the corresponding symmetry operations.

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UNIT - IV

Lesson - II

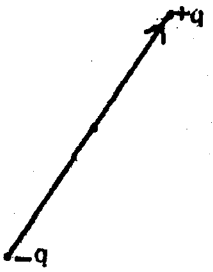
PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

4.2.1

Orientation of dipoles in an electric field, dipolemoment, induced dipolemoment, dipolemoment and structure of molecules, magnetic properties paramagnetism, diamagnetism and ferromagnetism.

4.2.2. DIPOLEMOMENT :

Dipolemoment is defined as the product of magnitude of charge and distance between the charges.



$\mu = q.\, r$

Where, μ. = dipolemoment

q = magnitude of charge

r - distance between the charges.

Units : It is a vector quantity, it is expressed in Debye units.

1 Debye = 10^{-18} esu.

Explanation : If a bond is formed between two atoms of different electronegativity values, negative charge is accumulated on a more electronegative atom and positive charge is accumulated on a more electropositive atom. Then the bond constitutes an electric dipole of equal positive and negative charge ±q, separated by a distance r. A dipole is characterized by its dipolemoment. It is a vector qr and direction is the line joining the negative to the positive charge.

If a polyatomic molecule contains two or more dipoles in different bonds, the net dipolemoment of the molecule is the resultant of vector addition of the individual bond moments.

Importance :

Dipole moments provide.

i) an insight into the geometric structure of the molecule.

ii) the extent to which a bond is polarized.

4.2.3. Orientation of dipoles in an electric field :

Molecules are made up of protons. Neutrons and electrons. When they are placed between two charged parallel plates, the electric field causes separation of positive and negative charges. Thus an electric field always induce dipoles whether the molecules contain dipoles or not in the begining. The electric field is said to polarize the dielectric.

Dielectric constant:

When dielectric is introduced between the plates of a capacitor, the capacitance is increased called dielectric constant.

$$C = \in C_o$$

Where,

C_0 = capacitance with vacuum

C = capacitance with dielectric

$\in$ = dielectric constant.

The dipolemoment perunit volume is called dielectric polarization. It is represented by *P*.

4.2.4. Induced dipolemoment :

An electric field acting on a dielectric causes polarization in two ways.

i) Induction effect

ii) Orientation effect

Thus polarization is the sum of two terms, $P = P_d + P_o . P_d$ is the orientation polarization caused by the preferential alinement of permanent dipoles in the direction of the electric field. P_0 is the induced or distortion polarization caused by the separation of positive and negative charges due to the action of electric field on the dielectric.

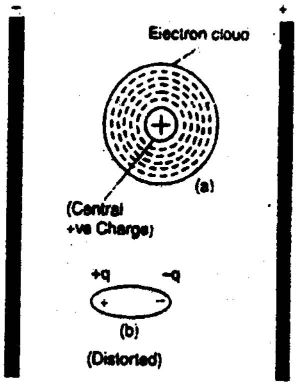


Fig. 2.1.

The polarized state of the molecule exists as Ion as it is in between the electrically charged plates. When once the charged plates are removed, the molecule gets initial state. So, it is called induced polarization.

The magnitude of induced dipolemoment is proportional to the strength of the field acting on it.

$\mu i \,\alpha\, F$

$\mu.i = \alpha\ F$

Where μi = magnitude of induced dipolemoment.

F = Field strength

α = proportionality constant called polarisability.

According to clausius and Mosotti equation .

$$Pi = \left(\frac{D-1}{D+2}\right)\frac{M}{p} = \frac{4}{3}\pi N\alpha$$

Where, Pi = induced polarization.

M = Mol. Wt.

P = density

N - Avogadro number

D = Electric distortion.

4.2.5. Dipolemoments and structure of molecules :

Dipolemoments provide two kinds of information about molecular structure.

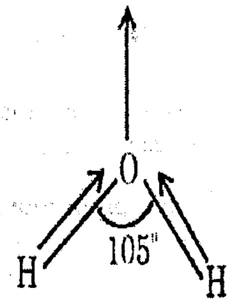
1. The extent to which a bond is permanently polarized.
2. An insight into the geometry of the molecules

Ex : 1. Carbondioxide :

$$\overleftarrow{O =}\ \overrightarrow{C = O}$$

Carbondioxide has no dipolemoment, despite the difference in electro negativity between carbo and oxygen. So, the molecule is linear. The dipolemoments due to C - 0 bonds exactly cancel each other b vector addition.

2. Water molecule :

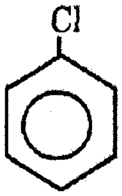


Water has dipolemoment 1.85 d. It must have a triangular structure. Each O — H bond has moment of 1.60 d. So, the bond angle must be 105° such that resultant dipolemoment is 1.85d.

3. Benzene and it's derivatives :

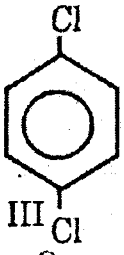
I

$\mu = 0$



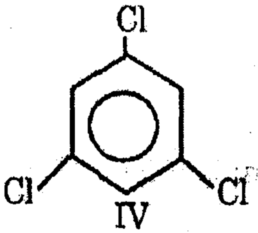
II

1.7 d



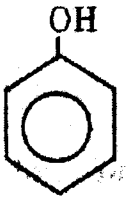
III

0



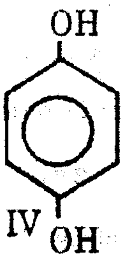
IV

0



V

1.4 d



IV

1.64 d

Benzene (I) P – dichloro bezene (III), Trichloro benzene (IV) have zero dipolemoments. So, benzene is planar and C-Cl bonds are in the plane of the ring, there by the moments due to C-Cl bonds cancel each other by vector addition.

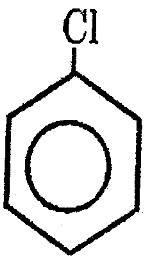
P-dihydroxy benzene (VI) has dipolemoment 1.64d. This shows that O - H bonds are not in the plane of the ring. They are directed at an angle to the ring, thus providing a net dipole moment.

4. Ethyl chloride and chlorobenzene :

$CH_3 CH_2 - Cl$

$\mu = 2.05$ d

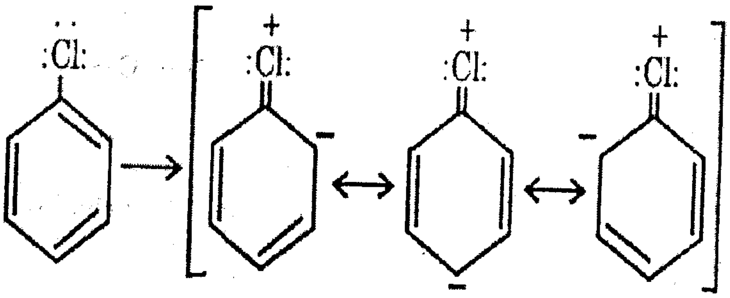
I



1.70d

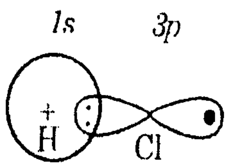
II

Chlorobenzene (II) has less dipolemoment than ethyl chloride(I). This is due to resonance in chlorobenzene which decreases negative charge on the aromatic chlorine.



5. Hydrogen chloride :

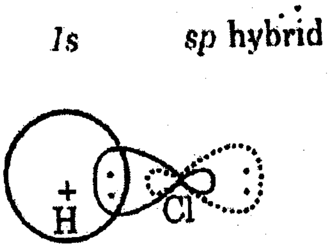
$\overset{\delta+}{H} — \overset{\delta-}{Cl}$



Internuclear distance in HCl = 1.26A°

Dipolemoment should be $\mu = 1.26 \times 4.8 = 6.05\ d$

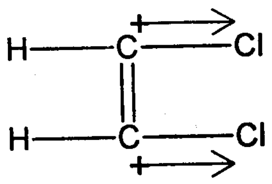
But HC1 has dipolemoment of *1.30 d* only. This shows that the pair of electrons in the non-bonding *sp* hybrid orbital are not symmetrically disposed. This makes substantial contribution in decreasing the dipolemoment. Thus HC1 was proposed the following model rejecting the older model.



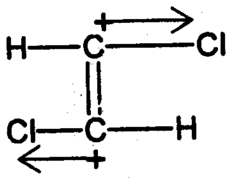
6. Differenciation of cis and trans - isomers :

This cis isomer of a symmetrical alkene has a definite dipolemoment while the trans isomer has zero dipolemoment.

Ex :1) 1,2 - dichloro ethylene.

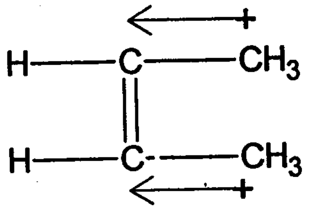


cis 1,2 - dichloro ethylene
μ = 1.9D

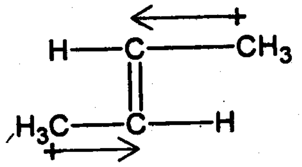


Trans 1,2 - dichloro ethylene
μ = 0D.

Ex :2) 2 -butene.



cis - 2 - butene



Trans -2 - butene μ = 0.

In symmetrical trans isomer the effect produced by one half of the molecule is cancelled by other half of the molecule.

4.2.6. Magnetic properties :

The theory for magnetic properties of molecules resemble that for electric polarization. Thus a molecule can have magnetic moment induced by magnetic field.

$$B = H + 4\pi I$$

Where, B = magnetic induction

H = field strength

I = Intensity of magnetism or magnetic moment per unit volume.

In a vacuum, $B = e^{1}H$

Where e^{1} = permeability.

Magnetic susceptibility :

Magnetic susceptibility per unit volume of the medium is given by,

$$X = \frac{I}{H}$$

Magnetic susceptibility per mole is

$$X_M = D + \frac{C}{T}$$

Where, D and C are constants.

X or X_M can be negative or positive. If X_M is negative, the medium is called diamagnetic. If X_M is positive, it is called paramagnetic.

Para magnetism :

Substances containing unpaired electrons are attracted by the magnetic field when placed in it. It is called paramagnetism.

Ex : Fe^{+2}, O_2, $K_3[Fe(CN)_6]$

It is caused by spin and orbital angular momentum of electrons. At 20°C, magnitude is positive and small. It is of the order of 10^{-6} pergram. It is dependent on temperature.

Diamagnetism :

Substances containing only pairs of electrons are repelled by the magnetic field when placed in it. It is called diamagnetism.

Ex : Zn^{+2}, H_2, KCl

It is caused by induced magnetic field or orbital electrons. At 20°C magnitude is negative and very small. It is of the order of 10^{-6} per gram. It is independent of temperature.

Ferromagnetism:

Some substances are attacted strongly by the magnetic field when placed in it.

Magnetism of substances increases millions of times when placed in a magnetic field. It is called Ferromagnetism.

They retain magnetic properties for some time even after removel of the field.

Ex : Fe, Co, Ni.

It is caused by particles arranged on lattice and electrons with parallel spin. At 20°C, magnitude is positive and very large. It is of the order of 10^{-2} per gram. There is big decline at Curie temperature.

4.2.7. Problems :

1. The bond length of H- Cl bond is 1.26A° and its dipole moment is 1.068D. Calculate percentage ionic character of the H- Cl bond (charge on the electron = $4.8 X 10^{-10}$esu).

Sol : μ (for 100% ionic bond) = ed

$= 4.8 X 10^{-10} X 1.26 X 10^{-8}$

$= 6.05 X 10^{-18}$esu.

= 6.05D

observed μ = 1.068D

$$\% \text{ ionic character} = \frac{1.068}{6.05} \times 100$$

= 17.66

4.2.8. Model Questions :

1. What is dipole moment? Explain with two examples. What are its units ?
2. How dipole moment is helpful in distinguishing.
   a) linear and non linear molecules.
   b) cis – and trans – isomers.
3. How is dipole moment useful in the determination of structures and shapes of molecules ?
4. Explain the following terms.
   a) diamagnetism
   b) Para magnetism
   c) Ferro magnetism
5. The bond length of H-I is 1.60A° and its dipole moment is 0.38D. Calculate percentage ionic character of the H- I bond.
6. Explain induced dipole moment.

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UNIT - IV

Lesson - III

MOLECULAR SPECTROSCOPY

4.3.1.

Electromagnetic radiation – different regions, Wave Length, Wave Number, Frequency and Energy. Interaction with molecules and types of molecular spectra. Concept of potential energy curves for bonding and antibonding molecular orbitals. Qualitative description of S,P and n M.O., their energy levels and respective transitions. Ultraviolet visible absorption spectroscopy – presentation and analysis of spectra, types of electronic transitions, effect of conjugation. concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts, examples.

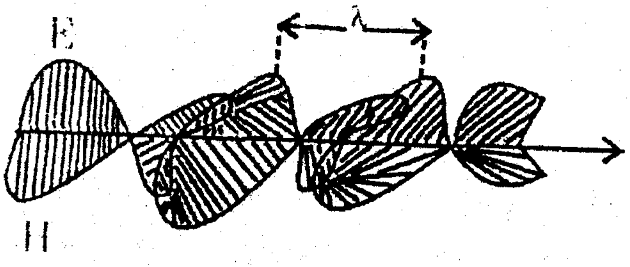
Infrared absorption spectroscopy – energy levels of simple harmonic oscillator, molecular vibrations, Hooke's law, intensity, determination of force constant and qualitative relation of force constant, bond energies, effect of an harmonic motion and isotope on the spectrum, modes of vibrations in polyatomic molecules, intensity and position of IR bands. Instrumentation characteristic absorption bands of various functional groups – interpretation of spectra of simple organic molecules.

4.3.2. Electro Magnetic Radiation :

The important characteristics of Electromagnetic radiations are

1. Electro magnetic radiations are produced by the Oscillation of electric charge and magnetic field residing on the atom.

2. These radiations are associated with electric and magnetic components which are mutually perpendicular and are coplanar.



Vertical component 'E' indicates change in strength of the electric filed.

Horizontal component 'H' indicates change in the strength of magnetic filed.

3. These radiations are characterized by their wave lengths or frequencies or wave numbers.
4. The energy carried by an electro magnetic radiation is directly proportional to it's frequency.
5. The emission or absorption of radiation is quantised.
6. Each quantum of radiation is called photon.

7. All types of radiations travel with the same velocity.
8. No medium is required for their propagation. They can travel through vacuum.
9. A group of electromagnetic radiations can be split up into various components for analysis.

Ex: When visible light is passed through the prism, it is split up into seven colours each with definite wave length.

4.3.3. Different Regions :

Electromagnetic spectrum covers entire range of Electromagnetic radiations from Cosmic rays at one end to radio waves at the other end. Different regions of the electromagnetic spectrum are identified by different names based on the range of their wave lengths or frequencies.

Cosmic rays	Gamma Rays	X - rays	Ultra violet	Visible	Infrared	Micro wave	Radio Waves
10^{20}	10^{18}	10^{17}	10^{16}	10^{14}	10^{13}	10^{12}	10^{10}

Frequency cycles / sec.

The major characteristics of various spectral regions are :

1. γ - ray region : It consists of cosmic rays and γ-rays. This region lies between 0.1 to 1A°. 1A° = 10^{-10} m

The γ - rays are shortest waves emitted by atomic nuclei.

2. X - ray region : This region lies between 1 to 10 A^0. X - rays are emitted by the transitions involving inner electrons of an atom or a molecule.

3. Visible and U.V. region : U.V region lies between 200 to 400 nm. Visible region lies between 400 - 800 nm.

1 nanometer (nm) - 10^{-9} meter.

The vacuum U.V region lies between 1 - 180 nm.

In U.V region electromagnetic spectrum is associated with the energy charges due to electronic transitions.

Infrared region : I.R. region lies between 0.7 - 200 μ

1 micron (μ) = 10^{-6} meter.

This region is further divided into sub regions.

Near Infrared 7—25 μ

Infrared 2.5 - 15 μ

Far Infrared 15-200 μ

In I.R. region electromagnetic spectrum is associated with the energy charges due to molecular vibrations.

Micro wave region :

This region lies between 0.1 mm to lcm wave length. This region corresponds to the energy changes due to rotation of the molecules.

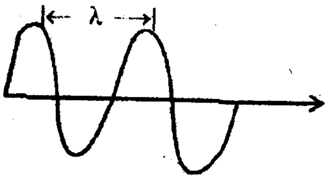
Radio waves :

This region lies between 1 to 10 cm wave length. The region corresponds to the energy changes due to reversal spin of nucleus or electrons.

4.3.4. Wave length (λ) :

Wave length is the distance between two adjacent crests or troughs in a particular wave. It is denoted by the letter λ (lamda). It can be expressed in Angastrom units (A°) or in millimicrons (mμ)

1A° = 10^{-8}cm; 1mμ = 10^{-7} cm



wave motion

Visible light region lies between 3800 - 760OA° wave length. Different colours of light have different wave lengths.

Wave number ($\bar{v}$) :

Wave number is the reciprocal of wave lengths expressed in centimeters. It is the total number of waves which can pass through a space of one cm. It is denoted by $\bar{v}$. It is frequently used in infrared technique. Units are cm^{-1}.

$\bar{v} = \frac{1}{\lambda}$ Where λ = Wave length in cm.

Frequency (v)

Frequency is defined as number of waves which can pass through a point in one second. It is expressed as v (nu). Units are cycles per second or Hertz (Hz).

Frequency $v = \frac{C}{\lambda}$ Where $C = 3 \times 10^{10}$ cm/sec.

As wave length increases frequency decreases.

Problem 1 : Calculate frequency and wave number range of visible light.

Ans : We know wavelength range of visible light is 3800°-7600A°.

Frequency $v = \frac{C}{\lambda}$

Where $\lambda = 3800\ A^0 = 3800 \times 10^{-8}$cm

C - 2.998×10^{10}cm/sec.

$$v = \frac{2.998\times10^{10}}{3800\times10^{-8}} = 7.88\text{x}10^{14}\ \text{Hz}$$

When, $\lambda = 7600A° = 7600 \times 10^{-8}$ cm

$$V = \frac{2.998\times10^{10}}{7600\times10^{-8}} = 3.94 \times 10^{14}\ \text{Hz}$$

∴ Frequency range of visible light is 7.88×10^{14} cycles/sec to 3.94×10^{14} cycles/sec.

Wave number $\bar{v} = \frac{1}{\lambda}$

Where, $\lambda = 3800A° = 3800 X 10^{-8}cm$

$$\bar{v} = \frac{1}{3800\times10^{-8}} = 2.63 \times 10^4\ \text{cm}^{-1}$$

When $\lambda = 7600A° = 7600 X 10^{-8}cm$

$$\bar{v} = \frac{1}{7600\times10^{-8}} = 1.315 \times 10^4\text{cm}^{-1}$$

Wave number range of visible light is 2.63×10^4 cm^{-1} to 1.315×10^4cm^{-1}

Energy (E) :

Energy of a wave of particular radiation is given by,

$$E = hv = h.\frac{C}{\lambda}\ \text{ergs.}$$

Where h = plancks constant = 6.626×10^{27} erg. sec.

C = 2.998×10^{10} cm sec^{1}.

X = Wave length in cm.

Problem 2 : Calculate the energy associated with a radiation having wave length 3800A°.

Ans : λ =3800A° = 3800 x 10^{-8} cm.

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-27} \times 2.998 \times 10^{10}}{3800 \times 10^{-8}} = 5.227 \times 10^{-12} \text{ ergs}$$

4.3.5. INTERACTION WITH MOLECULES :

Atomic Spectroscopy :

It is connected with interaction of electromagnetic radiations with atoms. Atoms are usually in their lowest energy state known as ground state. Here transition of electrons occur from one electronic energy evel to another,

olecular Spectroscopy :

It is connected with interaction of electromagnetic radiations with molecules. Here transitions occur etween rotational and vibrational energy levels also along with electronic transitions.

Molecular spectra extend from visible to micro wave region. It provides information about molecular brations and rotations which is useful to know molecular structure.

It is possible to get lot of information about molecular structure from atomic and molecular spectra.

nteraction of Radiant energy and Matter :

There are number of interactions between radiation and Matter. Specific instruments were developed o measure each interactive property. The properties that are most prominent in instrumental analysis are

1. Absorption and transmission.
2. Emission and fluorescence.

4.3.6. Types of molecular spectra :

There are two types of spectra.

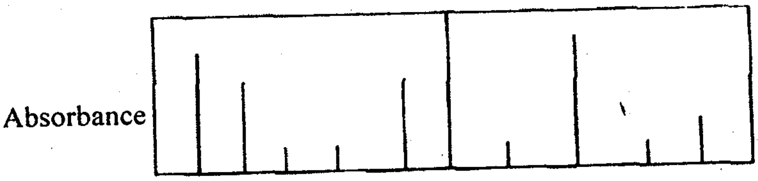
1. Absorption spectrum
2. Emission spectrum

Absorption spectrum :

The spectrum with dark lines against a white background is called absorption spectrum. Electrons absorb energy when light is passed through the molecules and then examined. It is obtained in the ground state. Absorption spectrum is obtained when electrons jump from lower to higher orbits.

Absorption line spectrum :

Due to limited number of permissible atomic energy levels, atoms can absorb only a few selected frequencies. The plot of absorbance vs. wave length is a line absorption spectrum.



Wavelength nm
line spectrum

Line spectrum :

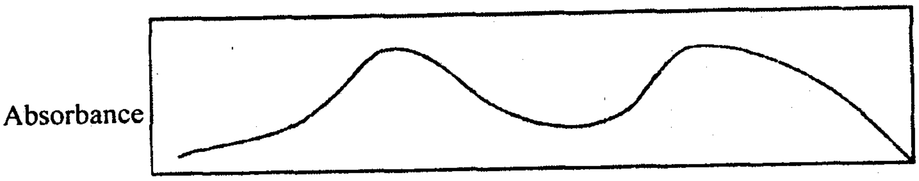
This type of spectrum is useful for atomic analysis in atomic absorption and X - ray absorption.

Absorption band spectrum :

The number of possible energy transitions in molecules is much greater than in atoms. In addition, energy is needed for vibrations of atoms with in the molecule and molecular rotations. Thus the total energy is

$$E_{total} = E_{elec.} + E_{vib} + E_{rot.}$$

The polot of absorbance Vs. wavelength is a band absorption spectrum.



Wave length nm.
Band spectrum

Emission spectrum :

The spectrum with bright lines against dark background is called emission spectrum. It is obtained in the excited state. Electrons emit energy when jump from higher orbits to lower orbits.

Emission line spectrum :

The spectrum with bright lines separated by dark spaces is emission line spectrum. It is the characteristic of all atoms. It is used as qualitative and quantitative in flame photometry and X- ray spectroscopy.

Emission band spectrum :

The spectrum with groups of lines packed together appearing as bands is emission band spectrum. It is the characteristic of all molecules.

The energies of various transitions to the ground state can not be separated. This principle is used in molecular fluorescence and phosphorescence.

4.3.7. Bonding and anti bonding molecular orbitals :

According to linear combination of atomic orbitals, atomic orbitals of the two atoms combine forming two molecular orbitals. They are

1. Bonding molecular orbital .
2. Anti bonding molecular orbital.

Bonding molecular orbital :

The molecular orbital which has lower energy than the combining atomic orbitals is called bonding molecular orbital.It gives rise to attractive state.

Anti bonding molecular orbital :

The molecular orbital which has higher energy than the combining atomic orbitals is called anti bonding molecular orbital. It gives rise to repulsive state.

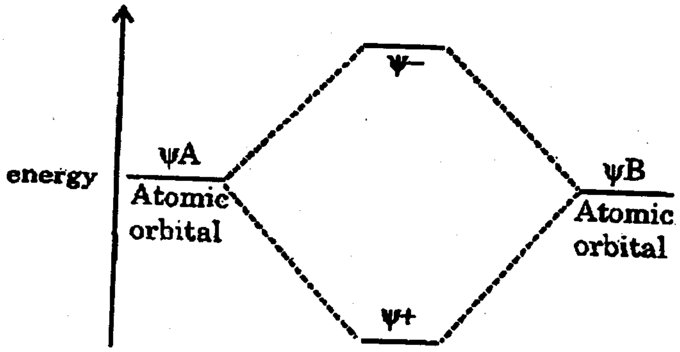
Let. the wave functions of the two atoms A and B be ψA and ψB. Then,

$\psi + = \psi A + \psi B$ (Bonding)

$\psi - = \psi A - \psi B$ (Anti bonding)

The relative energies of molecular orbitals and their constituent atomic orbitals are illustrated in the following diagram.

Anti bonding molecular orbital



Bonding molecular orbital

A detailed examination of the energy associated with the function ψ^{-} shows that effective combination of ψA and ψB occurs when

i) They represent similar states of energy.

ii) They have same symmetry w.r.t molecular axis A — B

If these conditions are not satisfied, then the wave functions contribute little to the linear combination. So. ψ - represents a state of high energy called anti bonding orbital.

In molecules electrons occupy both bonding and anti bonding molecular orbitals. The presence of an electron in an anti bonding molecular orbital introduces a factor opposing the formation of a stable molecule.

4.3.8. Ultra Violet - Visible absorption spectroscopy :

Ultra violet spectroscopy involves the measurement of absorption of radiations by the substance in the U.V and visible regions.

Range : Ultra violet 10 - 400 nm Visible 400 - 800 nm

Near or Quartz U.V. region 200 - 400 nm Far U.V region 10 - 200 nm

The common U.V spectrometer record the spectra over the range of 200 - 800 nm . The far U.V region below 200nm was not much studied due to absorption by air.

Units :

The U.V spectra is recorded on wave length scale in Nanometers (nm). An old word for Nanometer is Millimicron (m μ)

1 nm = 1 m μ = 10A°.

Presentation of spectra :

The spectrum of the compound is presented in the form of a continuous graph by plotting Absorption of electro magnetic radiations vs. wave length over a particular range.

The absorption of light by the molecule is governed by the following laws.

Beer's Law :

When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

Mathematically, $-\frac{dI}{dx} = KI$

Where, I = Intensity of radiation ofter passing through thickness x of the medium

$-\frac{dI}{dx}$ = rate of decrease of intensity of radiation.

K = Proportionality constant depending on the nature of the absorbing medium.

Beer's law :

When a beam of monochromatic radiation is passed through a homogeneous absorbing medium the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as concentration of the solution.

Mathematically, $-\frac{dI}{dx} = K^{1} IC$

Where, C = Concentration of the solution in moles litre^{-1}.

K^1 = Molar absorption coefficient

I = Intensity of radiation after passing through a thickness x of the medium.

$-\frac{dI}{dx}$ = rate of decrease of Intensity.

From these laws the **Lambert - Beer's law** is formulated, Mathematically, $A = log\frac{I_0}{I} = \epsilon cl$

Where, A = Absorbance = $log\frac{I_0}{I}$ (I_0= intensity of incident light I = Intensity of transmitted light)

C = Concentration in moles, litre^{-1} of the absorbing compound.

l = length in cm of sample tube.

ϵ = Mollar extinction coefficient.

The Lambert'- Beer's law gives relationship between the-amount of light absorbed and concentration of the solution, length of the solution through which light passes.

The wave length at which a molecule has its highest absorption coefficient (ϵ_{max}) is designated as λ_{max}

A spectrum may have several different maxima each with its characteristic value of λ_{max}

4.3.9. Principle of U.V. spectroscopy : (Types of electronic transitions).

Principle :

The U.V and visible radiations are more energetic than I.R. radiations. They promote valency electrons from lower energy level to higher energy level. The electrons to be promoted are

1. σ electron, an electron forming a bond.
2. π electron, an electron forming a bond.
3. n electron, an electron of unshared pair of electrons.

According to molecular orbital theory, when a molecule is excited by absorbing U.V or Visible light, the electrons are promoted from a bonding to an anti bonding orbital.

Types of electronic transitions :

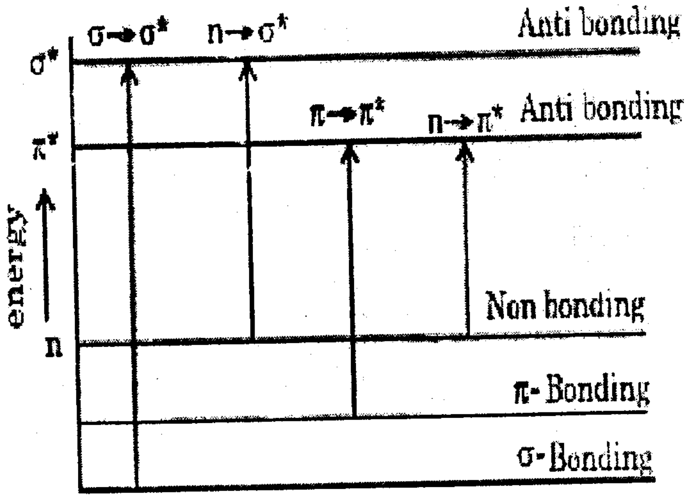
1. $\sigma \rightarrow \sigma^*$ Transition : The anti bonding orbital which is associated with the excitation of σ electron is called anti bonding sigma orbital (σ^*)

σ to σ^* transition takes place when σ electron is promoted to anti bonding sigma orbital (σ^*). It is represented as $\sigma \rightarrow \sigma^*$ transition.

2. n $\rightarrow \sigma^*$ Transition : n to σ^* transition takes place when a non bonding electron (n) is promoted to anti bonding sigma orbital (σ^*). It is represented as n $\rightarrow \sigma^*$ transition.

3. $\pi \rightarrow \pi^*$ Transition : The anti bonding orbital which is associated with the excitation of π electron is called anti bonding pi orbital (π^*). π to π^* transition takes place when π electron is promoted to anti bonding pi orbital (π^*). It is represented as $\pi \rightarrow \pi^*$ transition.

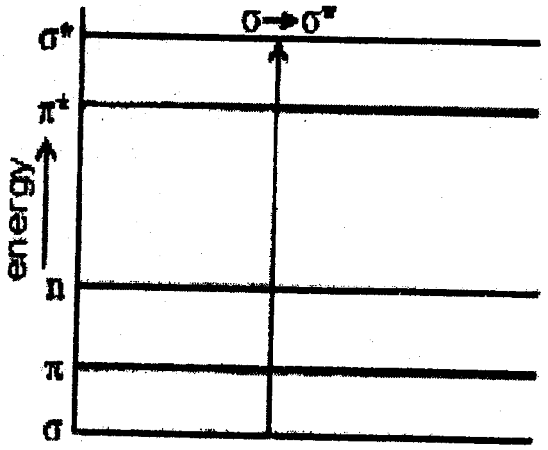
4. n $\rightarrow \pi^*$ Transition : **n** to n^* transition takes place when an electron of unshared pair of electrons (n) is promoted to anti bonding pi orbital (π^*). It is represented as n $\rightarrow \pi^*$ transition.



Electronic excitations

Various transitions involved in U.V. spectroscopy :

1. $\sigma \rightarrow \sigma^*$ **Transition** : σ bonds are very strong. So $\sigma \rightarrow \sigma^*$ transition is a high energy process. These transitions do not show absorption in the normal U.V region of 400 — 180 mμ .



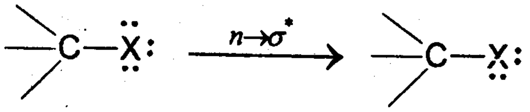
C - C
$\sigma \longrightarrow \sigma^*$transition ion

Saturated hydrocarbons

Ex : For Methane, Ethane, Propane etc., absorption occurs near 150 mμ. The region below 200 mμ is vacuum U.V region. In this region oxygen present in the air also absorbs. So, the entire path must be evacuated. This region is less informative.

2. n $\rightarrow \sigma^*$ transitions : n $\rightarrow \sigma^*$ transitions show absorption from 165 - 175 mu.

Ex : Saturated halides, alcohols, ethers, aldehydes, ketones, amines etc.

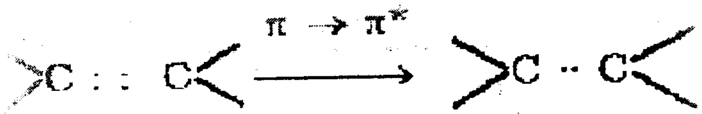


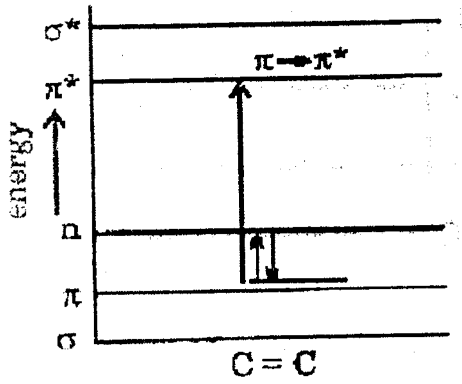
Water – 167 mμ
Methyl alcohol – 167 mμ

n $\rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding. Hydrogen bonding shifts U.V absorptions to shorter - wave lengths.

3. $\pi \rightarrow \pi^*$ Transition : π - bonds are weak. So $\pi \rightarrow \pi^*$ transition occurs at longer wave length. They show absorption from 170 - 190 mμ. They are also high energy transitions.

Ex : Compounds containing double or triple bonds, Aromatic compounds. Alkenes. Alkynes, Carbonyl compounds. Cyanides. Azo compounds etc.

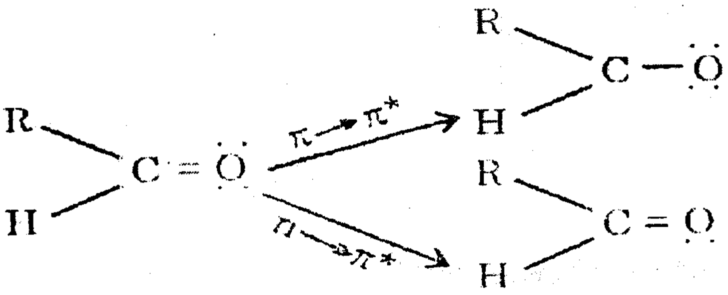




π ---> π * transition in alkenes

4. n → π * transitions : n → π * transitions require least amount of energy.

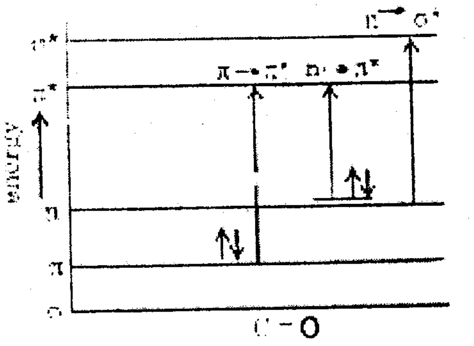
Ex : Saturated aldehydes show absorptions at 290 mμ, due to n → π * transition.



$n \rightarrow \sigma^*$160 nm

$\pi \rightarrow \pi^*$180 mμ

$n \rightarrow \pi^*$290 mμ



Transitions in Carbonyl compounds

Allowed transitions :

The transitions with extinction coefficient ($\in_{max}$) more than 10^4 are usually called allowed transitions.

Ex : Butadiene λ_{max} 217 $\in_{max}$ 21000. It is allowed transition.

Forbidden transition :

The transitions with extinction coefficient ($\in_{max}$) below 10^4 are called forbidden transitions.

Ex : Benzophenone λ_{max} 252 $\in_{max}$ 20,000 (allowed) λ_{max} 352 $\in_{max}$ 180 (Forbidden)

To decide whether the transition is allowed or forbidden for a molecule, it is important to consider,

1) The geometry of molecular orbital in the ground state.
2) The geometry of molecular orbital in the excited state.
3) The orientation of electronic dipole of the incident light.

4.3.10. Chromophore concept :

Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or visible region.

They are two types.

1. Chromophores in which the group contains *n* electrons. They undergo $\pi \rightarrow \pi^*$ transitions.

Ex : Ethylenes ($>C=C<$), Acetylenes ($-C\equiv C-$)

2. Chromophores in which the group contains both π electrons and n - electrons (non bonding). They undergo $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

Ex : Carbonyls ($>C=O$), Nitriles ($-C\equiv N$), Nitro compounds ($-NO_2$), Azocompounds ($-N=N-$).

Auxochromes : An Auxochrome is defined as any group which does not itself acts as a chromophore but whose presence brings an absorption shift towards longer wave length {towards red end):

Ex : $-OH$, $-OR$, $-NH_2$, $-SH$.

Explanation :

The absorption shift towards longer wave length is due to the combination of Chromophore and Auxochrome to give raise to another chromophore. The Auxochrome group is called colour enhancing group. The effect of Auxochrome depends on its ability to extend conjugation of a chromophore by sharing the non -bonding electrons.

Benzene λ_{max} 255 mμ $\in_{max}$ 203

Aniline λ_{max} 280mμ $\in_{max}$ 1430.

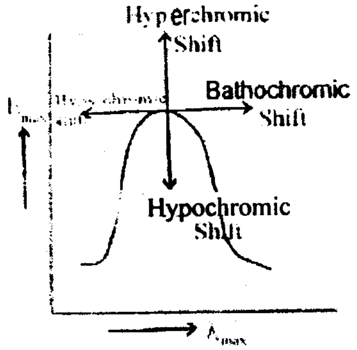
In Aniline Amino ($-NH_2$) group is an Auxochrome.Hence absorption shift is towards longer wave length.

4.3.11. Absorption and Intensity shifts :

Bathochromic effect : (Red shift) :

The effect in which absorption maximum is shifted towards longer wave length is called Bathochromic shift. It is also called Red shift because the shift is towards red end of the spectrum.

Ex : The n $\rightarrow \pi$ * transition of carbonyl group experiences bathochromic shift when polarity of the solvent is decreased.



Absorption and Intensity shifts

Hypochromic effect : (Blue shift) :

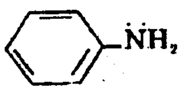
The effect in which absorption maximum is shifted towards shorter wave length is called Hypsochromic shift. It is also called Blue shift because the shift is towards the blue end of the spectrum.

Ex : Aniline λ_{max} 280 mμ

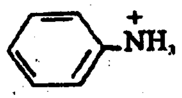
Aniline (in acid solution) λ_{max} 203 mμ

Explanation :

In Aniline the electron pair on Nitrogen atom are in conjugation with π - bonds of Benzene ring. In acid solution the electron pair on Nitrogen atom is no longer present and hence conjugation is removed. Removal of conjugation is responsible for Blue shift.



Aniline



Aniline in acid solution

Hyperchromic effect :

The effect in which the intensity of absorption maximum increases is called Hyperchromic effect.

Here extinction coefficient E_{max} increases .

Ex : B - band for pyridine λ_{max} 25.7mμ $\in_{max}$2750.

B - band for 2 - methyl pyridine λ_{max} 26.2 mμ $\in_{max}$3560

Explanation :

The introduction of Auxochrome usually increases intensity of absorption. The methyl group in 2-methyl pyridine is responsible for Hyperchromic shift.

Hypochromic effect :

The effect in which the intensity of absorption maximum decreases is called Hypochromic effect. Here extinction coefficient $\in_{max}$decreases.

Ex : Biphenvl λ_{max} 250mμ $\in_{max}$19000.

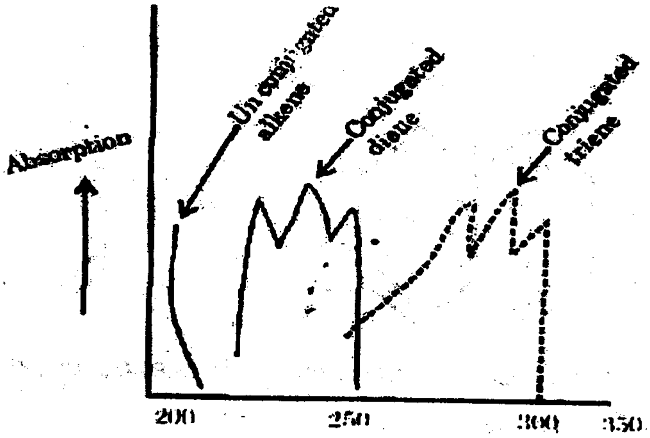
2-Methyl Biphenyl λ_{max} 237mμ $\in_{max}$10250.

Explanation :

The introduction of a group which causes distortion in geometry of the molecule leads to Hypochromic shift. Here distortion in geometry caused by Methyl group in 2-Methyl Biphenyl is responsible for Hypochromic effect.

4.3.12. Effect of conjugation : (Wood ward Fieser rules) :

As conjugation increases, wave length of the absorption maximum (λ_{max}) and also intensity of absorption ($\in_{max}$) increases.



Absorption in conjugated and un - conjugated systems:

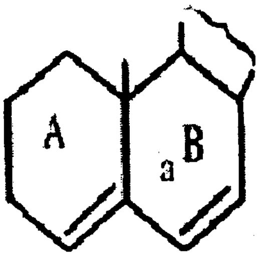
The conjugated polyene system appears coloured to the naked eye if there are more than five double bonds in conjugation.

This is because absorption occurs in visible region above 400 mμ. The actual rules for predicting absorption maximum (λ_{max}) were first made by wood ward and later modified by Fieser and Scott.

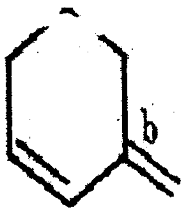
Rules for diene and triene absorption :

Value assigned to Parent - Hetero annular or open chain diene	217 nm
Value assigned to parent Homo annular diene	253 nm
Increment for	
a) Each alkyl substituent or ring residue	5 nm
b) The exocyclic nature of any double bond	5 nm
c) a double bond extension	30 nm
d) Auxochrome - O Acyl	0 nm
-O Alkyl	6 nm
- S Alkyl	30 nm
-Cl, -Br	5 nm
-N Alkyl	60 nm
λ_{max} Total	

Ex : 1



'a' is endocyclic double bond.



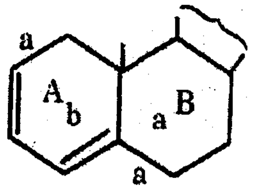
'b' is exocyclic double bond.

Hetero annular diene

(The two = bonds are indifferent rings, parent value	217 nm
Three ring residues (marked a) 3 x 5	15 nm
One exocyclic double bond (marked b, exocyclic t ring B)	5nm
λ_{max} **Total**	**236 nm**

Observed value is λ_{max} 235 nm (ϵ_{max} 19,000)

2.



(Homo annular diene)

(The two double bonds are in the same ring).

Parent value	253 nm
Three ring residues (marked a) 3 x 5	15 nm
One exocyclic double bond (marked b, exocyclic to ring B)	5 nm
λ_{max} **Total**	**273 nm**

Observed value is λ_{max} 275nm

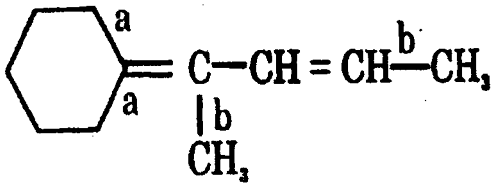
3. Calculate λ_{max} for 2,4 - Hexadiene :

$CH_2 - CH = CH - CH = CH - CH_2$

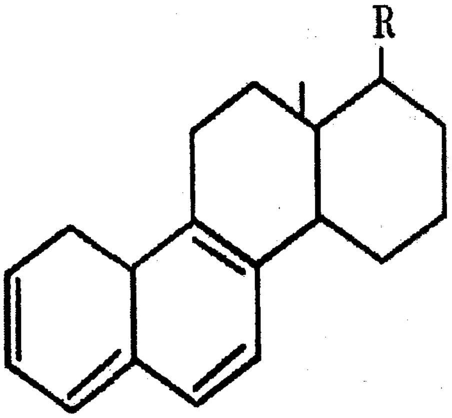
It is open chain diene.

Basic value	217 nm
Two alkyl substituents (2 x 5)	10 nm
Calculated value λ_{max}	227 nm
Observed value λ_{max}	227 nm

4. Calculate Absorption maximum in U.V. spectrum of



It is open chain diene	
Basic value	217 nm
Two alkyl substituents (marked b) 2 x 5	10 nm
Two ring residues (marked a) 2x5	10 nm
One exocyclic double bond	5 nm
Calculated value λ_{max}	242 nm
observed value λ_{max}	242nm



It is a Homodiene system.	
Basic value	253 nm
two - bonds extending conjugation 2 x 30	60 nm
Five ring residues 5x5	25 nm
One exocyclic double bond	5 nm
Calculated λ_{max}	343 nm
Observed λ_{max} 345 nm	

6. **Cyclohexadiene :**

It is Homodiene system.

Basic value	253 nm
Two ring residues 2 x 5	10 nm
Calculated λ_{max}	263 nm

Observed λ_{max} 238.5 nm ϵ_{max} 3400.

The cause for blue shift is distortion in chromophore system. The molecule no longer remains planar.

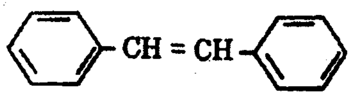
7. Acetaldehyde has U.V absorption at 160, 180, 290 nm. Which type of absorption is responsible for each of these?

Ans : 160 nm - This peak is due to $\pi \rightarrow \pi^*$ transition.

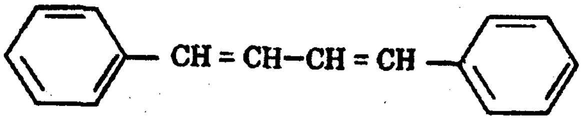
180 nm - This peak is due to $n \rightarrow \pi^*$ transition.

290 nm - This peak is due to $n \rightarrow \sigma^*$ transition.

8. Which of the following will have greater λ_{max} ?



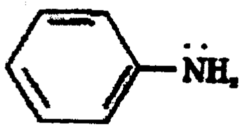
I



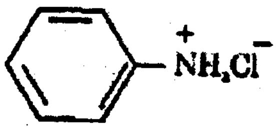
(II)

Structure II will have greater λ_{max}, because as conjugation increases λ_{max}, value increases.

h)



III



IV

In structure III lone pair of electrons are available for conjugation. In structure IV no such pair of electrons are available for conjugation with the ring. So, structure IV will have greater λ_{max}

9. Which of the following compounds absorbs U.V radiation. Heptane, Benzene, Butadiene, Heptene, Acetone, Ethylene, Nitrobenzene, Benzoic acid

Compound	Absorption	Reason
1. Heptane	No	$\sigma \rightarrow \sigma^*$ transition needs high energy.
2. Benzene	Yes	$\pi \rightarrow \pi^*$ transition
3. Butadiene	Yes	$\pi \rightarrow \pi^*$ transition
4. Heptene	Yes	$\pi \rightarrow \pi^*$ transition
5. Acetone	Yes	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions
6. Ethylene	Yes	$\pi \rightarrow \pi^*$ transition
7. Nitrobenzene	Yes	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.
8. Benzoic acid	Yes	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Infrared absorption spectroscopy :

This is the most important type of spectroscopic method used for elucidating the structure of organic compounds

Range :		
	Near IR	12500 - 4000 cm^{-1}
	Proper IR	4000 - 667 cm^{-1}
	Far IR	667 - 50 cm^{-1}

Most of the I.R spectrometers have a range of 5000 - 580 cm^{-1}. I.R. spectra are visually described in terms of frequencies of Radiations absorbed (v).

Units : The **I.R.** spectra is recorded on wave number scale in inverse centimeters (cm^{-1}). Wave number is defined as the number of vibrations of radiations per centimeter (cm^{-1}).

Wave number $\bar{V} = \frac{1}{\lambda}$

Where λ is in microns (μ),

$$\bar{V} = \frac{10^4}{\lambda} cm^{-1} \qquad (\because 1\,\mu = 10^{-4}\,cm)$$

4.3.13. Principle of I.R. Spectroscopy :

Molecular vibrations :

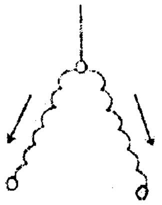
Due to lower amounts of energy associated with I.R. radiations, they cann't cause electronic transitions. They cause molecular vibrational and rotational changes.

In the I.R. Spectroscopy the absorbed energy (2.5 - 15 μ) brings predominant changes in vibrational energy There are two kinds of fundamental vibrations.

1. Stretching vibrations. 2. Bending vibrations.

1. Stretching vibrations :

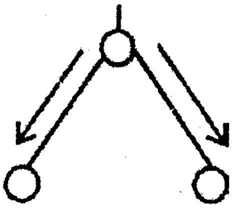
In stretching vibrations, the distance between two atoms increase or decrease but the atoms remain in the same bond axis



Stretching vibrations

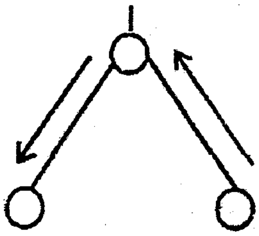
There are two types of stretching vibrations.
a) Symmetric stretching
b) Asymmetric stretching

a) Symmetric stretching : In these vibrations, the movement of atoms with respect to a particular atom is in the same direction.



Symmetric stretching

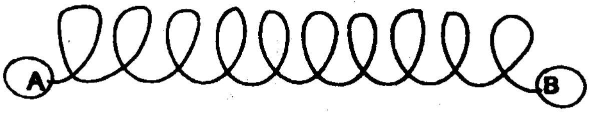
b) Asymmetric stretching : In these vibrations, one atom approaches the central atom while the other atom departs from it.



Asymmetric stretching

2. Bending vibrations :

In bending vibrations the positions of the atoms change with respect to the original bond axis.

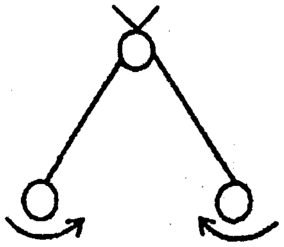


Bending vibrations

There are four types of Bending vibrations or deformations.

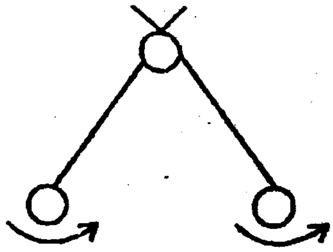
1. Scissoring. 2. Rocking
3. Wagging 4. Twisting.

1. Scissoring : In these vibrations the two atoms approach each other.



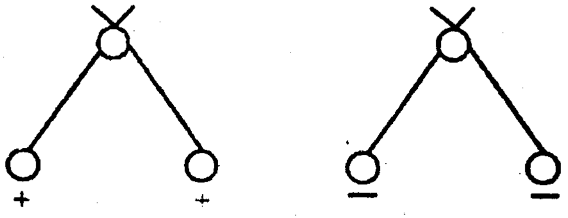
Scissoring

2. Rocking : In these vibrations the movement of the twoatoms is in the same direction.



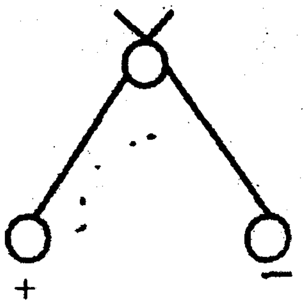
Rocking

3. Wagging : In these vibrations the two atoms move either up or down with respect to the central atom.



Wagging

4, Twisting : In these vibrations one of the two atoms move up while the other atom move down with respect to the central-atom.



Twisting

Bending vibrations require lower energy and occur at lower wave numbers than stretching vibrations.

4.3.14. Hook's Law : (Determination of force constant)

The value of stretching vibrational frequency of a bond is calculated by application of Hook's law.

Hook's law can be represented as

$$\bar{V} = \frac{\nu}{c} = \frac{1}{2\pi c}\left[\frac{K}{\frac{m_1 m_2}{m_1 + m_2}}\right]^{\frac{1}{2}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Where, μ = reduced mass

m_1 and m_2 = masses of the atoms concerned in gms.

K = force constant

C = Velocity of radiation = 2.998×10^{10} cm/sec

v =frequency

$\bar{V}$ = wave number

∴ The vibrational frequency or wave number depends on

i) Bond strength. ii) Reduced mass.

4.3.15. Force constant (K) :

In harmonic motion force constant is defined as the restoring force per unit displacement. Force constant is regarded as stiffness of the bond. For a single bond it is approximately 5×10^5 dynes/ cm. It's value becomes double for a double bond and triple for a triple bond. Thus it is related to the strength of the bond.

Ex :

Compound	**Force constant dynes/cm**	**Type of vibration**	**Bond order**	**Region in cm^{-1}**
Alkanes	5×10^5	C - C	Str. 1.	1300 - 800
Alkenes	10×10^5	C = C	Str. 2	1650 - 1600
Alkynes	15×10^5	C = C	Str. 3	300 - 2100

Ex : C = C stretching absorpts at higher frequency than C — C stretching.

This is due to higher bond strength in higher value of K of the double bond compared to single bond. As K value increases, bond strength increases. It absorbs at higher frequency.

Reduced mass : O - H stretching absorbs at higher frequency than C - C stretching.

Compound	Type of vibration	Region cm^{-1}
Alkanes	C - C Str	1300 - 800
Alcohols	O - H Str	3600 - 3650.

This is due to smaller value of reduced mass for O - H bond compared to C - C bond. It absorbs at higher frequency as reduced mass decreases.

4.3.16. Energy levels of simple harmonic Oscillator :

The Infrared spectrum of a molecule results due to the transitions between two different vibrational energy levels. The vibrational motion resembles the motion observed for a ball attached to a spring that is simple harmonic oscillator. A chemical bond can be visualized as two balls attached to a spring. But the difference is that only certain vibrational energy levels are allowed in molecules. The vibrational energy of a chemical bond is quantised.

$$E_{vib} = \left(V + \frac{1}{2}\right)hv$$

Where, V = Number of vibrational level (0,1,2,3 ....)

h = Planck's constant

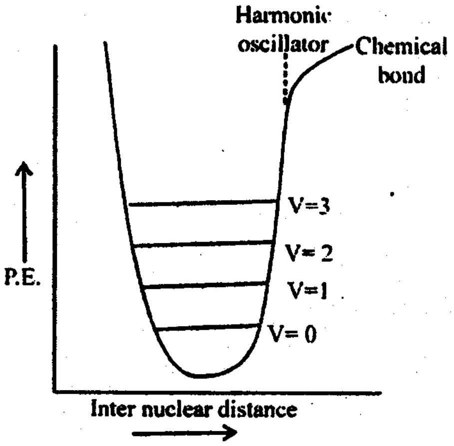
v = Vibrational frequency.

We know, $v = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

The energy difference between the two vibrational energy levels is

$\Delta E_{vib} = hv$

At ordinary temperature, the molecules are in their lowest vibrational energy levels. The potential energy diagram is approximately that of a simple harmonic oscillator.



The allowed vibrational energy levels for a diatomic molecule undergoing simple harmonic motion.

4.3.17. Selection rules : (Fundamental vibrations)

It was found that the energy for a transition from energy level 1 to 2 or 2 to 3 is same and identical to that from 0 to 1.

Transitions from ground state V = O to the first excited state V = 1 absorb strongly and gives intense bands called Fundamental bands.

$\Delta E_{vib} = E_{vib}(V = 1) - E_{vib}(V=2)$

$= \left(1+\frac{1}{2}\right)hv - \left(0+\frac{1}{2}\right)hv = hv$ $\left[\because E_{vib} = \left(v+\frac{1}{2}\right)hv\right]$

This gives frequency of a Fundamental band.

Transitions from 0 to 2 gives rise to weak bands called overtones. The first over tone is given by

$\Delta E_{vib} = E_{vib}(V = 2) - E_{vib}(E = 0)$

$\left(2+\frac{1}{2}\right)hv - \left(0+\frac{1}{2}\right)hv = 2hv$

Polyatomic molecules exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degrees of freedom in a molecule. Each atom has three degrees of freedom corresponding to the three Cartesian Co-ordinates (x,y,z). A molecule which is of finite dimensions will be made up of rotational, vibrational and translational degrees of freedom. So, the molecule containing 'n' number of atoms has 3n degrees of freedom. It is equal to Translational + Rotational + Vibrational degrees of freedom.

Since only three Co-ordinates are necessary to locate a molecule in space, a molecule has always three translational degrees of freedom.

Linear molecules : For linear molecule there are only two degrees of rotation. So, for linear molecule containing *n* atoms.

Total degrees of freedom = 3n

Translational degrees of freedom = 3

Rotational degrees of freedom = 2

∴ Vibrational degrees of freedom = 3n - 3 - 2 = 3n - 5

Hence, theoretic-ally there will be 3n - 5 possible fundamental bands for linear molecules.

Ex : Carbondioxide (CO_2). It is a linear molecule.

No. of atoms (n) = 3

Total degrees of freedom = 3n = 3x3 = 9

Translational degrees of freedom = 3

Rotational degrees of freedom = 2

Vibrational degrees of freedom = 9-3-2

(3n - 5) = 4.

Hence for CO_2 molecule, the theoretical fundamental bands should be four in I.R. Spectrum.

Non - linear molecules : For non — linear molecules, there are three degrees of rotation. So, for a non — linear molecule containing *n* atoms.

Total degrees of freedom = 3n

Transnational degrees of freedom = 3

Rotational degrees of freedom = 3

Vibrational degrees of freedom = 3n -3 - 3 = 3n - 6

Ex : Benzene (C_6H_6). It is a non -linear molecule.

No. of atoms n = 12

Total degrees of freedom = 12 x 3 = 36

Translational degrees of freedom = 3

Rotational degrees of freedom = 3

$\therefore$ Vibrational degrees of freedom = $\{3n - 6) = 36 - 3 - 3 = 30$

Hence for Benzene molecule there should be 30 fundamental bands theoretically in the I.R. Spectrum.

It was found that the theoretical number of fundamental bands are obtained very rarely. The reasons are

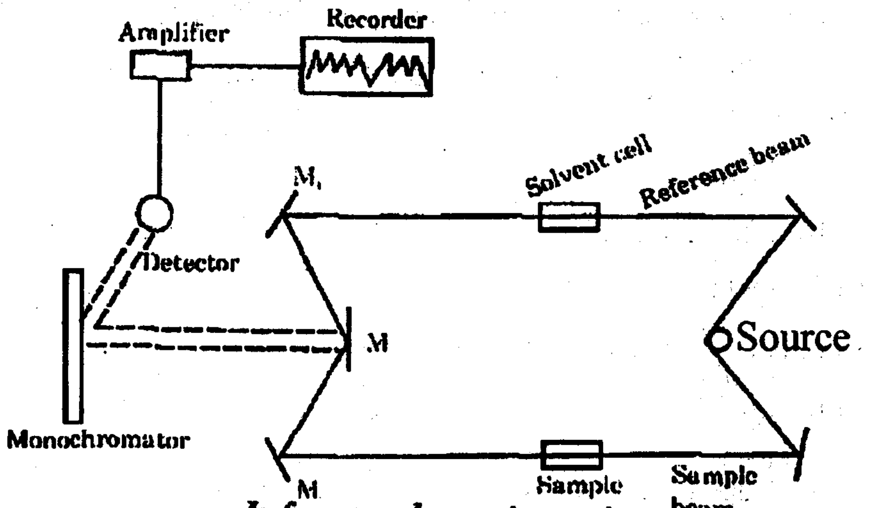
1. Fundamental vibrations fall outside the region 2.5 - 15
2. Fundamental vibrations are too weak to be observed as bands.
3. Fundamental vibrations are too close that they overlap.
4. Additional bands may appear. They are
   - a) Overtone bands
   - b) Combination bands
   - c) Difference bands.

These additional bands are usually 10 - 100 times less intense as compared to fundamental bands.

4.3.18. Finger print region :

The region below 1500 cm^{-1} is called Finger print region. Due to bending vibrations, overtones and combination bands along with fundamental bands these are not useful for structural information as confusion of one with the other occurs. But this region is very important for comparing the identity of the two compounds and also for detection of certain functional groups. For example esters, ethers, type of disubstitution in Benzene ring etc.

4.3.19. Instrumentation :



Infra – red spectrometer

Radiation source :

The source of radiation in a typical Infrared spectrometer is a small ceramic rod, heated electrically to 1100 - 1800°C or Nernst filment. The radiation is divided into two beams, one of which is passed through the sample while the other is a reference beam.

Absorption cells :

The cells generally employed are made up of rock salt or potassium bromide. Identical absorption cells are used.

Sample preparation :

0.55mg compound in a suitable minimum solvent acts as a liquid film. In case of solids a pellet is obtained by pressing the sample.

Mono chromator :

The pulse beam enters the monochromator through a slit and dispersed by a grating or by a prism. In the mono chromator the beam is sorted out into individual wave lengths by a sodium chloride prism through out the range 4000 - 650 cm^{-1}

Detector :

The signal beam emerging from monochromator is focussed on to a detector by means of a mirror system.

Amplifier and Recorder :

The signals from detector are amplified electronically and recorded on a special graph paper mounted on a drum.

Calibration of spectral chart :

A very sharp absorption band at 1603 found in the spectrum of polystyrene is often used to calibrate the spectral chart.

4.3.20. Characteristic absorption bands of functional groups :

Band	Frequency	Intensity
C - H (Alkanes)	2850 - 2960	m — s
= C - H (Alkenes)	3010-3100	m
≡C - H (Alkynes)	3300	s
Ar C - H (Aromatic)	3010 - 3100	m
C - H (Aldehyde)	2650 - 2880	two bands
C = C (Alkenes)	1620 - 1680	w
C ≡ C (Alkynes)	2100 - 2660	w

C = C (Aromatic)	1500- 1600	w
C - O(alcohol, ether)	1000 - 1300	s
>C = O(Aldehydes, Ketones)	1680 - 1760	s
0 - H (Alcohols, Phenols)	3600 - 3650	w
Hydrogen bonded	3200 - 3400	s
0 - H (Carboxylic acids)	2500 - 3000	w
N - H (Amines)	3300 - 3500	m
C - N Amines	1130- 1360	w
C = N Nitriles	2230 - 2260	w
- NO_2 Nitro	1345- 1385	s

Here w = weak, m = medium, s = strong

4.3.21. Important tips for interpreting I.R. spectrum :

1. Always place more reliance upon the negative evidence.

Ex : If there is no band at 1900 - 1600 cm^{-1}, then the carboxyl >C = O group must be absent.

2. Vibrations occur in the region above 1500 cm^{-1}, are most informative. So, always start from higher frequency of-the spectrum.

3. 3600 - 3200 cm^{-1} : Appearance of bands in this region shows the presence of -OH, -NH_2, >NH groups, ≡C - H str. shows medium band near 3300 cm^{-1}.

4. 3200 - 3000 cm^{-1} : Appearance of bands in this region shows C - Hstr and Ar - H str. Sharp bands of weak to medium intensities are observed.

5. 3000 - 2500 cm^{-1} : The presence of bands in this region shows C - H str. from Methyl or Methylene groups, a very broad band shows - COOH and two weak bands (2720, 2820) shows C - H str. from - CHO.

6. 2300 - 2100 cm^{-1} : The bands in this region shows alkynes, cyanides. cyanates and isocyanates.

7. 1900 - 1650 cm^{-1} : Strong bands are due tc >C = O stretching from Anhydrides, Esters, Aldehydes, Ketones, Carboxylic acids. Amides, Imides and lactones.

8. 1600 - 1000 cm^{-1} : This region is useful for confirmation of Nitro compounds, ethers and Alcohols.

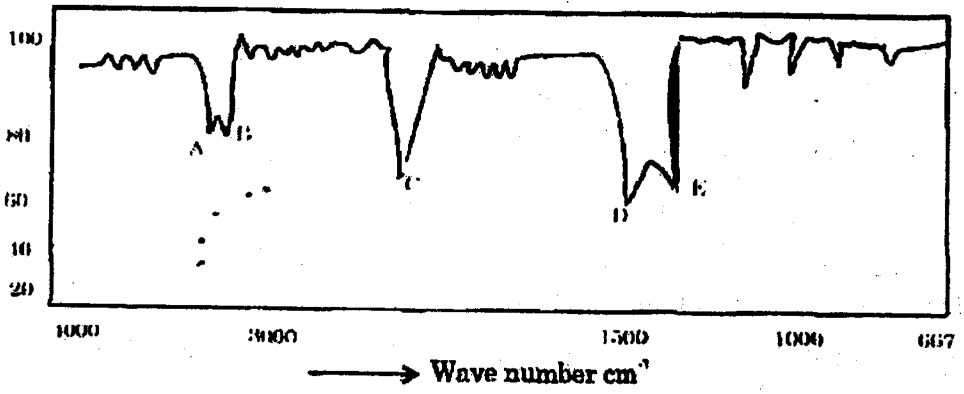
For Aromatic rings, medium bands around 1600 cm^{-1} 1580 cm^{-1} and 1500 cm^{-1} are observed.

9. Below 1000 cm^{-1} : This region is very useful for identifying the type of substitution on the aromatic ring.

i) Mono substitution, 770 - 730 cm^{-1} strong band
ii) Meta disubstituted, 850 - 710 cm^{-1} two medium bands.
iii) Ortho and para disubstituted. One band each. Para at higher wave number.

10. To distinguish intermolecular and intra molecular hydrogen bonding, the spectra to be taken at different concentrations.

Examples : 1



A = 3002 cm^{-1} C -H Str. in CH_3

B = 2940 cm^{-1} C - H Str

C = 2256 cm^{-1} $C\equiv N$

D = 1440 cm^{-1} C - H def: in CH_3

E = 1370 cm^{-1} C - H def.

Ans. Alkyl nitrile $CH_3 - C\equiv N$

For Alkyl nitrile $C\equiv N$ shows band at 2250 cm^{-1}

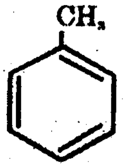
For Aryl nitrile $C\equiv N$ shows band at 2230 cm^{-1}

Isocyanides show band in the region on 2200 - 2075 cm^{-1}

For Azo compounds, N = N str. 1630 - 1570 cm^{-1}

For Isocyanates, $C\equiv N$ absorb in the region 2275 - 2250 cm^{-1}

2. Write various infrared bands for Toulene.



Toulene

Ar - H Str. ~ 3030 cm^{-1}

C - H Str. in CH_3 2850 - 2960 cm^{-1}

C = C Str. ~ 1600 cm^{-1} ~ 1580 cm^{-1} ~ 1460 cm^{-1}

C - H Mono substituted Benzene 730 - 770 cm^{-1}

3. Write various I.R.. bands for 1-Hexyne

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

1-Hexyne

$\equiv C - H$ Str.	~ 3300 cm^{-1}
C - H Str. in CH_2	~ 2860 - 2950 cm^{-1}
$C \equiv C$ Str.	~ 2100 cm^{-1}
C - H bending	~ 1465 cm^{-1}

4. Describe various I.R. bands for 2-Hexene

$CH_3 - CH_2 - CH_2 - CH = CH - CH_3$

2- Hexene

= C - H str -3050 cm ‘

C - H Str. in CH_3 -2860 - 2950 cm^{-1}

C = C Str. -1680 cm^{-1}

C - H bending -1465 cm^{-1}

- CH = CH - (cis, trans) 700 - 970 cm^{-1}

5. How would I.R. spectrum of the following differ.

a) Acetone	and	Ethanol
CH_3COCH_3		CH_3CH_2OH
C = O Str. 1710 cm^{-1}		Hydrogen bonded -OH
		3200 - 3600 cm^{-1}

b) Acetic acid	and	Methanol
CH_3COOH		CH_3OH
C = O Str. 1700 - 1725 cm^{-1}		P - OH 1050 cm^{-1}
Hydrogen bonded — OH		Hydrogen bonded - OH
2500 - 3000 cm^{-1}		3200 - 3600 cm^{-1}

c) Ethanol	and	dimethyl ether
CH_3 CH_2 OH		CH_3 O CH_3
Primary - OH 1050 cm^{-1}		Alkyl ether 1100 cm^{-1} C - O - C
Hydrogen bonded - OH		
3200 - 3600 cm^{-1}		

d) Ethyl Methyl Ketone and	unsaturated Ether.
$CH_3CH_2COCH_3$	$CH_2 = CH - CH_2 - O - CH_3$
C = O Str. 1700 - 1725 cm^{-1}	= CH Str. 3010 - 3050 cm^{-1}
	Alkyl ether 1100 cm^{-1} C-O-C
e) 3- Chloro butanoic acid and	Acetyl chloride
$Cl.CH_2CH_2\ CH_2COOH$	$CH_3\ COCl$
Saturated acid - COOH 800 cm^{-1}	Acid chloride - COCl 1795 cm^{-1}

6. **A compound A has molecular formula $C_7H_6O_2$ *it* gives I.R. absorption band at 1771 cm^{-1}. In treatment with $LiAlH_4$, it gives B which shows I.R. band at 3330 cm^{-1} and 1050 cm^{-1}, Write the structures for A and B.**

1771 cm^{-1} absorption band shows — COOH.

∴ Structure of A is C_6H_5COOH.

$$C_6H_5COOH \xrightarrow{LiAlH_4} C_6H_5CH_2OH$$

3300 cm^{-1} absorption band shows hydrogen bonded - OH. 1050 cm^{-1} absorption band shows primary — OH.

∴Structure A is Benzoic acid C_6H_5COOH

Structures B is Benzyl Alcohol $C_6H_5CH_2OH$

7. **How many fundamental frequencies would you expect in the I.R. spectrum of CO_2?**

CO_2 is a linear molecule

∴ No. of fundamental vibrations = 3n - 5

(Where n = no. of atoms) = 3 x 3 — 5 = 4

They are,

Symmetrical stretching. It is inactive.

Asymmetrical stretching. It is active.

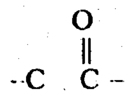
Two bending vibrations. These are degenerate and appear as combination band.

Thus two bands at 2349 cm^{-1} and 667 cm^{-1} are observed.

4.3.22. Comparison of UV- visible and IR Spectroscopy :

S.no	UV- Visible Spectroscopy	IR Spectroscopy
1.	The region is from 10- 800nm.	The region is from 800 – 20,000nm.
2.	These radiations are strong.	These radiations are weak.
3.	Only unsaturated and conjugated groups absorb in this region.	All organic bonds and groups absorb in this region.
5.	Usually expressed in terms of Wavelength. Units : nm	Usually expressed in terms of frequencies Units : Cm^{-1}.
6.	It shows broad absorption bands.	It shows sharp peaks.
7.	It gives idea about the conjugated system.	It gives idea about the nature of functional groups in the molecule.

4.3.23. Model Questions :

1. What type of changes will take place when an organic molecule absorpts UV and IR radiations?
2. What is meant by by Transitions? Explain with suitable examples
3. Match the following UV absorption bands to the chromophores
   a) 250 nm (intense peak)
   b) 255 nm (medium intensity)
   c) 280 nm (low intensity)
4. Using Wood ward Fischer rules calculate λ_{max} for the compound ($(CH_3)_2C = CHCOCH_3$.
5. Give IR absorption bands for the following.
   a) – CHO
   b) $>C = O$
   c) –OH
   d) –COOH
   e) $-C \equiv C-$
   f) $-NH_2$
6. What is spectroscopy ? What are the advantages of using spectroscopic methods? Give the principle of UV spectroscopy in brief. What wavelengths are absorbed by the following groups?
   a) $> C = C<$
   b) $> C = C - C = C<$
   c) 
   $-C \quad \overset{\overset{O}{\|}}{C}-$

7. How the following compounds are distinguished by their UV Spectra ?
   a) n – hexane and 1,3,5 – hexatriene.
   b) Cyclohexane and benzene
   c) Ethyl benzene and styrene
   d) Cis and trans – stilenes.
8. How do you differenciate the following in each pair using IR spectra ?
   a) Aniline from n – methylaniline.
   b) Acetaldehyde from ethanol
   c) Acetone from acetylene
   d) Acetonitrile from acetylene
   e) PhCN and PhNC
9. Explain the bathochromic shift and hypsochromic shift. Write an account of the usefulness of UV and IR spectroscopy in the structural determination of organic compounds with suitable examples.

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UNIT - IV

Lesson - IV

STEREO CHEMISTRY OF CARBON COMPOUNDS

4.4.1. Molecular Representations :

Wedge, Fischer, Newman and Saw - horse formula. Isomerism - definition of homomers and isomers. Classification of isomers - constitutional and stereoisomers, definition and examples. Constitutional isomers - Chain, functional, positional isomers and metamerism. Stereoisomers - enantiomers and diastereomers, definitions and examples. Conformational and configurational isomerism, definiton.

Enantiomers :

Optical activity - wave nature of light, plane polarised light, interaction with molecules, optical rotation and specific rotation. chiral molecules - definition and criteria - absence of plane, centre and Sn axis of symmetry. Asymmetric and disymmetric molecules - examples of asymmetric molecules (Glyceraldehyde, Lactic acid, Aniline) and disymmetric molecules (trans -1-2- dichloro cyclopropane). Chiral centres - definition, molecules with similar chiral carbons (Tartaric acid), defintion of mesomers, molecules with dissimilar Chiral carbons (2, 3 - dibrompentane). Numbers of enantiomers and mesomers - calculation. D,L - and R,S configuration of asymmetric and disymmetric molecules. cahn- Ingold - prelog rules. Recemic mixture, Recimisation and Resolution techniques.

Diastereomers :

Definition. geometrical isomerism with reference to alkenes - cis, trans and E, Z - Configuration.

4.4.2 MOLECULAR REPRESENTATIONS :

Dashed - Wedged Representation :

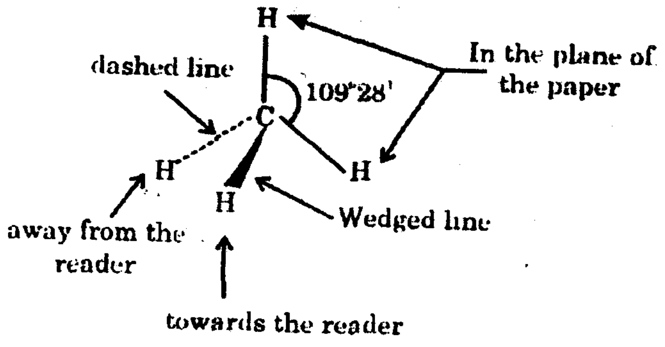
Dashed - Wedged representations illustrate the structures of molecules in three dimensions. Drawing the structures of three dimensional molecules on a two dimensional paper is difficult. For example a Tetra hedron should look three dimensional. So, a short hand notation is used to simplify three dimensional drawings known as Dashed - Wedged line drawings.

In this representation Dashed lines (are used to) show the bonds that go backward, away from the reader.

Thick lines are used to show the bonds that come forward, towards the reader.

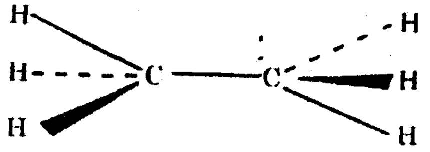
Straight lines are used to show the bonds in the plane of the paper.

Ex : 1. Methane molecule :



Three - dimensional molecule Methane (CH_4)

2. Ethane molecule :

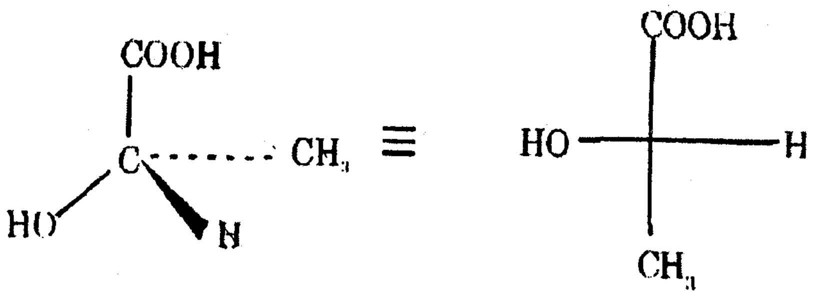


Three dimensional structure of Ethane (C_2H_6). As the number of chiral carbons in a molecule increases, it becomes difficult to draw the structures in three dimension.

Fischer projection :

The Fischer projection is a standard way to project the three dimensional configuration of each chiral carbon in a molecule. The Fischer projection can be written in the following way.

Ex : 1. Lactic acid CH3. CHOH. COOH.

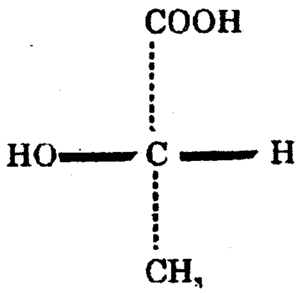


S - Lactic acid
Three dimensional projection

S - Lactic acid
Fischer projection

1. The molecule is written with its main carbon chain vertical and C_1 is at top.
2. The structure is flattend at chiral carbon to a plane surface.
3. The horizontal line at the chiral carbon represent bonds that project forward.
4. The vertical line at chiral centre represent bonds that project backward.

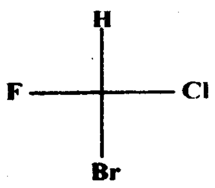
Thus the Fischer projection of S - Lactic acid indicates.

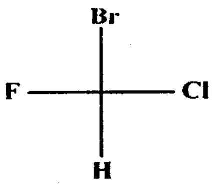


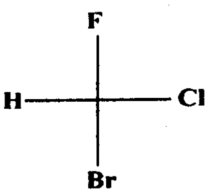
Illustraton :

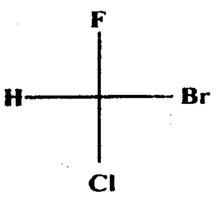
If two structural formula differ by odd number of interchanges, they are enantiomers. If by even number they are identical.

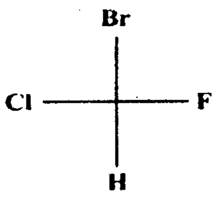
Ex :


(I)


(II)

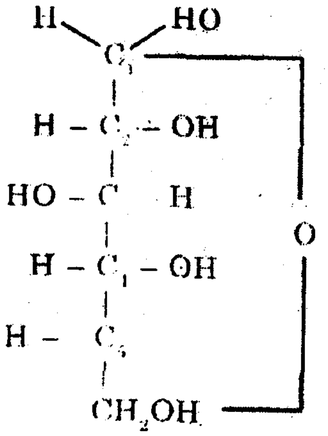

(III)


(IV)

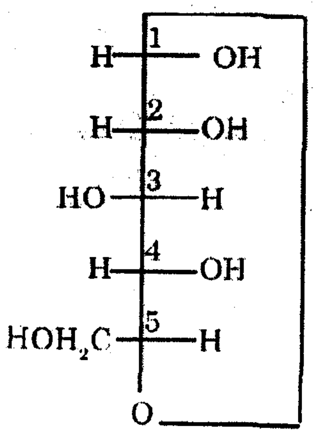

(V)

Relation of structures (II) to (v) W.r.t. (I)

Structure	Sequence of interchange	No.of interchanges	Relation ship w.r.t. (I)
II)	H, Br	1(odd)	enantiomer
III)	H, F	1(odd)	enantiomer
IV)	H,F ; Br, Cl	2(even)	identical
V)	H, Br ; Cl, F	2(even)	identical



Common Fischer projection



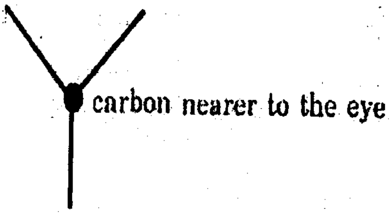
Modified Fischer projection

Advantage : It can not only be drawn quickly, but it facilitates comparision of Stereo isomers easy.

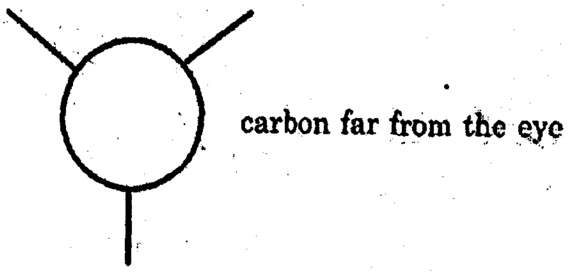
NEWMAN PROJECTION :

Newman projections are useful for drawing conformations.

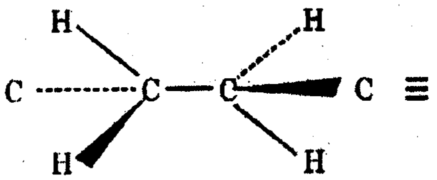
1. The front carbon is represented by three equally spaced lines coming together in 'Y' shape. These three lines represent three bonds.



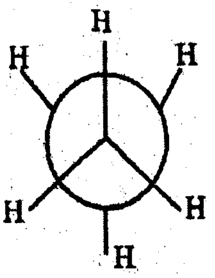
2. The back carbon is represented by a circle with three equally spaced radial extensions. These three radial extensions represent three bonds.



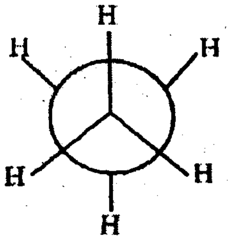
Ex : 1. Ethane molecule



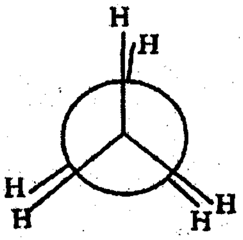
Three dimensional projection formula



Newman projection formula.



Staggend form of ethane
These are also called
Anti forms. More stable.



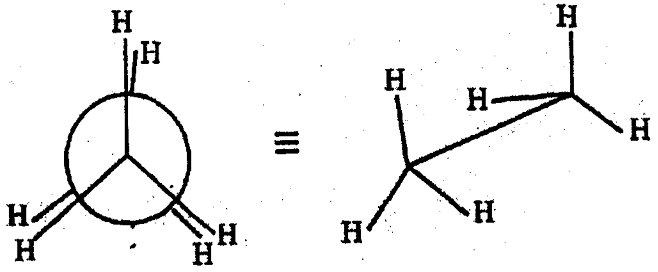
Eclipsed form the Ethane
These are also called
Synforms. These are less stable.

SAWHORSE FORMULA :

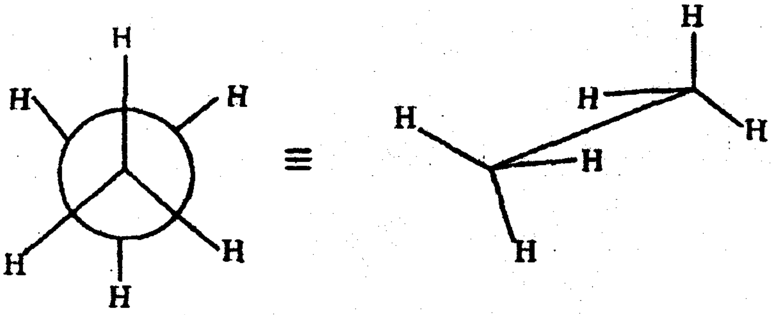
Sawhorse formula is used to specify conformation like Newman projection.

In Sawhorse representation the C - C bond is viewed side ways where as in Newman projection the C - C bond is along the line of vision. In Sawhorse representation C - C bond can be seen while in Newman projection the C - C bond can not be seen.

Ex. Ethane molecule



Newman projection Sawhorse model
Eclipsed form of Ethane



Newman projection Sawhorse model

Staggered form of Ethane

4.4.3. ISOMERISM

The phenomenon of different compounds having same molecular formula is called isomerism.

Isomers :

Isomers are different compounds having same molecular formula.

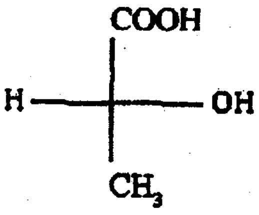
Ex : Glucose and Fructose. They are having same molecular formula $C_6H_{12}O_6$.

Homomers :

Homomers are the identical representations of the same compound. The molecular models of these representations are superimposable.

At different times two molecules of the same compound occupy same position in space. They are identical and called Homomers.

Ex : Lactic acid $CH_3CHOHCOOH$.



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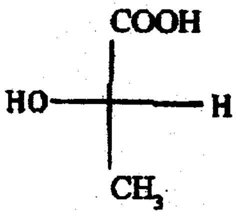

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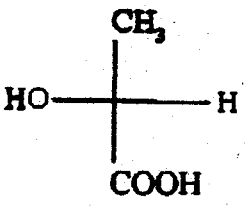


III

Structures I and II are Isomers. Structure II -is the mirror image of structure I. They are not super imposable called Enantiomers.

Structures I and III are same. They are Homomers. When structure I is rotated by 180°. structure III is obtained.

Molecules with same molecular formula

superimposable | non – superimposable

Homomers | Isomers

CLASSIFICATION OF ISOMERS

Isomers

Constitutional Isomers
1. Chain Isomers.
2. Functional Isomers
3. Positional Isomers
4. Metamers.

Stereo Isomers
1. Enantiomers.
2. Diastereomers

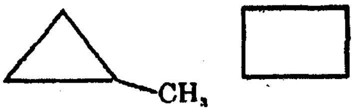
4.4.3.1. Isomers are two types.

1. Constitutional Isomers 2. Stereo Isomers.

1. Constitutional Isomers :

Isomers with different constitutions are called constitutional Isomers, This phenomenon is called structural Isomerism.

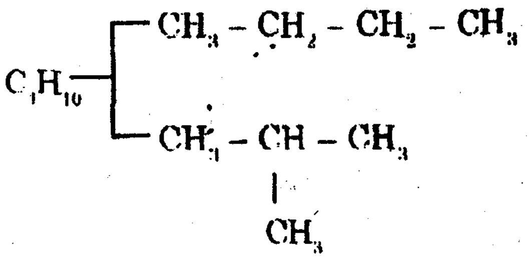
Ex : Methyl Cyclopropane and Cyclobutane.



Chain Isomers :

Isomers which differ in carbon chains are called chain Isomers. Such phenomenon is called chain Isomerism.

Ex : Butane C_4H_{10}



C_4H_{10}: $CH_3 - CH_2 - CH_2 - CH_3$ n – Butane

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$ iso – Butane

Functional Isomers :

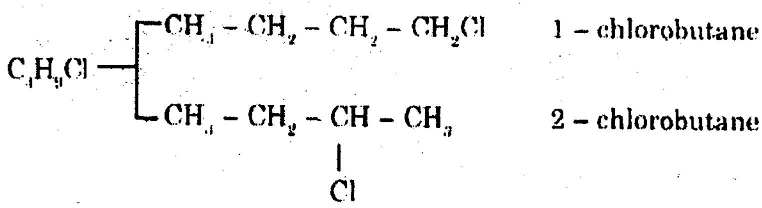
Isomers which differ in the nature of the functional group are called Functional Isomers. Such phenomenon is called Functional Isomerism.

$C_4H_{10}O$ — $CH_3CH_2CH_2CH_2\ OH$ n – Butanol

$C_4H_{10}O$ — $CH_3CH_2 - O - CH_2\ CH_3$ Diethyl ether.

Positional Isomers :

Isomers which differ in the position of an atom or group are called positional Isomers. Such phenomenon is called position Isomerism. **Ex :** Chloro – Butane C_4H_9Cl



$$C_4H_9Cl \begin{cases} CH_3 - CH_2 - CH_2 - CH_2Cl & \text{1 – chlorobutane} \\ CH_3 - CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3 & \text{2 – chlorobutane} \end{cases}$$

Metamers :

Isomers which differ in the distribution of carbon atoms on either side of the functional group are called Metamers.Such Phenomenon is called Metamerism **Ex :** $C_4H_{10}O$

$C_4H_{10}O$ — $CH_3CH_2OCH_2CH_3$ Diethyl ether

$C_4H_{10}O$ — $CH_3OCH_2CH_2CH_3$ Methyl propyl ether

4.4.3.2. Stereo Isomers :

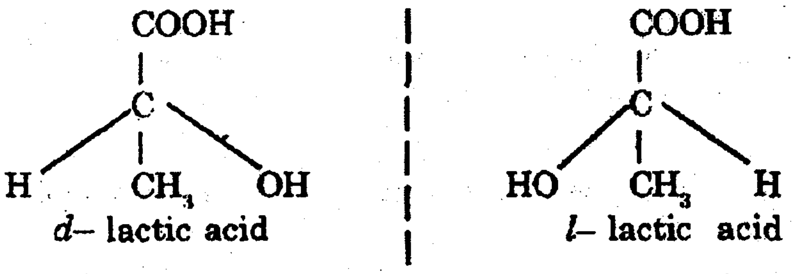
Isomers with same constitution which differ in special arrangement are called Stereo Isomers.This phenomenon is called Stereo isomerism.

They are two types

1. Enantiomers 2. Diastereomers.

Enantiomers :

Isomers which are mirror images and non -super imposable are called Enantiomers.



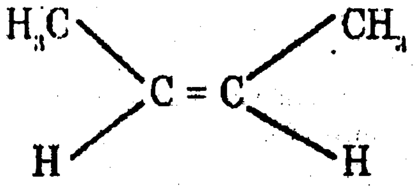
$d-$ lactic acid | $l-$ lactic acid

d- lactic acid rotates the plane of polarized light to right. It is a dextro isomer. *l*- lactic acid rotates the plane of polarized light, to left. It is a leavo isomer. These two are mirror images and non -super imposable. Hence they are enantiomers.

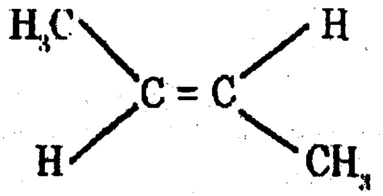
Diastereomers :

Stereo Isomers which are not enantiomers are called Diastereo Isomers. They are not mirror images.

Ex : Cis - 2 - butene and trans - 2 - butene



Cis – 2 – butene



trans – 2 – butene

Conformational and configurational Isomerism :

Stereo Isomerism can be classified into two types. Conformational and Configurational Isomerism.

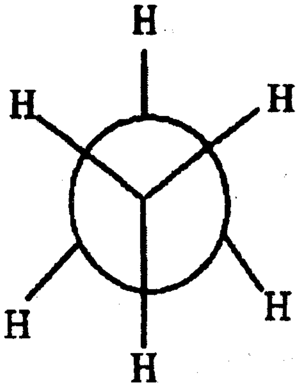
Conformational Isomerism :

The formation of different easily interconvertible structures by rotation about a single bond is called conformational Isomerism. Such compounds are called conformations or conformers. These are non - super imposable. A single conformation can not be physically separated because the energy required for rotation about a single bond is neglisible and different conformers are easily interconvertible.

Ex : Conformers of Ethane

Staggered form:

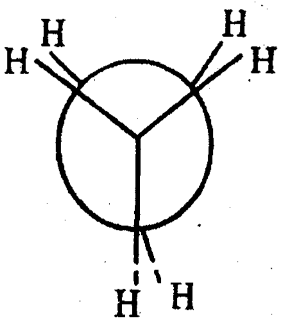
In staggered form the atoms on the two carbons are as far as possible. These are also called Anti forms.



Staggered form of Ethane

Eclipsed form :

In Eclipsed form atoms on the two carbons are as close as possible. These are also called synforms. They are less stable.



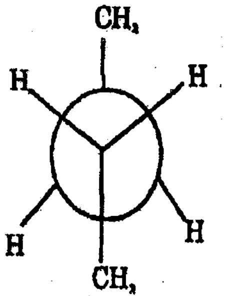
Eclipsed form of Ethane

Skew forms :

The infinite number of conformers existing between staggered and Eclipsed forms are called Skew forms.

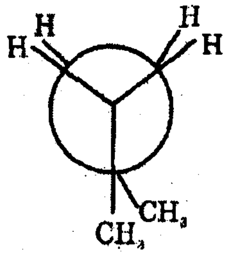
Conformers of n - Butane : Staggered form :

In staggered form of n- Butane the Methyls are at an angle of 180°.



Staggered form of n - butane

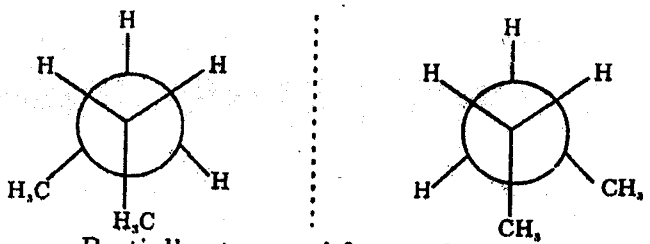
Eclipsed form : In Eclipsed form of n-butane the Methyls are at an angle of 0°.



Eclipsed form of n - butane

Gouche forms : Partially staggered forms :

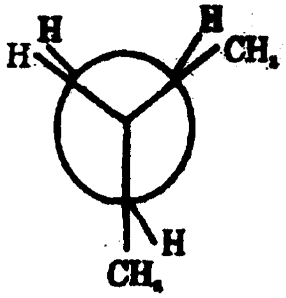
In partially staggered forms, the Methyls are at an angle of 60°.

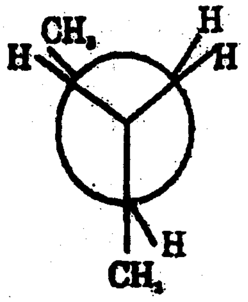


Partially staggered forms of *n* - butane.
These are mirror images. enantiomers

Partially Eclipsed forms :

In partially Eclipsed forms the Methyls are at an angle of 120°.



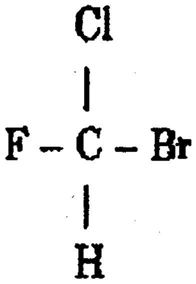


Configurational isomerism :

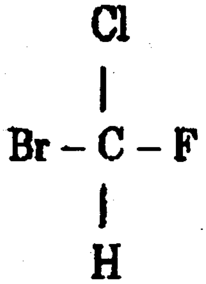
The formation of different non - interconvertible structures by rotation about a single bond is called configurational Isomerism. Such compounds are called configurational isomers. They are non - super imposable.

A single configuration can be physically separated because they are non - interconvertible.

Ex : 1. Configurational Isomers of Bromochlorofluoro Methane. CHBrFCl :

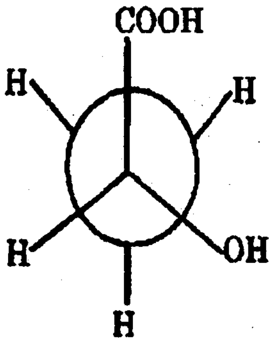


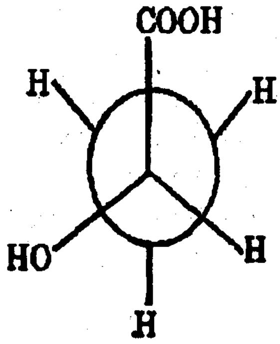
$$\begin{array}{c} Cl \\ | \\ F-C-Br \\ | \\ H \end{array}$$



$$\begin{array}{c} Cl \\ | \\ Br-C-F \\ | \\ H \end{array}$$

2. Configurational Isomers of Lactic acid (CH$_3$CHOH COOH) .





4.4.4. OPTICAL ACTIVITY :

The phenomenon of rotating the plane of polarized light is called optical activity. The compounds exhibiting this property are called optically active compounds.

The compounds which have similar physical and chemical properties and differ only in their optical activity are called optical isomers. This phenomenon is called optical Isomerism.

Ex : Lactic acid, Tartaric acid.

Condition for optical activity:

The necessary and only sufficient, condition for a molecule to show optical activity is that the geometrical structure of the molecule should not super impose on its mirror image.

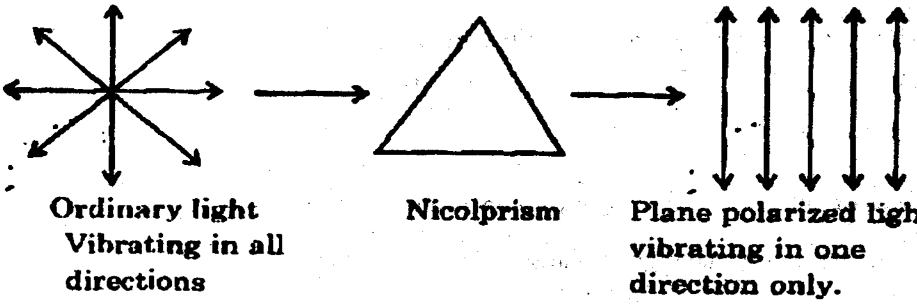
Wave nature of light:

Light is propagated in all directions in the form of waves. It is an electromagnetic radiation. It is associated with electric and magnetic fields.

The vertical component of the wave E indicates change in the strength of the electric field. The horizontal component of the wave H indicates change in the strength of the magnetic field.

Plane polarized light :

An ordinary light vibrates in all planes at right angles to the plane of propagation.



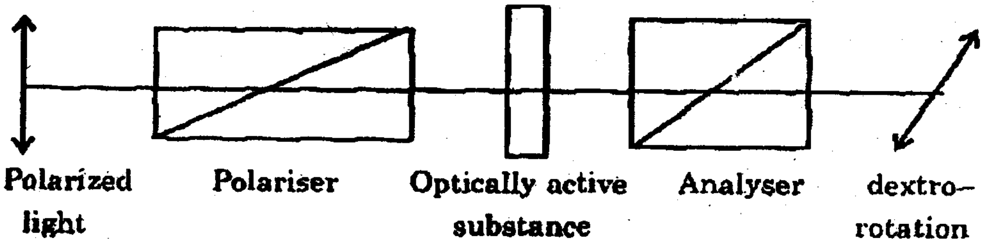
When light is passed through a NiCol prism, the emergent beam vibrates only in one direction. This type of light, which vibrates only in one plane, is called polarized light.

Interaction with molecules:

A plane polarized light consists of a right handed and a left handed circularly polarized light. Therefore it represents a chiral environment. Because of opposite chiralities, the rays establish diastereomeric relationship with any particular enantiomer and interact differently. As a result the plane of polarization is rotated either towards right (clock wise) or towards left (anti-clock wise) by a certain angle.

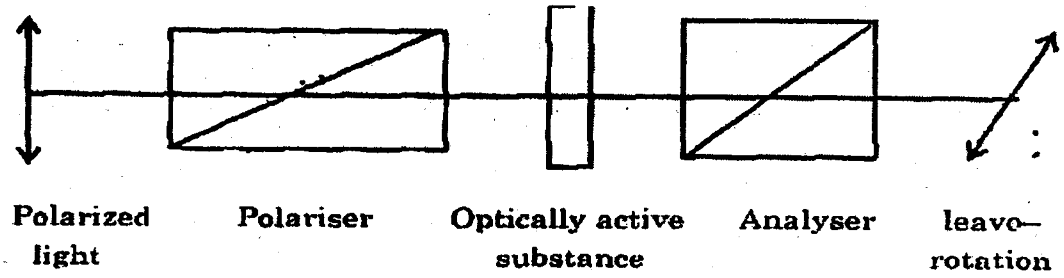
4.4.4.1. OPTICAL ROTATION : Dextro- rotatory :

Substances which rotate the plane of polarized light to right are called dextro rotatory. It is indicated by d or (+).



Leavo- rotatory :

Substances which rotate the plane of polarized light to left are called leavorotatory. It is indicated by / or (-).



On the basis of optical activity organic compounds are divided into three types.

1. Dextro - rotatory : It rotates the plane polarized light to right (dextro = right), d or (+) form

Ex : *d*— Tartaric acid.

2. Leavo - rotatory : It rotates the plane of polarized light to left, (leavo = left). It is l or (-) form.

Ex : *l* - Tantaric acid.

3.Optically inactive : The compounds do not rotate the plane polarized light in any direction.

Ex : Meso - tartaric acid

4.4.4.2.Factors Effecting Optical rotation :

The magnitude of optical rotation depends upon the following factors.

1. Nature of the substance.
2. Concentration of the solution

3. Length of the tube containing the solution.
4. Nature of the solvent
5. Temperature of the solution
6. Wave length of the light used.

Specific rotation :

Specific rotation is defined as the observed rotation when polarized light is passed through 1 decimeter of the solution having concentration of 1 gram per milli litre.

Specific rotation $[\alpha]_D^{t^\circ C} = \frac{\alpha}{lc}$

Where,
α = Observed rotation
l = Length of the solution in decimeters. (1 decimeter = 10cmsj
C = No. of'grams of substance in 1 ml of the solution
D = The Sodium D line corresponding to 589 $m\mu$ wave length
t = Temperature.

The sign (+) attached with the angle of rotation indicates rotation towards right and (-) sign indicates rotation towards left.

Ex : $[\alpha]_D$ of α - glucose is +112°.

4.4.5. CHIRALITY :

On studying several optically active organic compounds it was found that chiral carbon or chirality is responsible for optical activity.

Chirality :

Chirality is the property of a molecule being non - super imposable on its mirror image.

Chiral Carbon :

A carbon atom having four different monovalent atoms or groups is called asymmetric or chiral carbon.

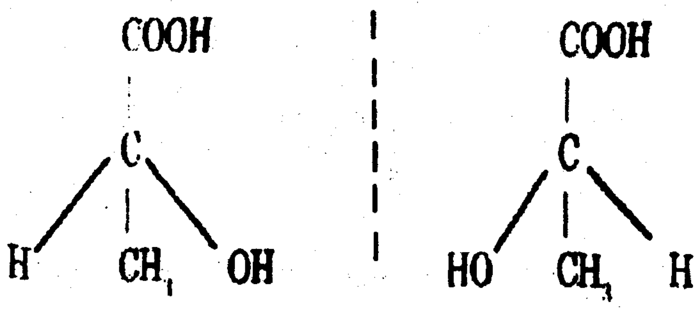
In Greek, cheir = hand. Chirality means handedness. The term chiral or chirality is used to a molecule whose mirror image is non - super imposable. It is responsible for optical activity.

Chirality was proposed by Kelvin. It largely displaced the earlier term dissymetric and still earlier term asymmetric. However on account of their popularity they are still used.

Explanation :

The left hand of a person looks similar to his right hand. But the left hand gloue does not fit to his right hand. The relation between two hands is that they are non - super imposable mirror images of each other. Molecules having left hand and right hand forms are called chiral molecules. They are optically active.

Ex : Lactic acid .



Lactic acid

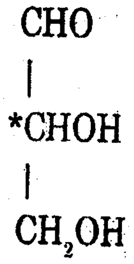
These are non - super imposable mirror images. Chiral and optically active.

Asymmetric Molecules : A molecule is said to be asymmetric if it has no elements of symmetry except C_1 symmetry.

Asymmetric molecule does not possess either of the following elements of symmetry

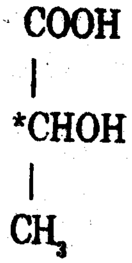
1. Plane of symmetry.
2. Centre of symmetry.
3. Alternating axis of symmetry.
4. Simple axis of symmetry except C_1.

Ex :



$$\begin{array}{c} CHO \\ | \\ {}^{*}CHOH \\ | \\ CH_2OH \end{array}$$

Glyceraldehyde



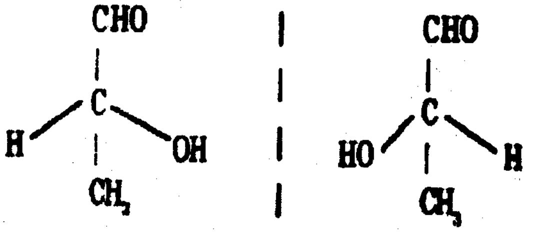
$$\begin{array}{c} COOH \\ | \\ {}^{*}CHOH \\ | \\ CH_3 \end{array}$$

Lactic acid

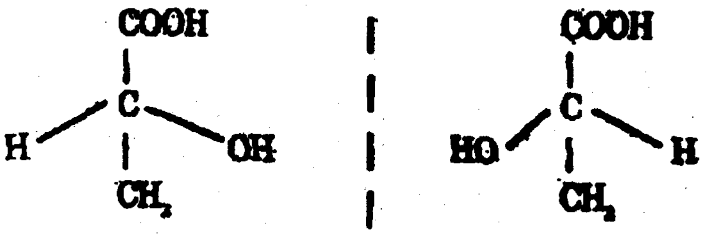
$$\begin{array}{c} COOH \\ | \\ {}^{*}CHNH_2 \\ | \\ CH_3 \end{array}$$

Alanine

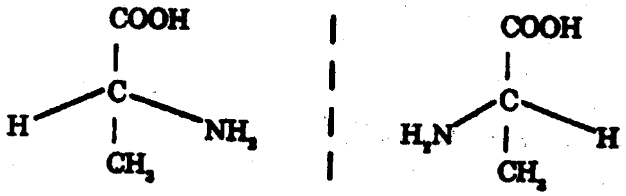
Each molecule has two non - super imposable mirror image structures. They are chiral and optically active.



non - super imposable mirror images of Glyceraldehyde



non - super imposable mirror images of Lactic acid.



non – super imposable mirror images of Alanine.

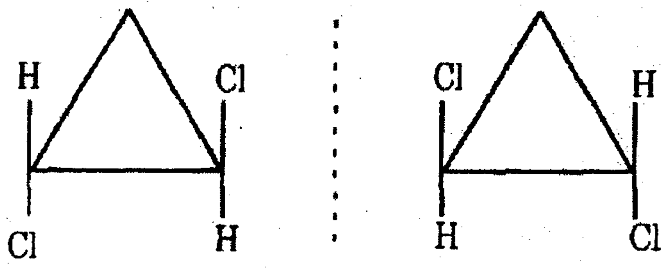
All molecules contain an infinity number of C_1 axes.

Disymmetric molecules : A molecule is said to be dissymmetric if it has no element of symmetry except simple axis of symmetry.

A disymmetric molecule does not possess either of the following elements of symmetry.

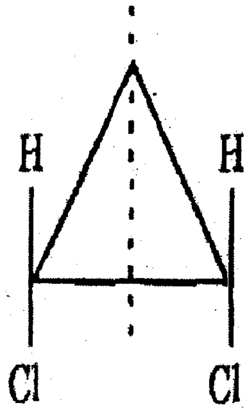
1. Plane of symmetry.
2. Centre of symmetry
3. Alternating axis of symmetry.

Ex : Trans 1. 2- dichloro cyclopropane.



non – super imposable mirror images of trans 1,2- dichloro cyclopropane

Cis - 1,2 - dichloro cyclopropane :



Cis – 1,2- dichloro cyclopropane has plane or symmetry, it is a Meso compound.

One fold alternating axis of symmetry corresponds to plane of symmetry. Two fold alternating axis of symmetry corresponds to centre of symmetry. So, a molecule that lacks alternating axis of symmetry is called disymmetric. These are usually optically active.

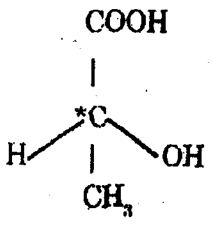
Symmetry designations

Term	Alternating axis	Simple axis	Optical activity
Symmetric	Present	May or may not be present	Inactive
Disymmetric	Absent	May or may not be present	Usually active
Asymmetric	Absent	Absent	Usually active

4.4.6. CHIRAL CENTRE :

A carbon atom containing four different monovalent atoms or groups is called chiral carbon or chiral centre.

Ex : Lactic acid



Explanation :

The term chiral is used to compounds whose mirror images are non - super imposable.

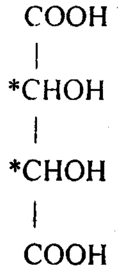
If a molecule has only one chiral centre, it is always chiral. But molecules having two or more chiral centres may be chiral or achiral.

Thus the presence of chiral centre is not the criterion of chirality. The only thing is that the molecule as a whole should be chiral.

4.4.6.1. Compounds containing similar chiral carbons :

The no.of optical isomers in a molecule containing ‘n’ number of similar chiral carbon atoms is always less than 2^n.

Ex : Tartaric acid $COOH\,(CHOH)_2\,COOH$.

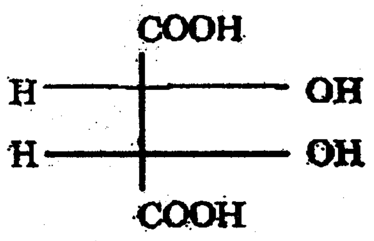


$$\begin{array}{c} COOH \\ | \\ {}^{*}CHOH \\ | \\ {}^{*}CHOH \\ | \\ COOH \end{array}$$

No. of chiral carbons = 2

No. of possible optical isomers = $2^n = 2^2 = 4$

But Tartaric acid has only three Isomers because it contains two similar chiral carbons.



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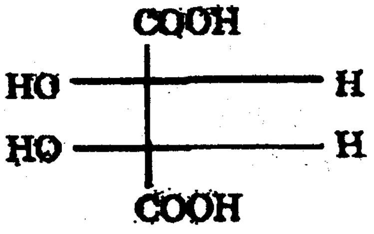
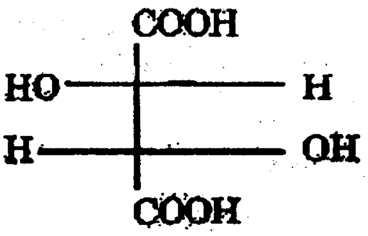
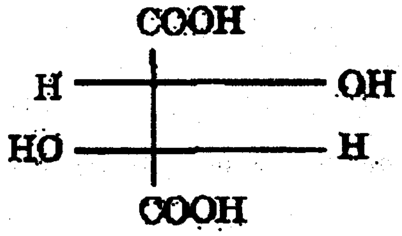


II

Mirror images are super imposable



III



IV

Mirror images are non - super imposable

Enantiomers :

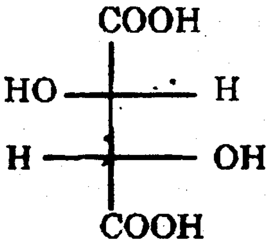
Stereo Isomers which are mirror images of each other and non-super imposable are called enantiomers. They are optically active. Structures III and IV are mirror images of each other and optically active. They are non-super imposable. They are enantiomers. They are not interconvertible by rotation about carbon - carbon bond.

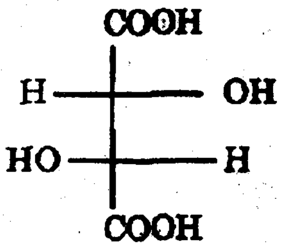
Mesomers :

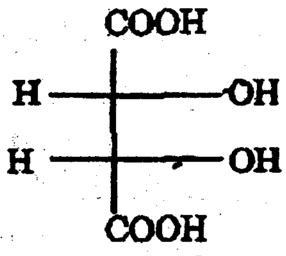
Stereo isomers which are optically inactive due to internal compensation are called Mesoisomers. They can not be separated into two optically active. forms In these molecules the rotation of upper half of the molecule is cancelled by the rotation of lower half of the molecule.

Structures I and II are mirror images of each other and optically inactive due to internal compensation. When one of these Isomers {I or II) is rotated through 180° with the plane of the paper, the second one is obtained. Hence these structures are identical.

Thus Tartaric acid has three Isomers only.


(+) form


(–) form


Mesoform

Recemic modification :

The mixture containing equimolar quantities of dextro and leavo forms is called Recemic mixture. **Equimolar** quantities of structures III and IV form a recemic mixture. Tt is optically inactive. It shows zero **rotation**. It can be separated into two optically active forms.

4.4.6.2.Compounds containing dissimilar chiral carbon atoms:

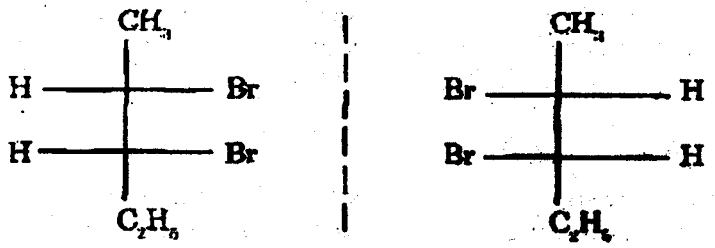
The no. of optical isomers in a molecule containing V number of different chiral carbon atoms is given by 2^n. There will be 2^{n-1} pairs of enantiomers and same number of Racemic modifications.

Ex : 2, 3 - dibromo pentane CH_3, CHBr CHBr C_2H_5.

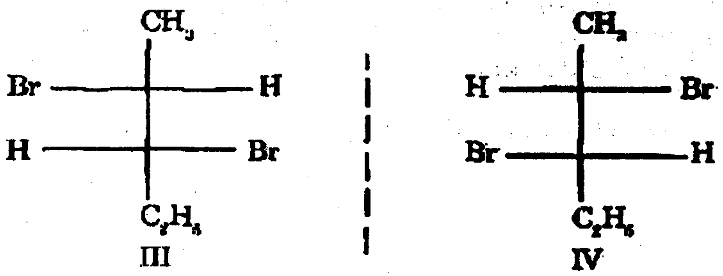
It has two dissimilar chiral carbon atoms.

No. of optically active Isomers = $2^n = 2^2 = 4$

No. of enantiomeric pairs = $2^{n-1} = 2^{2-1} = 2$


I II

Pair of enantiomers


III IV

Pair of enantiomers

Enantiomers :

Stereo Isomers which are non - super imposable mirror images of each other and optically active are called enantiomers. Structures I and II (or) III and IV are two pairs of enantiomers.,

Diastereo Isomers :

Stereo isomers which are not mirror images of each other are called diastereo isomers.

Structures I and 111 are not mirror images of each other. They are optically active. So, they are diastereo isomers.

Similarly structures II and III (or) II and IV (or) I and IV are also diastereo isomers.

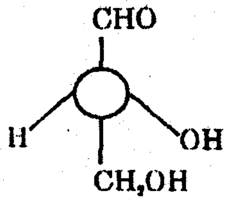
Recemic modifications :

The mixtures containing equimolar quantities of dextro and leavo forms are called recemic mixtures. They are optically inactive. They show zero rotation separated into two optically active forms.

Mixtures of equimolar quantities of I and II (or) III and IV form two different Recemic modifications.

4.4.7. DL - Configuration (Or) Relative configuration :

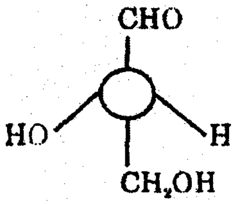
Fischer arbitrarily proposed the following configuration for dextro (+) - Glyceraldehyde and named it as D - glyceraldehyde.



D(+) glyceraldehyde.

All Isomers prepared from or converted into D- glyceraldehyde are named as D - Isomers whether they are dextro or leavo rotatory.

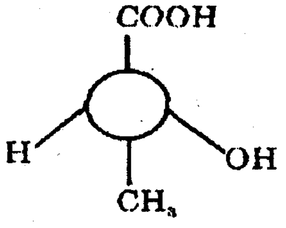
Fischer arbitrarily proposed the following configuration for leavo (-) - glyceraldehyde and named it as L - glyceraldehyde.



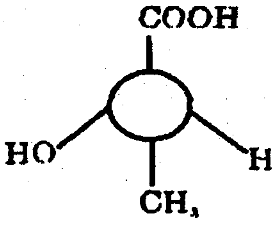
L(-) glyceraldehyde

All Isomers prepared from or converted into L-glyceraldehyde are named as L - Isomers whether they are dextro or leavo rotatory.

Ex : Lactic acid

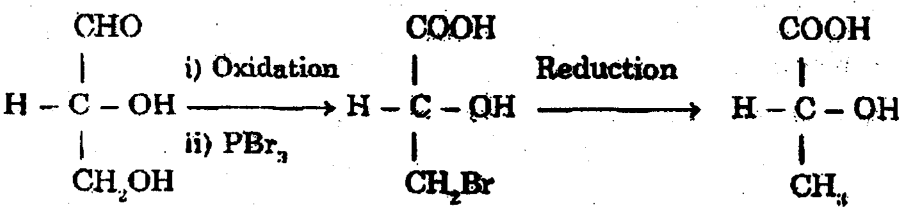


D- Lactic acid



L- Lactic acid

Lactic acid obtained from D(+)- glyceraldehyde was assigned D - configuration.



$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{ii) } PBr_3]{\text{i) Oxidation}} \begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_2Br \end{array} \xrightarrow{\text{Reduction}} \begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_3 \end{array}$$

D(+) - glyceraldehydes D - Lactic acid

Similarly Lactic acid obtained from L (-) - glycer aldehyde was assigned L - configuration.

Defects : 1. It is only a relative configuration.

2. The basic defect is that some times the same molecule may be related to both D and L series.

3. It is cumbersome to apply it to complicated molecules.

4.4.8. ABSOLUTE CONFIGURATION OR R, S - CONFIGURATION :

R. S- configuration is an unambiguous system devised by Cahn, Ingold and Prelog. It is based on the actual three -dimensional formula.

Sequence rules :

The order of priority of atoms or groups directly attached to the asymmetric centre is given by the sequence rules.

1. The atom of highest atomic number gets highest priority and that of lowest atomic number gets lowest priority.

Ex : I > Br > Cl > F >. O > N > C > H.

2. If two atoms attached to the asymmetric centre have same atomic number, then priority is given by comparing next atom in the group.

Ex : $CH_3CH_2 > CH_3$

3. A doubly bonded atom attached to the asymmetric centre is considered as two such atoms attached.

Ex : $>C = O > -CH_2OH$

4. A triply bonded atom attached to the asymmetric centre is considered as three such atoms attached.

$-C \equiv N > >C = O$

In $C \equiv N$, carbon is considered as attached to three Nitrogen atoms where as in $>C = O$, carbon is considered as attached to two oxygen atoms.

Assignment of configuration :

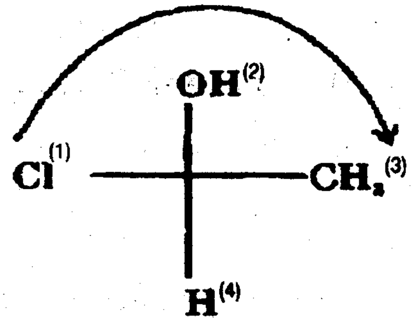
Configuration of the molecule is represented by the projection formula such that least priority atom or group must present, on the lower vertical position .

R - Configuration :

If decreasing order of priority is clock-wise, then the molecule is assigned R - configuration (Rectus = right)

Ex : 1-chloro ethanol. Priority order of the atoms is

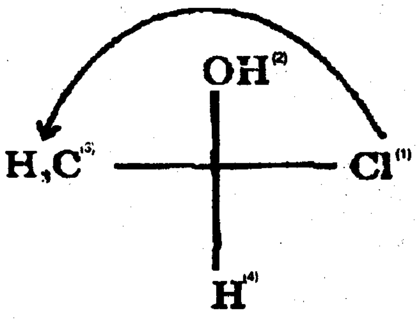
$$Cl > OH > CH_3 > H.$$



R- Configuration

S - configuration :

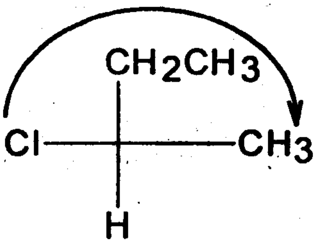
If decreasing order of priority is anti clock wise, then the molecule is assigned S - configuration (Sinister = left).



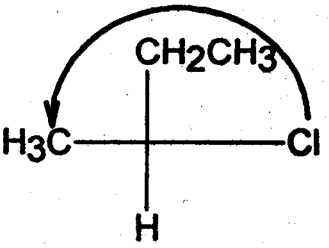
S - Configuration

Here lowest priority atom - H is present, on the lower vertical position.

Ex : 2. 2 - chloro butane.



R - 2 - Chlorobutane

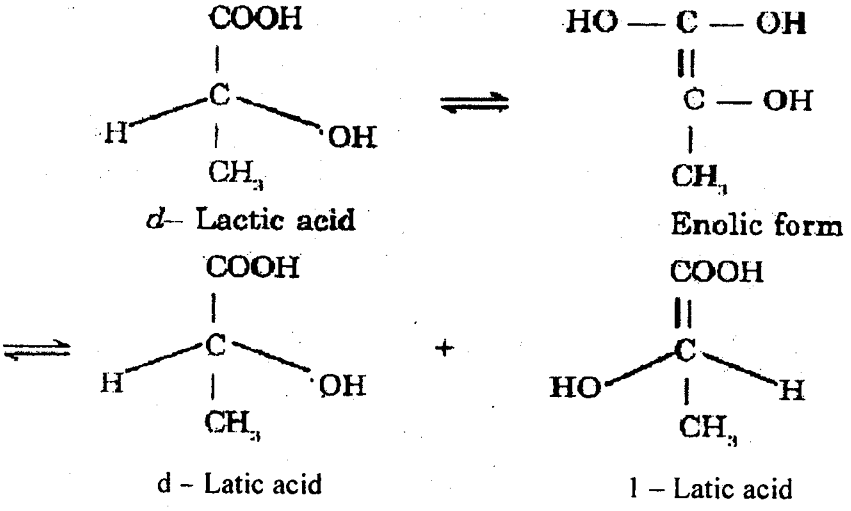


S - 2 - Chlorobutane

4.4.9. Recemisation :

The process of conversion of an optically active compound into a recemic mixture is called recemisation.

Ex : Lactic acid undergoes recemisation in the presence of a base.



Recemic mixture

Resolution :

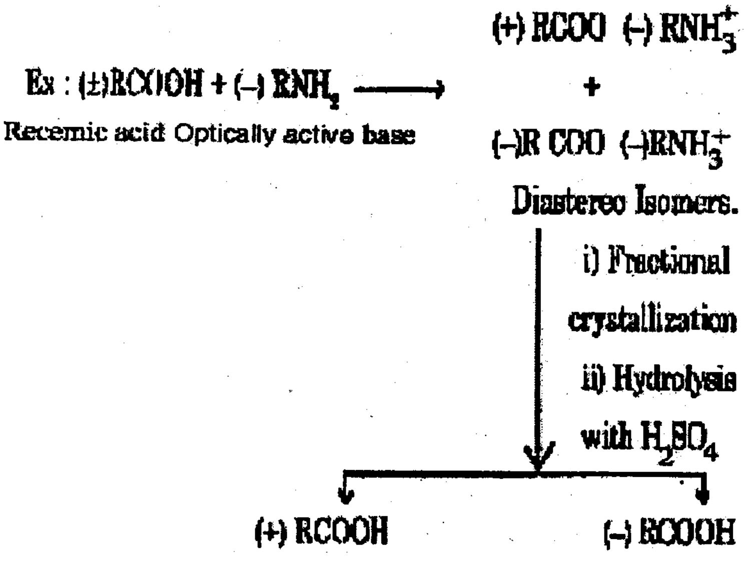
The process of separation-of a recemic mixture into *d*- and *l*- forms is called Resolution.

Resolution of Recemic acids :

Resolution of recemic acids is carried with the help of optically active bases such as Brucine and Strychnine.

Resolution of Recemic bases :

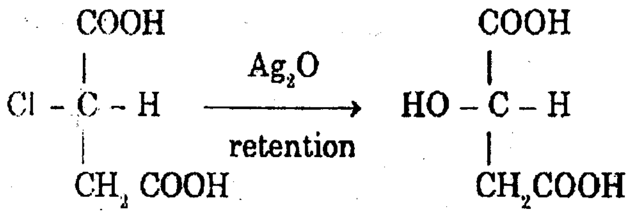
Resolution of recemic bases is carried out with the help of optically active acids such as Camphor and Menthol derivatives.



Retention :

The process in which attacking groups takes the position of the leaving group is called retention.

Ex : L- Chlorosuccinic acid undergoes retention on hydrolysis with mild reagents like Ag_2O.



$$\begin{array}{c} COOH \\ | \\ Cl-C-H \\ | \\ CH_2COOH \end{array} \xrightarrow[\text{retention}]{Ag_2O} \begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ CH_2COOH \end{array}$$

l - Chloro succinic acid *l* - Malic acid

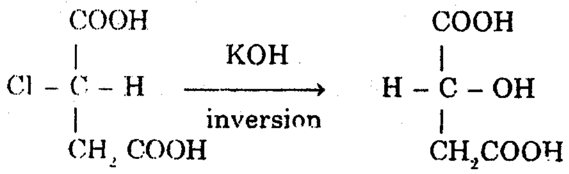
Inversion:

The process in which attacking group takes any position other than that of the leaving group is called inversion.

Walden inversion :

The conversion of *d*- form of an optically active compound into *l*- form and vice versa is called Walden inversion.

Ex : *l*- Chloro succinic acid undergoes inversion on hydrolysis with strong reagents like KOH.



$$\begin{array}{c} COOH \\ | \\ Cl-C-H \\ | \\ CH_2COOH \end{array} \xrightarrow[\text{inversion}]{KOH} \begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_2COOH \end{array}$$

l-chloro succinic acid *d* - Malic acid

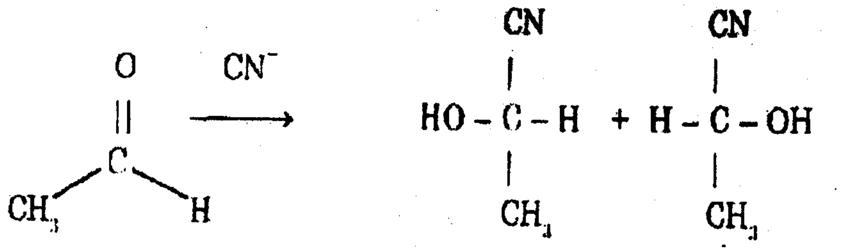
4.4.10. Recemic mixtures :

The mixture containing an equimolar quantities of dextro and leavo forms is called Recemic mixture. It. shows zero rotation. It can be resolved into two optically active forms.

By synthesis :

The synthesis of chiral compounds from symmetrical compounds in the absence of optically active agent always produce a recemic mixture.

Ex : The formation of lacto nitrile from Acetaldehyde always produce a recemic mixture.

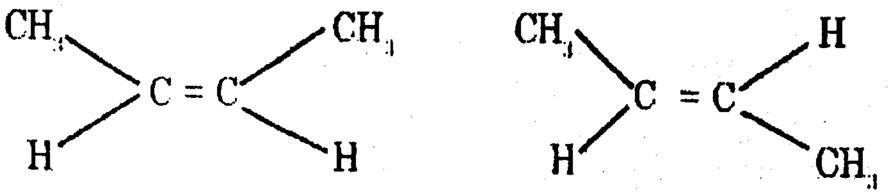


Acetaldehyde l – Lacto nitrile d– lacto nitrile

4.4.11. Geometrical Isomerism :

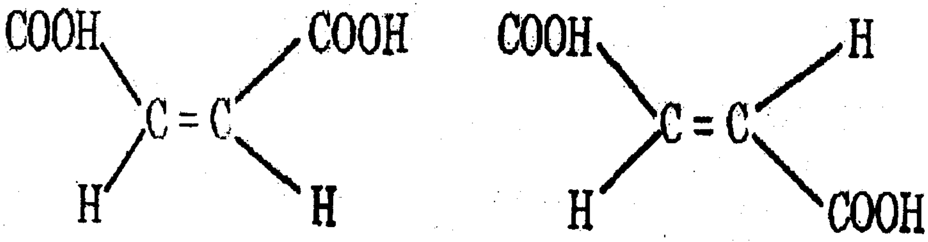
1. Isomerism due to hindered rotation of a double bond is called Geometrical Isomerism.

Ex : 1. 2 - Butane



Geometrical Isomers of 2-Butene

2. Maleic acid and fumaric acid :



Maleic acid
less stable

Fumaric acid
more stable

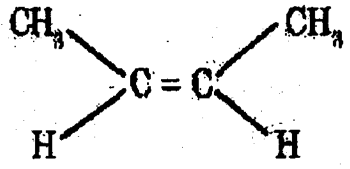
These Isomers can be separated.

Cis, trans - Configuration :

Cis - Isomers :

In Cis - Isomers similar atoms or groups are present on the same side of the double bond.

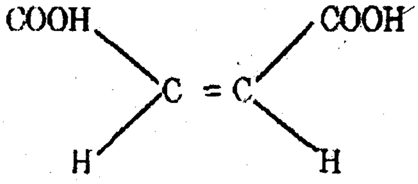
Ex :1.



Cis -2- Butene

In Cis -2 - butene the two Methyl groups are present on the same side of the double bond. It is Cis - Configuration.

Ex : 2.

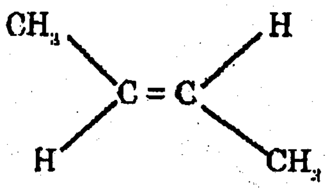


Cis- Isomer
Maleic acid

In Maleic acid the two - COOH groups are present on the same side of the double bond. Hence it is Cis- configuration.

Trans - configuration : In Trans - Isomers similar atoms or groups are present on the opposite sides of the double bond.

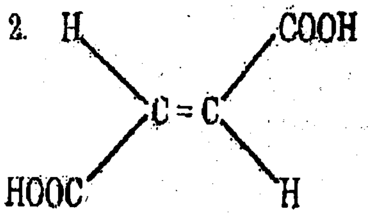
Ex : 1.



Trans - 2- butene

In Trans - 2 - butene the two Methyl groups are present on the opposite sides of the double bond. It is trans configuration.

Ex : 2.

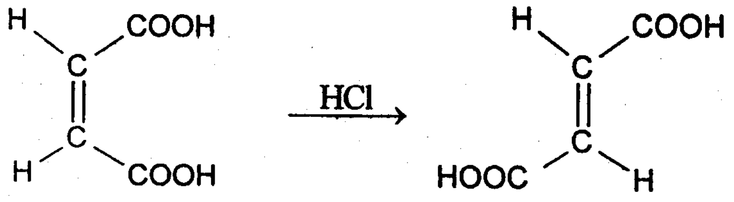


Trans - Isomer
Fumaric acid

In Fumaric acid the two carboxylic acids groups are present on the opposite sides of the double bond. It is trans - configuration.

Stability : Cis --Isomers are less stable while Trans -Isomers are more stable.

Ex : At room temperature in the presence of HCl less stable Maleic acid converts into more stable Fumaric acid.



Maleic acid
less stable

Fumaric acid
more stable

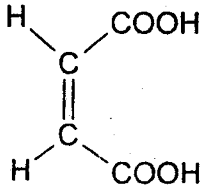
Dipolemoments :

Cis - Isomers are unsymmetrical. They show definite dipolemoment.

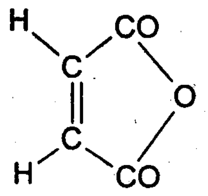
Trans - Isomers are symmetrical. ∴ They show zero dipolemoment.

Dehydration :

In Maleic acid both the -COOH groups are on the same side. It easily forms anhydride.

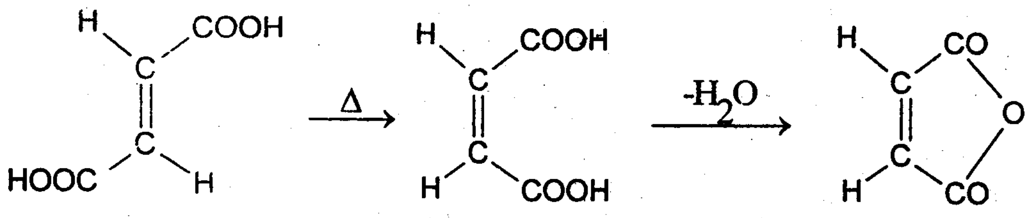


Maleic acid



Maleic anhydride

On heating Fumaric acid converts into Maleic acid and forms anhydride.



Fumaric acid
trans - isomer

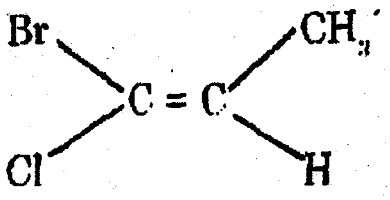
Maleic acid
cis - isomer

anhydride

Defect :

Cis, trans- nomenclature is failed when Alkenes have no identical substituents on the ends of the double bond.

Ex : 1 - bromo - 1 - chloro propene



4.4.12. E, Z - Configuration :

To solve the problem of compounds containing no identical substituents on the ends of the double bond. E, Z - configuration is introduced.

In E, Z - nomenclature the order of priority of atoms or groups attached directly to the double bonded carbon atoms is given by sequence rules. For this Cahn - Ingold - Prelog convention for chiral carbon atoms is used.

Sequence rules :

1. The atom of highest atomic number gets highest priority and that of the lowest atomic number gets lowest priority.

Ex : I > Br > Cl > F > O > N > C > H.

2. If two atoms attached to the double bonded carbon atom have same atomic number, then priority is given by comparing next atom in the group.

Ex : CH_3 CH_2- > CH_3-

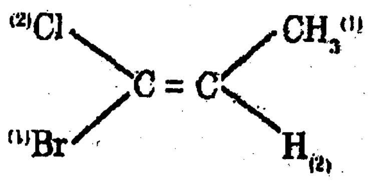
E - Isomer :

In E - Isomer the two atoms or groups of highest priority are on the opposite sides of the double bond.

In German, E = Entegen means opposite.

Ex : 1 - bromo - 1 - chloro propene

The order of priority is Br > Cl and CH_3 > H.

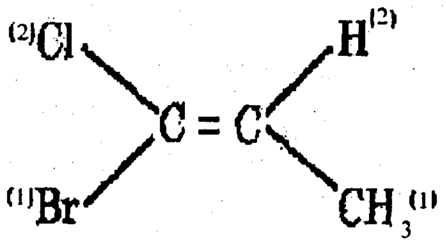


E - 1 - bromo - 1 - chloro propene

Here the highest priority Br and CH_3 are on the opposite sides of the double bond. Hence it is E-configuration.

Z - Isomer :

In Z - Isomer the two atoms or groups of highest priority are on the same side of the double bond. In German, Z = Zusammen means 'together'.



Z - 1 - bromo - 1 - chloro Propane

4.4.13. Model Questions :

1. What are enantiomers ? What are the necessary conditions for a compound to exhibit enantiomerism ? illustrate with the help of a suitable example.
2. Write notes on diastereo isomers and mesoisomers giving example.
3. Explain optical isomerism with suitable examples.
4. Explain Walden inversion.
5. Write Fischer projection formula of D – glyceraldehyde , L- alanine and L- tartaric acid.
6. Write the configurations of

   a) E- But - 2-ene

   b) Z- 2 – chloro but – 2 – ene
7. Explain resolution and recimisation with examples.
8. Write the optical isomers of Tartaric acid.

9. Assign R and S – configuration to

   a) glyceraldehyde

   b) Amino Propionic acid

10. Explain Racemisation and Asymmetric synthesis.

11. What are the sequence rules for determining absolute configuration of optically active molecule.

12. What is Chiral Centre ? Explain molecules with similar chiral carbons and molecules with dissimilar Chiral Carbons.

13. Explain asymmetric and dissymmetric molecules with examples.

14. Define homomers and isomers. Explain conformational and configurational isomerism with example.

15. Write about classification of isomers.

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UNIT - IV

Lesson - V

THEORY OF SEMI MICRO QUALITATIVE ANALYSIS

4.5.1 :

Principles involved - solubility product, common ion effect, classification and reactions of anions classification seperation and reactions of cations into groups - group reagents.

4.5.2. Semimicro qualitative analysis :

Semimicro qualitative analysis is the systematic identification of the constituents of materials using small amounts of 1ml or 0.1g of the material.

Advantages :

1. Reduced consumption of chemicals
2. Saving of time
3. Space required is also reduced.

4.5.3. Principles :

1. Solubility product.
2. Common ion effect.

1. Solubility product :

Solubility product is defined as the product of ionic concentrations of a sparingly soluble salt present in a solution at a given temperature.

Derivation :

Let us consider the saturated solution of a sparingly soluble salt AB.

$AB(s) \rightleftharpoons A^+ + B^-$

According to law of Mass Action,

$$K = \frac{[A^+][B^-]}{[AB]}$$

$K[AB] = [A^+][B^-]$.

At a given temperature [AB] is a constant in a saturated solution.

$\therefore$ K[AB] = K_s = $[A^+][B^-]$

Where K_s is called solubility constant.

Results :

1. In a saturated solution solubility product and ionic product are equal.

2. When ionic product exceeds solubility product, the solution is supersaturated and precipitation occurs.

3. When ionic product is less than solubility product, the solution is unsaturated and no "precipitation occurs.

2. Common ion effect :

The solubility of a sparingly soluble salt decreases in the presence of another salt with common ion. This effect is called common ion effect.

Ex : 1. The solubility of soap decreases in the presence of NaCl due to the common ion Na^+. So, soap is precipitated due to common ion effect. It is called salting out of soap.

$\underset{\text{Soap}}{RCOONa} \rightleftharpoons RCOO^- + Na^+$

$NaCl \rightleftharpoons Na^+ + Cl^-$

Here the common ion is Na^+

2. Ionisation of NH_4OH decreases in the presence of NH_4Cl due to the common ion NH_4^+

$NH_4OH \rightleftharpoons NH_4^+ + \overline{O}H$

$NH_4,Cl \rightleftharpoons NH_4^+ + Cl^-$

Here the common ion is NH_4^+

Applications of solubility product :

Precipitation of II and IV group metals as sulphides :

Solubility product of II group metal sulphides is less than that of IV group metal sulphides.

a) In the presence of HCl, ionisation of H_2S decreases due to common ion effect. Here the common ion is H^+.

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

$HCl \rightleftharpoons H^+ + Cl^-$

∴ The ionic product is greater than the solubility product of II group metal sulphides and less than that of the IV group metal sulphides. Hence only II group metal sulphides are precipitated in the presence of HCl.

b) In the presence of NH_4OH, $\bar{OH}$ ions remove H^+ ions.So, ionisation of H_2S increases. Now ionic product, exceeds the solubility product of IV group metal sulphides also.

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

$NH_4OH \rightleftharpoons NH_4^+ + \bar{OH}$

$H^+ + \bar{OH} \rightleftharpoons H_2O$

So, IV group metal sulphides are also precipitated in the presence of Ammonium hydroxide.

Precipitation of III group metals as hydroxides :

Solubility product of III group metal hydroxides is less than that of IV, V and VI group metal hydroxides.

In the presence of Ammonium chloride, ionisation of NH_4OH decreases due to common ion effect. Here the common ion is NH_4^+.

$NH_4OH \rightleftharpoons NH_4^+ + \bar{OH}$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

∴ Ionic product is greater than the solubility product of III group metal hydroxides and less than that of the IV, V and VI group metal hydroxides. Hence only III group metal hydroxides are precipitated.

4.5.4 Classification and reactions of anions :

Anions are generally classified in the following way.

1. Anions which evolve gases with dil. HCl.
2. Anions which evolve gases with conc. H_2SO_4.
3. Anions which can be identified by other reactions like precipitation.

a) Anions which evolve gases with dilute HCl :

This group is also known as carbonate group. This group includes carbonate. sulphide, sulphite, nitrite and Acetate. When these ions are treated with dilute HCl the following gases are evolved.

Anion **Gas evolved**

Before heating :

1.Carbonate (CO_3^{-2}) A colour less gas (CO_2) is evolved with quick effervescence

$$Na_2CO_3+2HCl \rightarrow 2NaCl + H_20 + CO_2 \uparrow$$

After heating :

2.Sulphide (S^{-2}) A colourless gas (H_2S) is evolved with rotten egg smell.

$$FeS+2HCl \rightarrow FeCl_2+H_2S \uparrow$$

3.Sulphite (SO_3^{-2}) A colourless gas (SO_2) is evolved with pungent smell.

$$Na_2SO_3+2HCl \rightarrow 2NaCl+H_2O+ SO_2 \uparrow$$

4. Nitrite (NO^-_2) Reddish brown gas (NO_2) is evolved.

$$NaNO_2+HCl \rightarrow NaCl+HNO_2$$

$$3HNO_2.+O_2 \rightarrow HNO_3+H_2O+2NO_2 \uparrow$$

5. Acetate (CH_3COO^-) Acetic acid vapours with smell of vinegar are evolved.

$$Pb(CH_3COO)_2 + 2HCl \rightarrow PbCl_2 + 2CH_3COOH$$

b) Anions which evolve gases with concentrated H_2SO_4 :

This group includes Chloride, Bromide, Iodide, Nitrate, Borate and organic acids (Acetate, Oxalate. Tartrate). When these ions are treated with Cone. H_2SO_4 the following gases are evolved.

Anion **Gas evolved**

Before heating :

1. Chloride (Cl^-) A colourless gas (HCl) is evolved with pungent smell.

$$NaCl+H_2SO_4 \rightarrow NaHSO_4+HCl \uparrow$$

2.Bromide (Br^-) Reddish brown vapours of Bromine (Br_2) are evolved.

$$2KBr + 3H_2SO_4 \rightarrow 2KHSO_4 + 2H_2O + SO_2 + Br_2 \uparrow$$

3.Iodide I^- Violet vapours of iodine (I_2) are evolved

$$8KI + 9H_2SO_4 \rightarrow 8KHSO_4+ 4H_2O + H_2S + 4I_2 \uparrow$$

After heating :

4. Nitrate (NO^-_3) — Reddish brown vapours of Nitrogen dioxide (NO_2) are evolved

$$4KN0_3 + 4H_2SO_4 \rightarrow 4KHSO_4, + 2H_20 + 4NO_2 \uparrow + O_2$$

5. Borate (BO_3^{-3}) — White fumes of Boric acid (H_3BO_3) are evolved

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 \uparrow + Na_2SO_4$$

6. Oxalate ($C_20_4^{-2}$) — Colourless gases of CO and CO_2 are evolved. CO burns with blue flame.

$$CaC_2O_4 + H_2,SO_4 \rightarrow CaSO_4 + H_2O + CO + CO_2 \uparrow$$

7. Tartrate ($C_4H_4\ O_6\ ^{-2}$) — The substance is charred with burning sugar smell CO and CO_2gases are evolved.

$$Na_2C_4H_4O_6 + H_2SO_4 \rightarrow Na_2SO_4 + \underset{\text{charring}}{2C} + CO + CO_2 + 3H_2O.$$

c). Anions which can be identified by precipitation reactions:

In regular course of analysis, precipitation tests are carried out by preparing sodium carbonate extract.

Preparation of Sodium Carbonate extract :

The substance is mixed three times with pure Sodium Carbonate. It is boiled for 5 minutes after adding distilled water and filtered. The filtrate is called Sodium Carbonate extract. It contains Anion as soluble Sodium salt.

Identification with Nitric Acid and Silver Nitrate solution :

The Sodium Carbonate extract is acidified with dil. $HN0_3$, and Silver nitrate solution is added in excess. It is filtered.

Residue	**Filtrate**
i) White precipitate insoluble in dil. HNO_3 and soluble in NH_3 is formed - chloride $NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$	i) Dilute ammonia is added drop by drop. Crimson red precipitate, is formed - Chromate $Na_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4 + 2NaNO_3$
ii) Whitish yellow precipitate. insoluble in dil. HNO_3 and soluble in NH_3 is formed -Bromide $NaBr + AgNO \rightarrow AgBr \downarrow + NaNO_3$	ii) Yellow precipitate is formed - phosphate $Na_3PO4 + 2AgNO_3 \rightarrow Ag_3PO_4 \downarrow + 2NaNO_3$
iii) Yellow precipitate, insoluble in dil. HNO_3 and insoluble in $NH._5$ is formed - Iodide.	iii) Chacolate brown precipitate is formed - Arsenate $Na_3.\ AsO_4 + 3\ AgNO_3 \rightarrow Ag_3AsO_4 \downarrow + 3NaNO_3$

Identification with HNO_3 and Ammonical $AgNO_3$ solution : (silver mirror test)

The extract is acidified with dilute Nitric acid and neutralized with dilute NH_3In another test tube Ammonia is added drop by drop to silver nitrate solution till a precipitate formed is almost dissolved, This solution is added to the neutralized solution and warmed.

Silver mirror is formed - Tartrate.

Identification with dilute HCl and $BaCl_2$ solution :

The extract is acidified with dilute HCl and $BaCl_2$ solution is added. It is filtered.

Residue	**Filtrate**
i) A white precipitate insoluble in excess HCl is formed - Sulphate	i) It is cooled and neutralized with NH_3 Yellow precipitate insoluble in acetic acid is formed - chromate
$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + 2NaCl$.	$Na_2CrO_4 + BaCl_2 \rightarrow BaCrO_4 + 2NaCl$

d) Identification with Acetic acid and $CaCl_2$ solution:

The extract is acidified with acetic acid and $CaCl_2$ solution is added. A white precipitate is formed - Sulphate or oxalate.

Test for oxalate : The precipitate is heated with dil. H_2SO_4 and few drops of dil. $KMnO_4$ solution are added.

Permanganate colour is decolourised - oxalate.

$$CaC_2O_4 + H_2SO_4 + (O) \rightarrow CaSO_4 + H_2O + 2CO_2$$

Identification with Acetic acid and $FeCl_3$ solution :

The extract is acidified with Acetic acid and $FeCl_3$ solution is added. A whitish yellow precipitate is formed - phosphate.

$$Na_3PO_4 + FeCl_3 \rightarrow FePO_4 \downarrow + 3NaCl.$$

Identification with H_2SO_4 and $FeSO_4$ solution : (Brown ring test) :

The extract is acidified with dil. H_2SO_4 and freshly prepared Ferrous sulphate solution is added. Then Conc. H_2SO_4 is added slowly by the sides of the test tube. A brown ring (Ferrous Nitrnso sulphate [$Fe(NO)SO_4$] is formed at the junction of the two layers - Nitrate.

$$6FeSO_4 + 2NaNO_3 + 5H_2SO_4 \rightarrow 2NaHSO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO \rightarrow Fe(NO)SO_4$$

4.5.5. Separation and reactions of cations in to groups :

Preparation of original solution : Original solution is prepared by dissolving the salt in water or dilute hydrochloric acid either in cold or in hot.

Group NO	Group reagent	Identification of group	Identification of cation
I.	Original solution + dil HCl	Precipitate is formed I group present	White - Silver - Ag+, Mercurous Hg+ or Lead Pb^{+2}

$$AgNO3 + HCl \rightarrow AgCl \downarrow + HNO_3$$

$$Pb(NO_3)_2 + 2HCl \rightarrow PbCl_2 \downarrow + 2HNO_3$$

Group NO	Group reagent	Identification of group	Identification of cation
II.	Original Solution + dil. HCl + H_2S gas.	Precipitate is formed- II group present.	Black - Mercuric mercury, Hg^{+3} Lead Pb^{+2} or Copper Cu^{+2}. Yellow - Cadmium Cd^{+2} or Arsenic. Brown - Bismuth Bi^{+3} Orange - Antimony Sb^{+3} red.

$$CuSO_4 + H_2S \rightarrow CuS \downarrow + H_2SO_4$$

$$CdCl_2 + H_2S \rightarrow CdS \downarrow + H_2SO_4$$

$$2BiCl_3 + 3H_2S \rightarrow Bi_2S_3 \downarrow + 6HCl$$

$$PbCl_2 + H_2S \rightarrow PbS \downarrow + 2HCl$$

$$2SbCl_3 + 3H_2S \rightarrow Sb_2S_3 \downarrow + 6HCl$$

Group NO	Group reagent	Identification of group	Identification of cation
III.	Original Solution $+NH_4Cl + NH_4OH$ in excess.	Precipitate is formed III group present.	White - Aluminium Al^{+3} Green - Chromium Cr^{+3} Light green - ferrous Fe^{+2} Brown - Feric Fe^{+3}

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 \downarrow + 3NH_4Cl$$

$$FeSO_4 + 2NH_4OH \rightarrow Fe(OH)_2 \downarrow + (NH_4)_2SO_4$$

$$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 \downarrow + 3NH_4Cl$$

$$CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 \downarrow + 3NH_4Cl$$

IV.	Orginal solution + NH_4Cl+ NH_4OH + H_2S gas	Precipitate is formed IV group present	Black - Cobalt CO^{+2} or Nickel Ni^{+2} Flesh - Manganese Mn^{+2} White - Zinc Zn^{+2}

$$COCl_3 + H_2S \rightarrow COS\downarrow + 2HCl$$

$$NiSO_4 + H_2S \rightarrow NiS\downarrow + H_2SO_4$$

$$MnCl_2 + H_2S \rightarrow MnS\downarrow + 2HCl$$

$$ZnSO_4 + H_2S \rightarrow ZnS\downarrow + H_2SO_4$$

V.	Original solution + NH_4 Cl + NH_4OH + $(NH_4)_2CO_3$	Precipitate is formed V group present	White - Barium, Ba^{+2}, Strontium, Sr^{+2} or Calcium Ca^{+2}

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3\downarrow + 2NH_4Cl$$

$$SrSO_4 + (NH_4)_2CO_3 \rightarrow SrCO_3\downarrow + (NH_4)_2SO_4$$

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4Cl$$

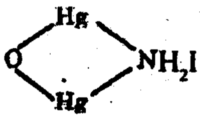
VI.	No Special reagent	VI group	Ammonium NH_4^+ Magnesium, Mg^{+2} Potasssium, K^+ Sodium Na^+

4.5.5.1. Identification of Ammonium (NH_4^+) :

a) The salt is heated with NaOH. A colourless gas Ammonia (NH_3) with smell of Ammonia is evolved - Ammonium NH_4^+.

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3\uparrow$$

b) The salt is warmed with NaOH and Nessler's reagent. A brown preciptate is formed Ammonium NH_4^+

$NH_4Cl + 4NaOH + 2K_2HgI_4 \rightarrow$  $\downarrow + 3NaI + NaCl + 4KI + 3H_2O$

4.5.6. Some Special tests :

1. Chromyl chloride test :

The chloride salt is heated with potassium dichromate salt and Conc. sulphuric acid. Red vapours of chromyl chloride (CrO_2Cl_2) are evolved. An yellow precipitate of Lead chromate is formed when the vapours are passed into Lead acetate solution.

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 4NaH\,SO_4 + 2KHSO_4 + 2CrO_2\,Cl_2 \uparrow + 3H_2O$$

2. Ammonium Molybdate Test :

The phosphate salt is heated with cone. Nitric acid and excess of Ammonium Molybdate. A canary yellow precipitate of Ammonium phosphomolybdate is formed.

$$Na_2HPO_4 + 12(NH_4)_2\,M_0O_4 + 23HNO_3 \rightarrow$$

$$(NH_4)_3\,[PMO_{12}O_{40}] \downarrow + 21NH_4NO_3 + 2NaN0_3 + 12H_2O$$

3.Ethyl Borate test :

The Borate salt is heated with few drops of Ethyl alcohol and Conc. Sulphuric acid. Ethyl borate vapours are evolved. They burnt with green flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$$

$$H_3BO_3 + 3C_2H_5OH \rightarrow B(OC_2H_5)_3 \uparrow + 3H_2O$$

4. Copper turnings tests :

The Nitrate salt is heated with copper turnings and Conc. sulphuric acid. Reddish brown vapours of Nitrogen dioxide (NO_2) are evolved.

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 \uparrow + 2H_2O$$

5. Manganese dioxide test :

The salt is treated with Manganese dioxide and Conc. suiphuric acid.

a) Greenish yellow chlorine (Cl_2) gas is evolved.

$$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2 \uparrow$$

b) Reddish brown vapours of Bromine (Br_2) are evolved.

$$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow$$

c) Violet vapours of Iodine (I_2) are evolved.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2 \uparrow$$

6. Golden yellow spangles test :

Potassium iodide solution is added to the Lead salt solution. An yellow precipitate of Lead Iodide is formed. It is dissolved in hot water and cooled. Golden yellow spangles are formed.

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2\downarrow + 2KNO_3$$

c) Violet vapours of iodine (I_2) are evolved.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$

7, Distinction between Ferrous an Ferric salts :

S.NO	Reagent	Ferrous salt (Fe^{+2})	Ferric Salt (Fe^{+3})
1.	Potassium Ferrocyanide solution	Light blue precipitate	Prussian blue precipitate
2.	Potassium Ferricyanide solution	Deep blue precipitate	No precipitate
3.	Ammonium Thiocyanate solution	No colour	Blood red colour
4.	Ammonia solution	Light green precipitate	Brown Precipitate

8. Ash test :

A filter paper is dipped in the salt solution and burnt to ash after adding a drop of cobalt nitrate solution.

a) Aluminum salts gave Thenald's blue ash

$$CoO + Al_2O_3 \rightarrow Co(Al_2O_2)_2$$

b) Zinc salts gave Rinmann's green ash.

$$CoO + ZnO \rightarrow CoZnO_2$$

9. Flame test :

The salt is made into paste with cone. Hydrochloric acid on a watch glass. It is introduced into non-luminous flame by a platinum wire. The colour of the flame is observed.

Bluish green	Copper
Bright green	Boron
Apple green	Barium
Flashes of green	Zinc
Crimson red	Strontium
Brick red	Calcium
Lilacviolet	Potassium.

The paste is made with Conc. HCl because chlorides are volatile salts.

4.5.6. Model Questions :

1. What are the principles involved in semimicro qualitative Analysis ?
2. Discuss the precipitation of II nd group and IV group metal sulphides in qualitative analysis.
3. Explain the chemistry involved in the test of the following.
   a) Sulphate
   b) Nickel
   c) Phosphate
   d) Ammonium
4. What is solubility product ? What are its applications in the qualitative analysis ?
5. Explain
   a) Chromyl Chloride test
   b) brown ring test
   c) golden spangles test
   d) flame test
6. What is sodium carbonate extract ? How does it help in identifying the anions ? Why potassium carbonate cannot be used in place of sodium carbonate?

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PRACTICAL
MANUAL

CONTENTS

PREPARATIONS :

SEMI MICRO QUALITATIVE ANALYSIS

Qualitative analysis deals with the analysis of quality of a mixture or a salt in general. Depending upon the amount of sample used, qualitative analysis is classified into different types namely macro analysis (0.1 - 1 gm or about 10 ml) ; semi micro analysis (0.01 - 0.1 gm or about 1ml) ; micro - analysis (0.001 - 0.01 gm or about 0.1 ml) and ultra - micro analysis (less than 1mg). In semi micro analysis, greater speed fo analysis is achieved by using smaller quantities of samples and saving of time in carrying out the operations like filtration, washing, evaporation etc.

Test tubes of volume 4 ml - 8 ml should be used for performing the tests.

Droppers are to be used for handling the liquids during the analysis. In semi micro technique, the precipitate is separated from a solution, by means of a centrifuge. The precipitate particles known as residue will settle at the bottom of the centrifuge tube. The supernatant liquid present over the residue is called the centrifugate. The centrifugate is removed from the residue by means of a capillary tube.

REACTIONS OF ANIONS :

Dry Tests :

Reactions of Carbonate (CO_3^{2-}) :

Normal carbonates of only Na^+; K^+ and NH_4^+ are soluble in water.

	EXPERIMENT	OBSERVATION
1.	To a pinch (10mg) of the carbonate, few drops of dil. Hcl is added, drop wise.	1. A colourless, odourless gas of CO_2 is evolved with quick effer vescence.
	$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$	
	a) A buring splinter is exposed to the gas. b) The gas is passed into lime water.	a) The buring splinter is put out. b) The lime water turned milky due to the formation of insoluble calcium carbonate.
	$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$	
	c) More of CO_2 gas is passed into the above milky solution.	c) The solution again became colourless due to the formation of soluble calcium bi carbonate.
	$\underset{\text{Insoluble}}{CaCO_3 + H_2O + CO_2} \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$	
2.	To the solution of carbonate, few drops of $BaCl_2$ solution is added.	2. White Precipitate of barium crbonate soluble in dil. HCl is formed.
	$Na_2CO_3 + BaCl_2 \rightarrow BaCO_3\downarrow + 2NaCl$ $BaCO_3 + 2HCl \rightarrow BaCl_2 + H_2O$	

Reactions of Chloride ion (Cl^-) :

<table>
<tr><th></th><th>EXPERIMENT</th><th>OBSERVATION</th></tr>
<tr><td>1.</td><td>A Pinch of the chloride salt is treated with few drops of conc. H_2SO_4.</td><td>1. Hydrogen chloride gas with pungent odour is evolved.</td></tr>
<tr><td colspan="3">$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$</td></tr>
<tr><td></td><td>a) A glass rod dipped in NH_4OH solution is exposed to the gas.</td><td>a) Dense white fumes of NH_4Cl are given out</td></tr>
<tr><td colspan="3">$NH_4OH + HCl \rightarrow NH_4Cl \uparrow + H_2O$</td></tr>
<tr><td></td><td>b) A glass rod dipped in AgNO3 solution is exposed to the gas.</td><td>b) A white curdy precipitate of AgCl is formed.</td></tr>
<tr><td colspan="3">$AgNO_3 + HCl \rightarrow AgCl + HNO_3$</td></tr>
<tr><td>2.</td><td>A small amount of the salt is mixed with MnO_2 and few drops of Conc. H_2SO_4 and then heated.</td><td>2. Greenish yellow gas of chlorine Cl_2 with pungent smell is evolved.</td></tr>
<tr><td colspan="3">$2NaCl + MnO_2 + 2H_2SO_4 \rightarrow NaHSO_4 + MnSO_4 + H_2O + Cl_2\uparrow$</td></tr>
<tr><td>3.</td><td>A small quantity of the salt is mixed with an equal amount of potassium dichromate ($K_2Cr_2O_7$) crystals and few drops of conc.H_2SO_4 and then warmed.</td><td>3. Orange red vapours of chromyl chloride (CrO_2Cl_2)are evolved.</td></tr>
<tr><td colspan="3">$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2CrO_2Cl_2\uparrow + 2KHSO_4 + 4NaHSO_4 + 3H_2O$</td></tr>
<tr><td></td><td>The above vapours are passed through NaOH solution and then lead acetate solution is added.</td><td>Yellow precipitate of lead chromate is formed.</td></tr>
<tr><td colspan="3">$CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$
$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow PbCrO_4 + 2CH_3COONa$</td></tr>
<tr><td>4.</td><td>The salt solution is treated with silver nitrate solution.</td><td>4. White curdy precipitate of silver chloride is formed.</td></tr>
</table>

Reactions of Bromide ion (Br^-) :

<table>
<tr><th></th><th>EXPERIMENT</th><th>OBSERVATION</th></tr>
<tr><td>1.</td><td>A small quantity of the salt is treated with few drops of conc. H_2SO_4.</td><td>1. Reddish brown vapours of bromine together with hydrogen bromide gas are evolved. The solution turned reddish brown.</td></tr>
<tr><td></td><td colspan="2">$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr\uparrow$
$2HBr + H_2SO_4 \rightarrow 2H_2O + 2SO_2 + Br_2\uparrow$</td></tr>
<tr><td></td><td>a) A rod dipped in $AgNO_3$ solution is exposed to the vapours.</td><td>a) Pale yellow precipitate of Ag Br is formed.</td></tr>
<tr><td></td><td colspan="2">$AgNO_3 + HBr \rightarrow AgBr\downarrow + HNO_3$</td></tr>
<tr><td>2.</td><td>A small quantity of the salt is mixed with MnO_2 and few drops of Conc. H_2SO_4 are added and warmed.</td><td>2. Orange red vapours of bromine with pungent smell are evolved.</td></tr>
<tr><td></td><td colspan="2">$2KBr + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2\uparrow$</td></tr>
<tr><td>3.</td><td>The salt solution is treated with few drops of $AgNO_3$ solution.</td><td>3. Pale yellow precipitate of AgBr is formed.</td></tr>
<tr><td></td><td colspan="2">$KBr + AgNO_3 \rightarrow KNO_3 + AgBr\downarrow$</td></tr>
<tr><td>4.</td><td>The salt solution is treated with few drops of lead acetate solution.</td><td>4. A white precipitate of $PbBr_2$ is formed which is soluble in hot water.</td></tr>
<tr><td></td><td colspan="2">$2KBr + (CH_3COO)_3 Pb \rightarrow PbBr_2 + 2(CH_3COO)K$</td></tr>
<tr><td>5.</td><td>The salt solution is mixed with chlorine water and few ml of carbon tetra chloride and then the mixture is shaken well.</td><td>5. Orange layer is formed, due to the dissolution of Br_2 in CCl_4.</td></tr>
<tr><td></td><td colspan="2">$2KBr + Cl_2 \rightarrow 2KCl + Br_2$</td></tr>
</table>

Reactions of Iodide ion (I^-) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the salt is warmed with few drops of conc. H_2SO_4.	1. Hydrogen iodide gas and violet vapours o iodine are evolved. Black solid is formed.
	$KI + H_2SO_4 \rightarrow KHSO_4 + HI\uparrow$ $2HI + H_2SO_4 \rightarrow 2H_2O + SO_2 + I_2\uparrow$	
2.	A small quantity of the salt is mixed with MnO_2 and few drops of Conc. H_2SO_4 are added and heated.	2. Violet vapours of iodine are evolved.
	$2KI + MnSO_4 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$	
3.	The salt solution is treated with few drops of $AgNO_3$ solution.	3. Yellow precipitate of AgI is formed which is insoluble in NH_4OH and HNO_3
	$KI + AgNO_3 \rightarrow KNO_3 + AgI\downarrow$	
4.	The salt solution is mixed with chlorine water and few ml of carbon tetra chloride and then the mixture is shaken well.	4. Violet coloured CCl_4 layer is formed.
	$2KI + Cl_2\text{ (water)} \rightarrow 2KCl + I_2$	

Reactions of Nitrate ion (NO_3^-) :

	EXPERIMENT	OBSERVATION
1.	The salt is heated in a dry test tue	1. Brown vapours of NO_2 are evolved in the case of nitrates of heavy metals like lead, copper etc.
	$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$	
2.	A small quantity of the salt is heated with few drops of conc.H_2SO_4	2. Brown vapours of NO_2 are evolved.
	$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ $4HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2$	
3.	A small quantity of the salt is mixed with copper turnings and few drops of Conc. H2SO4 and then heated.	3. Brown vapours of NO_2 are evolved. The solution turned to blue colour due to the formation of cupric nitrate.
	$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$	

Reactions of Borates (BO_3^{3-}) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the salt is heated in a dry test tube.	1. Some borates swell on heating.
2.	A small amount of borate salt is heated with conc.H_2SO_4	2. White fumes of boric acid are evolved.
	$Na_3B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$	
3.	**Ethyl borate test :** A Pinch of the salt is heated with few drops of ethyl alcohol and few drops of Conc H_2SO_4 and the vapours are exposed to the flame.	3. A green edged flame is observed. Ethyl borate is formed in the reaction.
	$H_3BO_3 + 3C_2O_5OH \rightarrow B(OC_2H_5)_3 + 3H_2O$	
4.	**Boron trifluoride test :** The salt is mixed with equal amount of calcium fluoride (CaF_2) and made into a paste with few drops of conc.H_2SO_4. This paste is taken on to a glass rod and kept very close to the non luminous flame near the base of the burner.	4. Green edged flame due to the formation o volatile boron trifluoride is observed.
	$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$ $Na_2B_4O_7 + H_2SO_4 \rightarrow 2B_2O_3 + Na_2SO_4 + 2H_2O$ $B_2O_3 + 6HF \rightarrow BF_3 + 3H_2O$	

Reactions of Acetate (CH_3COO^-) :

	EXPERIMENT	OBSERVATION
1.	To a small quantity the salt, few drops of dill.HCl is added and warmed.	1. Acetic acid with the smell of vinegar is given.
	$CH_3COONa + HCl \rightarrow NaCl + CH_3COOH$	
2.	A small amount of the salt is rubbed with oxalic acid and few drops of water in a watch glass.	2. Smell of vinegar is observed.
3.	To a small amount of acetate salt, few drops of conc. H_2SO_4 is added and warmed.	3. Acetic acid vapour with smell of vinegar is evolved.
	$CH_3COONa + H_2SO_4 \rightarrow CH_3COOH + NaHSO_4$ $2CH_3COONa + H_2SO_4 \rightarrow 2CH_3COOH + Na_2SO_4$	

Ethyl acetate test : A small quantity of the acetate salt is warmed with few drops of conc.H2SO4 and few drops of ethyl alcohol and then poured into a beaker full of water.	A fruity odour like that of an apple is obsered. This is due the formation of ethyl acetate.
$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$	
Amyl acetate test : To a small quantity of the acetate salt, few drops of Conc. H_2SO_4 few drops of amyl alcohol are added and warmed and then, the mixture is poured into a beaker full of water.	A fruity odour like that of banana is observed, due to the formation of amyl acetate.

Reactions of Sulphate (SO_4^{2-}) :

	EXPERIMENT	OBSERVATION
1.	The salt solution is treated with $BaCl_2$ solution.	1. A White precipitate of $BaSO_4$ is formed.
	$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2\ NaCl$	
2.	The salt solution is treated with lead acetate solution.	2. A white precipitate of lead sulphate is formed.
	$Na_2SO_4 + Pb(CH_3COO)_2 \rightarrow PbSO_4 + 2\ CH_3COONa$	

Reactions of Oxalates ($C_2O_4^{2-}$) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the oxalate salt is heated with few drops of Conc. H_2SO_4.	1. A mixture of CO and CO_2 gases are evolved.
	$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$ $H_2C_2O_4 \rightarrow H_2O + CO + CO_2$	
2.	A small quantityof the oxalate salt is mixed with MnO_2 and dil. H_2SO_4 and warmed.	2. CO_2 gas with effervescence is evolved.
	$Na_2C_2O_4 + 2\ H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + 2CO_2$	
3.	Salt solution is treated with $CaCl_2$ solution.	3. A white crystalline precipitate of calcium oxalate is formed insoluble in acetic acid an soluble in dil. H_2SO_4
	$Na_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 + 2\ NaCl$	

Reactions of Tartrate ($C_4H_4O_6^{2-}$) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the salt is heated in a dry test tube	1. Charring took place with the smell of burn sugar.
2.	A small amount of the tartrate salt is heated with few drops of Conc. H_2SO_4	2. Charring took place with the smell of burn sugar.
	$H_2C_4H_4O_6 \xrightarrow{H_2SO_4} CO_2 + CO + 2C + 3H_2O$	
3.	The salt solution is treated with silver nitrate solution.	3. A white precipitate of silver tartrate is formed, soluble in dilute HNO_3 and in ammonium hydroxide.
4.	The salt solution is treated with calcium chloride solution.	4. A white precipitate of calcium tartrate is formed which is soluble in acetic acid.
	$CaCl_2 + H_2C_4H_4O_6 \rightarrow 2HCl + Ca(C_4H_4O_6)\downarrow$	
5.	To a few drops of salt solution, few ml of dilute H_2SO_4 and a very small amount of resorcinol are added and warmed. After cooling the solution few drops of Conc. H_2SO_4 is added from the sides of the test tube.	5. A white precipitate of calcium tartrate is formed which is soluble in acetic acid.

Reactions of Phosphate ($PO_4)^{3-}$:

	EXPERIMENT	OBSERVATION
1.	To a solution of phosphate, few drops of conc.HNO_3 and excess of ammonium molybelate are added.	1. A canary yellow precipitate of ammonium phosphomolybdate is formed.
2.	$BaCl_2$ solution is added to the salt solution.	2. White precipitate of secondary barium phosphate, $BaHPO_4$ is formed. The precipitate is soluble in dilute mineral acids and acetic acid.
	$Na_2HPO_4 + BaCl_2 \rightarrow BaHPO_4 + 2NaCl$	
3.	A few ml of magnesia mixture ($MgSO_4$ + NH_4Cl + NH_4OH) is added to the salt solution.	3. A white crystalline precipitate of magnesium ammonium phosphate is formed.
	$Na_2HPO_4 + MgSO_4 + NH_4OH \rightarrow MgNH_4PO_4\downarrow + Na_2SO_4 + H_2O$	
4.	To the salt solution ferric chloride solution is added.	4. A light yellow precipitate of ferric phosphate is formed.
	$Na_2HPO_4 + FeCl_3 \rightarrow FePO_4 + 2NaCl + HCl$	

Reactions of Chromate (CrO_4^{2-}) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the chromate salt is heated with Conc. HCl.	1. Green solution of chromic chloride is formed.
2.	The salt solution is treated with $BaCl_2$ solution.	2. Pale yellow precipitate of barium chromate is formed.
	$K_2CrO_4 + BaCl_2 \rightarrow BaCrO_4 \downarrow + 2\ KCl$	
3.	The salt solution is treated with $AgNO_3$ solution.	3. Scarlet or deep red precipitate of silver chromate is formed. The precipitate is soluble both in dilute HNO_3 and NH_4OH
	$K_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4 \downarrow + 2\ KNO_3$	
4.	The salt solution is treated with lead acetate solution.	4. yellow precipitate of lead chromate is formed. The precipitate is insoluble in acetic acid.
	$K_2CrO_4 + Pb(CH_3COO)_2 \rightarrow PbCrO_4 \downarrow + 2CH_3COO\ K$	
5.	A small amount of chromate salt is mixed with equal amount of NaCl. The mixture is then treated with few drops of Conc. H2SO4 and warmed gently.	5. Reddish brown vapours of chromyl chloride are evolved.

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.	a) A white curdy precipitate of AgCl which is soluble in NH_4OH and insoluble in HNO_3 is formed.	Chloride, $\bar{Cl}$
		b) A Pale yellow precipitate of AgBr which is sparingly soluble in NH_4OH and insoluble in HNO_3 is formed.	Bromide, $B\bar{r}$
		c) An yellow precipitate of Ag I which is insoluble both in NH_4OH and HNO_3 is formed.	Iodide is confirmed.
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.	A brown ring ($FeSO_4.NO$) is formed at the junction of two layers.	Nitrate is confirmed
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.	Red coloured solution which on boiling gives red precipitate.	Acetate is confirmed
4	**Test for oxalate :**		
	a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.	A white precipitate of calcium oxalate is formed.	
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.	The $KMnO_4$ solution is decolourised.	Oxalate is confirmed

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.	A silver mirror is formed on the inner walls of the test tube.	Tartrate is confirmed.
6	**Test for phosphate :**		
	a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added.	white crystalline precipitate is formed	Phosphate is confirmed
	b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.	Light yellow precipitate is formed	
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.	A white precipitate of $BaSO_4$ which is insoluble in Conc. HCl is formed.	Sulphate is confirmed

Interfering anions - their Elimination :

Elimination of oxalates and tartrates :

These are eliminated by ignition of the mixture in a china dish for about twenty to thirty minutes.The residue is cooled and digested with dil. HCl and centrifuged. The centrifugate is taken as original solution and tested for cations using group analysis.

Elimination of Chromates :

The given mixture is taken in a china dish and boiled with conc. HCl until the solution is perfectly green. The solution is diluted with water and taken as original solution for group analysis.

If chromate is present as anion, chromium cation is identified in the third group as blue precipitate of $Cr(OH)_3$ in addition to the normal two cations present in the mixture.

Elimination of Phosphates :

If phosphate is present in the mixture, cation iron is to be tested in the solution from the second group. The remaining part of the solution is treated with excess of NH_4Cl and NH_4OH is added drop wise till the smell of ammonia is observed. Then it is neutralised with 6N acetic acid and then neutral ferric chloride solution is added drop wise till reddish brown precipitate is formed. It is centrifused. The residue is tested for III group cations and the centrifugate is tested for further groups cations.

Alternative method :

The cetrifugate from group II is taken in a test tube and boiled to expel H2S gas. 1-2 drop of Conc. HNO_3 is added, boiled gently for 2 minutes. To this, few ml of distilled water, 2 drops of NH_4Cl solution and 2-3 drops of Zirconium. nitrate reagent are added, warmed on a water bath for 2 minutes and centrifuged. Tested for completeness of the precipitate by adding a drop of zirconium nitrate reagent to the centrifugate. (If precipitate forms, centrifuge again and repeat the process until the addition of one drop of the reagent to the centrifugate gives no precipitate). If is heated on a boiling water both and centrifuged.

Reactions of Cations :

Reactions of Group I Cations (Pb^{2+}, Hg^{+}, Ag^{+}) :

Reactions of lead ion (Pb^{2+}) :

	EXPERIMENT	OBSERVATION
1.	The salt is dissolved in dil. HNO_3 and is treated with few drops of dil. HCl.	1. white precipitate of $PbCl_2$ which is soluble in boiling water is formed.
	$Pb(NO_3)_4 + 2HCl \rightarrow PbCl_2 + 2\,HNO_3$	
2.	The salt solution is treated with potassium iodide solution.	2. Yellow precipitate of lead iodide is formed. The precipitate is soluble in boiling water and on sudden cooling PbI_2 reappeared as golden yellow spangles.
	$Pb(NC_3)_2 + 2KI \rightarrow PbI_2\downarrow + 2\,KNO_3$	
3.	The salt solution is treated with potassium chromate solution.	3. Yellow precipitate of $PbCrO_4$ which is soluble in HNO_3 is formed.
	$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2\,KNO_3$	

Reactions of Group II Cations :

Reactions of Group IIA Cations - Copper group.

Reactions of Mercuric ion (Hg^{2+}) :

	EXPERIMENT	OBSERVATION
1.	To the salt solution dil. HCl is added.	1. No precipitate is formed.
2.	The salt solution is treated with NH_4OH solution.	2. White precipitate is formed.
	$HgCl_2 + NH_4OH \rightarrow (HgNH_2Cl)\downarrow + HCl + H_2O$	
3.	To the salt solution KI solution is added.	3. Red precipitate of mercuric iodide which is soluble in excess of KI is formed.
	$HgCl_2 + 2KI \rightarrow HgI_2\downarrow + 2KCl$ $HgCl_2 + KI \rightarrow KHgI_3$	
4.	The salt solution is treated with stannous chloride solution.	4. White precipitate which finally changed to gray precipitate of Hg is formed.
	$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + 2Hg_2Cl_2\downarrow$ $Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + 2Hg\downarrow$	

Reactions of Cupric ion (Cu^{2+}) :

	EXPERIMENT	OBSERVATION
1.	The salt solution is treated with NaOH solution.	1. Pale blue precipitate of $Cu(OH)_2$ which is insoluble in excess of NaOH is formed.
	$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2\downarrow + Na_2SO_4$	
2.	To the salt solution NH_4OH solution is added.	2. Pale blue precipitate of Cu $(OH)_2$ which is soluble in excess of NH_4OH is formed.
	$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$ $Cu(OH)_2 + 4NH_4OH \rightarrow [Cu(NH_3)_4(OH)_2] + 4H_2O$	
3.	H_2S is passed through the salt solution.	3. Black precipitate of Cu S is fromed.
	$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$	
4.	The salt solution is treated with Potassium ferro cyanide solution.	4. Chacolate brown precipitate which is soluble in NH_4OH is formed.
	$2CuSO_4 + K_4Fe(CN)_6 \rightarrow Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4$	

Reactions of Cadmium ion (Cd^{2+}) :

<table>
<tr><th></th><th>EXPERIMENT</th><th>OBSERVATION</th></tr>
<tr><td>1.</td><td>To the salt solution NaOH solution is added.</td><td>1. white precipitate of Cd $(OH)_2$ is formed.</td></tr>
<tr><td></td><td colspan="2">$CdSO_4 + 2NaOH \rightarrow CdOH)_2\downarrow + Na_2SO_4$</td></tr>
<tr><td>2.</td><td>The salt solution is treated with NH_4OH solution.</td><td>2. white precipitate of Cd $(OH)_2$ which is soluble in excess of NH_4OH is formed.</td></tr>
<tr><td></td><td colspan="2">$CdSO_4 + 2NH_4OH \rightarrow Cd(OH)_2 + (NH_4)_2SO_4$</td></tr>
<tr><td>3.</td><td>H_2S is passed into the salt solution.</td><td>3. yellow precipitate of Cd S which is souble in HNO_3 is formed.</td></tr>
<tr><td></td><td colspan="2">$CdSO_4 + H_2S \rightarrow CdS \downarrow + H_2SO_4$</td></tr>
</table>

Reactions of Bismuth ion (Bi^{3+}) :

<table>
<tr><th></th><th>EXPERIMENT</th><th>OBSERVATION</th></tr>
<tr><td>1.</td><td>The salt solution is treated with NaOH solution.</td><td>1. White precipitate of $Bi(OH)_3$ which is insoluble in excess of NH_4OH is formed.</td></tr>
<tr><td></td><td colspan="2">$Bi\ (NO_3)_3 + 3NH_4OH \rightarrow Bi(OH)_3 + 3NH_4NO_3$</td></tr>
<tr><td>2.</td><td>To the salt solution added dil. HCl and passed H_2S gas.</td><td>2. Dark brown precipitate of Bi_2S_3 is formed</td></tr>
<tr><td></td><td colspan="2">$2Bi\ (NO_3)_3 + 3H_2S \rightarrow Bi_2S_3 \downarrow + 6HNO_3$</td></tr>
<tr><td>3.</td><td>To the salt solution excess of KI solution is added.</td><td>3. Black Bi I_3 precipitate is formed which gradually changed to orange yellow coloured solution.</td></tr>
<tr><td></td><td colspan="2">$Bi\ (NO_3)_3 + 3KI \rightarrow Bi\,I_3 \downarrow + 3KNO_3$
$Bi\ I_3 + KI \rightarrow K\,Bi\,I_4$</td></tr>
<tr><td>4</td><td>NaOH solution is added drop wise to stannous chloride solution till the precipitate of stannous hydroxide fromed is just dissolved. The solution so formed is known as sodium stannite solution. To this solution, bismuth salt solution is added dropwise.</td><td>4. A black white precipitate of bismuth is formed</td></tr>
<tr><td></td><td colspan="2">$SnCl_2 + 2NaOH \rightarrow Sn(OH)_2 + 2\ NaCl$
$Sn(OH)_2 + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O$
$2Bi(OH)_3 \rightarrow Bi_2O_3 + 3H_2O$
$Bi_2O_3 + 3Na_2SnO_2 \rightarrow 2Bi \downarrow + 3Na_2SnO_3$</td></tr>
</table>

Reactions of Group IIB Cations - Tin group.

Reactions of Arsenic ion (As^{3+}) :

	EXPERIMENT	OBSERVATION
1.	As_2O_3 is dissolved in NaOH and H_2S gas is passed in presence of dil. HCl	1. Yellow precipitate of As_2S_3 is formed.
	$AS_2O_3 + 3H_2S \rightarrow AS_2S_3 \downarrow + 3H_2O$	

Reactions of Antimony ion (Sb^{3+}) :

	EXPERIMENT	OBSERVATION
1.	H_2S gas in passed into the salt solution in presence of dil HCl.	1. Orange red precipitate of Sb_2S_3 is formed.
2.	The antimony chloride, $SbCl_3$ is shaken with H_2O	2. Basic chloride of the metal is precipitated.
	$SbCl_3 + H_2O \rightarrow SbOCl \downarrow + 2\ HCl$	

Reactions of Stannous ion :

	EXPERIMENT	OBSERVATION
1.	H_2S gas in passed into the stannous chloride solution in presence of dil HCl.	1. Brown precipitate of Sn S is formed.
2.	To the stannous salt solution, mercuric chloride solution is added.	2. white precipitate of mercurous chloride is formed.

Reactions of Group III Cations :

Reactions of Aluminium ion (Al^{3+}) :

	EXPERIMENT	OBSERVATION
1.	NH_4OH solution is added to the salt solutioin.	1. white gelatinous precipitate of Al $(OH)_3$ is formed.
	$Al\,Cl_3 + 3NH_4OH \rightarrow Al\,(OH)_3\downarrow + 3NH_4Cl$	
2.	NaOH solution is added to the salt solution.	2. white gelatinous precipitate of Al $(OH)_3$ which is soluble in excess of NaOH solution is formed.
	$Al\,Cl_3 + 3NaOH \rightarrow Al\,(OH)_3 + 3\,NaCl$ $Al\,(OH)_3 + 3\,NaCl \rightarrow Na\,AlO_2 + 2H_2O$	
3.	$K_4[Fe\,(CN)_6]$ solution is added to the salt solution.	3. No precipitate is formed.

Reactions of Chromium ion (Cr^{3+}) :

	EXPERIMENT	OBSERVATION
1.	NH_4OH solution is added to the salt solutioin.	1. Green precipitate of Cr $(OH)_3$ which is soluble in excess of NH_4OH is formed.
2.	NaOH solution is added to the salt solution.	2. Green precipitate of $Cr(OH)_3$ soluble in excess of NaOH solution is formed.

Reactions of ferric ion (Fe^{3+}) :

	EXPERIMENT	OBSERVATION
1.	NH_4OH solution is added to the salt solutioin.	1. Dark brown precipitate is formed.
2.	Potassium ferro cyanide solution is added to the salt solution.	2. Deep blue precipitate is formed.
3	Potassium ferri cyanide solution is added to the salt solution.	3. Deep blue precipitate is formed.
4.	To the salt solution, added ammonium thiocyanate solution.	4. Blood red colouration is observed.

Reactions of Group IV Cations :

Reactions of Zinc ion (Zn^{2+}) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the salt is heated in a dry test tube.	1. Yellow colour when hot and white when cold is observed.
2.	The salt solution is treated with NH_4OH solution.	2. white precipitate of $Zn(OH)_2$ is formed. The precipitate is soluble in excess of NH_4OH solution.
	$Zn\,SO_4 + 2\,NH_4OH \rightarrow Zn\,(OH)_3 + (NH_4)_2\,SO_4$ $Zn\,(OH)_2 + 4NH_4OH \rightarrow Zn(NH_3)_4\,(OH)_2 + 4H_2O$ $Zn\,(OH)_2 + 2\,NaOH \rightarrow Na_2ZnO_2 + 2H_2O$	
3.	Potassium ferro cyanide solution is added to the salt solution.	3. A white precipitate of Zinc ferro cyanide is formed.
4.	The salt solution is treated with excess of solid NH_4Cl and NH_4OH solution is added till the smell of ammonia is observed.	4. No precipitate is formed.

Reactions of Manganese salt (Mn^{2+}) :

	EXPERIMENT	OBSERVATION
1.	NH_4OH solution is added to the salt solution	1. Pale brown precipitate of $Mn(OH)_2$ is formed.
	$Mn\,SO_4 + 2\,NH_4OH \rightarrow Mn\,(OH)_2 + (NH_4)_2\,SO_4$	
2.	A small amount of the salt is mixed with a little amount of PbO_2 and few ml conc. HNO_3. The mixture is boiled diluted and cooled.	2. The solution appeared pink in colour due to the formation of permanganic acid.

Reactions of Cobalt ion (Co^{3+}) :

	EXPERIMENT	OBSERVATION
1.	The salt solution is treated with NaOH solution.	1. Blue precipitate of cobalt hydroxide is formed.
	$Co\,(NO_3)_3 + 3\,NaOH \rightarrow 3Na\,NO_3 + Co(OH)_3\downarrow$	
2.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution and passed H_2S gas.	2. Black precipetate of CoS is formed.

Reactions of Nickel ion (Ni^{2+}) :

	EXPERIMENT	OBSERVATION
1.	The salt solution is treated with NaOH solution.	1. Bluish green precipitate of Ni $(OH)_2$ is formed.
	$Ni\,SO_4 + 2\,NaOH \rightarrow Ni\,(OH)_2 + Na_2SO_4$	
2.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution and passed H_2S gas.	2. Black precipitate of Ni S is formed.
3.	The salt solution is made alkaline with NH_4OH and then added few drops of dimethyl glyoxime.	3. Scarlet red precipitate of nickel dimethyl glyoxime is formed.

Reactions of Group V Cations :

Reactions of Barium ion (Ba^{2+}) :

	EXPERIMENT	OBSERVATION
1.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution and then ammonium carbonate solution is added.	1. White precipitate of barium carbonate which is soluble in acetic acid is formed.
	$BaCl_2 + (NH_4)_2CO_3 \rightarrow NH_4Cl + BaCO_3\downarrow$	
2.	The salt solution is treated wiht potassium chromate solution.	2. Yellow precipitate of $BaCrO_4$ is formed. The precipitate is insoluble in acetic acid.

Reactions of Strontium ion (Sr^{2+}) :

	EXPERIMENT	OBSERVATION
1.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution and then few drops of ammonium carbonate solution are added.	1. White precipitate of strontium carbonate which is soluble in acetic acid is formed.
2.	Potassium Chromate solution is added to the salt solution.	2. Yellow precipitate of strontium chromate is formed. It is soluble in acetic acid.
3.	To the salt solution ammonium oxalate solution is added.	3. White precipitate of strontium oxalate is formed. It is soluble in acetic acid.

Reactions of Calcium ion (Ca^{2+}) :

	EXPERIMENT	OBSERVATION
1.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution and then few drops of ammonium carbonate solution are added.	1. White precipitate of calcium carbonate is formed. It is soluble in acetic acid.
2.	The salt solution is treated with potassium chromate solution.	2. No precipitate is formed.
3	The salt solution is treated with ammonium oxalate solution.	3. A white precipitate of calcium oxalate is formed. The precipitate is soluble in acetic acid.

Reactions of Group VI Cations :

Reactions of Potassium ion (K^+) :

	EXPERIMENT	OBSERVATION
1	Tartaric acid is added to the saturated solution of the salt and then scratched the walls of the test tube with a glass rod.	1. White crystalline precipitate of potassium tartrate is formed.
2	Acetic acid and sodium cobalti nitrite solution are added to the salt solution.	2. Yellow precipitate of potassium cobaltinitrite is formed.
3	Picric acid is added to the salt solution and shaken well.	3. Yellow precipitate of potassium picrate is formed.

Reactions of Magnesium ion (Mg^{2+}) :

	EXPERIMENT	OBSERVATION
1.	NaOH solution is added to the salt solution.	1. white precipitate of magesium hydroxide is formed.
	$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2\downarrow + Na_2SO_4$	
2.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution.	2. No precipitate is formed.
3.	Ammonium carbonate solution is added to the salt solution and heated.	3. White precipitate of $MgCO_3$ is formed.
	$MgSO_4 + (NH_4)_2CO_3 \rightarrow MgCO_3\downarrow + (NH_4)_2SO_4$	
4.	Solid NH_4Cl and NH_4OH solution are added in excess to the salt solution. To the above solution Na_2HPO_4 solution is added and scratched the inner walls of the test tube with a glass rod.	4. White crystalline precipitate is formed.

Reactions of Ammonium ion (NH_4^+) :

	EXPERIMENT	OBSERVATION
1.	A small quantity of the **ammonium salt is heated in a dry test tube.**	1. Sublimation took place.
2.	A small quantity of the salt is **heated with NaOH solution.**	2. A colourless gas of NH3 with pungent smell is evolved. A glass rod dipped in dil. HCl is exposed to the gas. Dense white fumes of NH_4Cl are given out.
	$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$ $NH_3 + HCl \rightarrow NH_4Cl$	
3.	To the salt solution NaOH solution is added. Then Nessler's reagent is added in excess.	3. Reddish brown precipitate or colour action $3HgO.\ Hg(NH_4)_2I$ is formed.
4.	To the salt solution picric acid is added.	4. yellow precipitate of ammonium picrate is formed.
5.	Tartaric acid is added to the salt solution.	5. White crystalline precipitate of ammonium tartrate is formed.
	$2NH_4Cl + H_2C_4H_4O_6 \rightarrow 2HCl + (NH_4)_2C_4H_4O_6$	

General Group Separation Table :

To the original solution dil Hcl is added and centrifuged.

<table>
<tr>
<td rowspan="5">Residue :
$PbCl_2$ – white.
AgCl – white
$Hg_2 Cl_2$ – White
indicates the presence of I group cations.</td>
<td colspan="5">Centrifugate : Added few ml of dil HCl and H_2S gas is passed and centrifuged.</td>
</tr>
<tr>
<td rowspan="4">Residue :
Hg S – Black
PbS – Black
Bi_2S_3 – Brown
Cu S – Black
Cd S – Yellow
As_2S_3 – Yellow
Sb_2S_3 – Orange
SnS – Brown
SnS_2 – Yellow
indicates the presence of II group cations.</td>
<td colspan="4">Centrifugate : Boiled to expel H_2S gas. 3,4 drops of Conc. HNO_3 is added and boiled. Soild NH_4Cl is added in excess and NH_4OH solution is added till smell of ammonia is observed and then centrifuged. If phosphate is present, it should be eliminated before testing cations.</td>
</tr>
<tr>
<td rowspan="3">Residue :
Fe $(OH)_3$ – Brown
Cr $(OH)_3$ – Green
Al $(OH)_3$ – White
indicates the presence of III group cations.</td>
<td colspan="3">Centrifugate : Few ml of NH_4OH is added. H_2S gas is passed and centrifuged.</td>
</tr>
<tr>
<td rowspan="2">Residue :
Co S – Black
Ni S – Black
Mn S – Pale pink or flesh coloured
Zn S – white
indicates the presence of IV group cations.</td>
<td colspan="2">Centrifugate : Boiled to expel H_2S gas. NH_4Cl ; NH_4OH and $(NH_4)_2CO_3$ are added in excess and then centrifuged.</td>
</tr>
<tr>
<td>Residue :
Ba CO_3 – White
Sr CO_3 – White
Ca CO_3 – White
indicates the presence of V group cations.</td>
<td>Centrifugate : Tested for VI group cations, K+ and Mg^{2-} Ammonium ion is tested along with the anions.</td>
</tr>
</table>

Group I -- separation table :

To the residue few ml of water is added , boiled and centrifuged while hot.

<table>
<tr><td colspan="2">Residue :
To the residue NH_4OH solution is added and centrifuged.</td><td rowspan="2">Centrifugate :
Contains $PbCl_2$ It is divided into two parts.
1. To the first part of solution, potassium chromate solution is added. yellow precipitate is formed.
2. To the second part, potassium iodide solution is added. Yellow precipitate is formed. It is heated and cooled suddenly. The precipitate reappered as golden yellow spangles, lead is confirmed.</td></tr>
<tr><td>Residue :
Black residue indicates the presence of Hg_2^{2+} . It is dissolved in Conc.HNO_3 and $SnCl_2$ solution is added. White or grey precipitate is observed. Mercurous, mecrcry is confirmed.</td><td>Centrifugate :
Few drops of dil. HCl is added to the centrifugate. White precipitate is formed. Silver is confirmed.</td></tr>
</table>

Separation of II group cations into II A and II B groups :

To the residue of II group, few ml of NaOH solution and few drops of yellow ammonium sulphide are added, heatead and centrifuged.

Residue :	**Centrifugate :**
Residue contains sulphides of II A group cations. Using II A group separation table II A group cations are identified.	The centrifugate is tested for II B group cations..

II A group - separation table :

The residue obtained in the separation of II group cations is boiled with dil HNO_3 and a small amount of dil H_2SO_4 is added and centrifuged.

<table>
<tr><td colspan="2">Residue :
The residue is boiled with ammonium acetate solution and centrifuged.</td><td colspan="2">Centrifugate :
NH_4OH solution is added till smell of ammonia is observed and centrifuged.</td></tr>
<tr><td>Residue :
The residue is boiled with Conc.HCl and 1 or 2 crystals of $KClO_3$. It is cooled, diluted and then added few drops of Sn Cl_2 solution. White silky precipitate is formed. Mercury is confirmed.</td><td>Centrifugate :
To the centrifugate K_2CrO_4 solution is added. Yellow precipitate is formed. Lead is confirmed.</td><td>Residue :
The residue is dissolved in few ml of hot dil HCl and divided into two parts.
1. Water is added drop wise. Turbidity is formed. Bi^{3+} is confirmed.
2. Magpie Test : $SnCl_2$ solution is added to NaoH solution till a precipitate formed is just dissolved. This solution is added to another portion. On warming black colour is observed. Bismuth is confirmed.</td><td>Centrifugate :
1. Blue colour indicates Cu^{2+} Acetic acid and Potassium ferro cyanide solution are added. Chacolate brown precipitate is formed. Cu^{2+} is confirmed.
2. When the solution is colourless; Cu^{2+} is absent May indicate Cd^{2+}.H_2S gas is passed Yellow precipitate is observed cadmium is confirmed.</td></tr>
</table>

II B group - separation table (As^{3+}, Sb^{3+}, Sn^{2+} and Sn^{4+}) :

The residue obtained in the separation of II group cations into II A and II B groups, contains As_2S_3, Sb_2S_3, SnS and SnS_2 is boiled with a small quantity of Conc HCl, diluted and centrifuged.

<table>
<tr>
<td rowspan="2">Residue :
Residue is yellow in colour. It is boiled with dilute ammonium carbonate solution till the residue is dissolved. Acidified with dil HCl. The yellow precipitate is reappeared. Arsenic is confirmed.</td>
<td colspan="2">Centrifugate :
The centrifugate is boiled to expel H_2S gas. It is then cooled and excess of NaOH solution is added. Bromine water is added till the solution is yellow and centrifuged.</td>
</tr>
<tr>
<td>Residue :
The residue is dissolved in conc. HCl, diluted, boiled with iron filings and centrifuged. Mercuric chloride solution is added to the centrifugate. Gray precipitate is formed. Tin is present. Testedfor Sn^{2+} and Sn^{4+}.</td>
<td>Centrifugate :
The centrifugate is made alkaline with few drops of Conc.NH_4OH; added oxalic acid solution and then passed H2S gas. Orange precipitate is formed. Antimony is confirmed.</td>
</tr>
</table>

Group III - separation table :

The residue formed in III group is suspended in water and boiled with a little amount of Na_2O_2 to expel the oxygen gas. The solution is diluted and centrifused.

Residue :	**Centrifugate :**
Brown indicates the presence of Fe^{3+} The residue is dissolved in dil. HCl and potassium ferro cyanide solution is added. Deep blue precipitate is formed. Iron is confirmed.	Yellow colour indicates Cr^{3+}. It is divided into two parts. 1. The first part of the centrifugate is acidified with acetic acid and then lead acetate solution is added. Yellow precipitate is formed. Chromium is confirmed. 2. To the second part dil. HCl and excess. NH_4OH Solution are added White gelatinous precipitate is formed. The precipitate is dissolved in few drops of dil HNO_3 and added few drops of cobalt nitrate solution. A paper dipped in this solution is burnt. Blue ash is formed. Aluminium is confirmed.

IV group - Separation table (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}) :

The residue formed in the IV group is stirred with dil. HCl and then centrifuged.

<table>
<tr>
<td rowspan="2">Residue :
Residue is black. The residue is taken into a china dish, added conc.HCl and few crystals of $KClO_3$ and evaporated to dryness. Yellow ring on the walls of the dish indicates the presence of Nickel. The residue is dissolved in water and divided into two parts.
1. To the first part NH_4Cl ; NH_4OH and dimethyl glyoxime are added, scarlet red precipitate is formed. Nickel is confirmed.
2. To the second part solid NH_4Cl, NH_4OH and potassium ferrocyanide solution are added, brown precipitate is formed. Cobalt is confirmed.</td>
<td colspan="2">Centrifugate :
The crntrifugate id boiled to expel H_2S gas. It is cooled and added NaOH solution is excess and centrifuged.</td>
</tr>
<tr>
<td>Residue :
Flesh coloured precipitate is formed.
To the residue added conc. HNO_3 and lead peroxide and boiled. It is then diluted with water and allowed to cool. Pink coloured solution is observed. Manganese is confirmed.</td>
<td>Centrifugate :
H_2S gas is passed . A white precipitate of ZnS is formed. The precipitate is dissolved in few drops of Conc. HNO3 and added few drops of cobalt nitrate solution. A filter paper dipped in this solution is burnt. Green mass is observed.
Zinc is confirmed.</td>
</tr>
</table>

V group Separation table (Ba^{2+}, Sr^{2+}, and Ca^{2+}) :

The V group residue is dissolved in hot dilute acetic acid and centrifuged. A small par tof the centrifugate is treated with K_2CrO_4 solution If an yellow precipitate is formed, Barium is present. If yellow precipitate is formed, K_2CrO_4 solution is added to the entirre centrifugate and again centrifuged.

<table>
<tr>
<td rowspan="2">Residue :
Yellow residue indicates barium. The residue is tested for flame colouration. Apple green flame is formed. Barium is present.</td>
<td colspan="2">Centrifugate :
The centrifugate is divided into two parts.
To the first part calcium sulphate solution is added, boiled and centrifuged.</td>
</tr>
<tr>
<td>Residue :
White precipitate is formed.
Strontium is present. The precipitate is tested for flame colouration. Crimson red flame is observed. Strontium is present.</td>
<td>Centrifugate :
(If strontium is present) To the second part added $(NH_4)_2SO_4$ solution, boiled and centrifuged. Rejected the residue. The centrifugate is treated with NH_4OH solution and then added ammonium oxalate solution. White precipitate is formed. Calcium is present. The precipitate is tested for flame colouration. Brick red flame is observed. Calcium is present.</td>
</tr>
</table>

VI group Separation table (K^+,Mg^{2+}, and NH_4^+) :

To the centrifugate from V group few drops of ammonium oxalate and ammonium sulphate are added, boiled and centrifuged. The residue is rejected. The centrifugate is evaporated to dryness and the residue is dissolved in water and divided into three parts.

Residue :	**Centrifugate :**
1) To the first part solid NH_4Cl, excess of NH_4OH solution and then sodium phosphate solution are added. White precipitate is formed . Magnesium is present.	a) To the second part saturated solution of tartaric acid is added and scratched the sides of the test tube with a glass rod. White crystalline precipitate is formed. Potassium is present. b) To the third part picric acid is added and scratched the sides of the test tube with a glass rod. Yellow precipitate is formed. Potassium is confirmed.

Systematic semi micro qualitative analysis :

	EXPERIMENT	OBSERVATION	INFERENCE
1	Colour	Blue	Copper (Cu^{2+})
		Pale green	Ferrous(Fe^{2+})
		Green	Nickel (Ni^{2+}) or some Copper (Cu^{2+}) salts
		Pale Pink	Manganese (Mn^{2+})
		Pink	Cobalt (Co^{3+})
		Brown	Ferric (Fe^{3+})
		Yellow	Chromates
2	State	Crystalline or amorphous	
3	Odour	Vinegar smell	May be acetate
		Smell of ammonia	May be ammonium salt
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.	water (cold or hot) Dil. HCl (cold or hot) Conc. HCl (cold or hot) Dil. HNO_3 (cold or hot) Conc. HNO_3 (col or hot)	
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.	a) Water drops are formed on the sides of the test tube (water of crystallisation).	May be hydrated salt
		b) White sublimation is formed.	May be Ammonium ion
		c) Yellow when hot, white when cold.	May be Zinc
		d) White when hot, blue when cold.	May be Copper
		e) Brown when hot, dark brown when cold.	May be cadmium
		e¹) Brown when hot, yellow when cold.	May be lead
		f) Colourless gas with smell of ammonia is evolved.	May be ammonium salt.

	EXPERIMENT	OBSERVATION	INFERENCE
		g) Reddish brown vapours of NO_2 are evolved.	May be nitrate.
		h) Substance charred with the smell of burnt sugar.	May be tartrate.
6	**Flame test** : A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame	Bluish green Flashes of green Apple green Crimson red Brick red Lilac violet	May be Copper May be Zinc May be Barium May be strontium May be calcium May be Potassium
7	**Charcoal test :**		
a)	A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.	White silvery mass Red scales Gray metallic Yellow when hot white when cold orange when hot yellow when cold	May be Silver May be Copper May be Iron May be Zinc May be Lead
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.	Blue mass Green Pink	May be Aluminium May be Zinc May be Magnesium
8	**Action of dil. HCl** : A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.	a) Colourless gas of CO_2 with quick effervascence is evolved. The gas turned lime water milky.	Carbonate is present
		b) Vinegar smell is observed on heating.	May be acetate.

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4	a) A colourless pungent smelled gas (HCl) is evolved with quick effervescence. The vapours gave dense white fumes of NH4Cl with a glass rod dipped in NH_4OH solution and also gave white precipitate with a drop of AgNO3 solution taken on a glass rod.	May be chloride.
		b) Reddish brown vapours of bromine are evolved.	May be bromide.
		c) violet vapours of iodine are evolved.	May be iodide.
	Action of Conc. H_2SO_4 : in hot condition : The above contents are heated.	a) Reddish brown vapours of NO_2 are evolved.	May be nitrate
		b) Vinegar smell like that of acetic acid is observed.	May be acetate
		c) Charring of the mixture with burnt sugar smell is observed.	May be tartrate
		d) White fumes of boric acid are evolved	May be borate
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.	a) Greenish yellow gas of chlorine is evolved.	May be chloride.
		b) Reddish brown vapours of bromine are evolved.	May be bromide.
		c) violet vapours of iodine are evolved.	May be iodide.
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc.H_2SO_4 and copper turnings.	Reddish brown vapours of NO_2 are evolved.	May be nitrate.

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.	Red vapours of chromyl chloride ($CrO_2\,Cl_2$) are evolved. The vapours are passed into NaOH solution and then added lead acetate solution. Yellow precipitate is formed.	Chloride is confirmed
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4	A colourless gas of CO_2 with quick effervescence is evolved.	May be oxalate.
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water	Smell of Vinegar is observed	Acetate
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.	Apple smell due to ethyl acetate is observed.	Acetate
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.	Banana smell due to formation of amyl acetate is observed.	Acetate
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.	Green edged flame is observed	Borate
18	**Boron Trifluoride test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.	Green edged flame is observed	Borate is confirmed

	EXPERIMENT	OBSERVATION	INFERENCE
19	**Test for phosphate :** To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated	Canary yellow precipitate is formed	Phosphate
20	**Test for tartrate :** To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.	A bright red colour is observed	Tartrate
21	**Test for Chomate :** To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.	Red vapours of chromyl chloride are evolved. The vapours gave yellow precipitate with lead acetate in NaOH solution	Chromate
22	**Test for Ammonium radical (NH_4^+) :** To a small quantity of the mixture, NaOH solution is added and heated.	Colourless gas with smell of ammonia is observed. The gas gave dense white fumes with HCl vapours.	May be ammonium salt.
23	**Test with Nessler's reagent :** A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.	Brown precipitate is formed.	Ammonium ion is confirmed.

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.	a) A white curdy precipitate of AgCl which is soluble in NH_4OH and insoluble in HNO_3 is formed.	Chloride, $\bar{Cl}$
		b) A Pale yellow precipitate of AgBr which is sparingly soluble in NH_4OH and insoluble in HNO_3 is formed.	Bromide, $\bar{Br}$
		c) An yellow precipitate of Ag I which is insoluble both in NH_4OH and HNO_3 is formed.	Iodide, $\bar{I}$
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.	A brown ring ($FeSO_4.NO$) is formed at the junction of two layers.	Nitrate is confirmed.
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.	Red coloured solution which on boiling gives red precipitate.	Acetate is confirmed
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.	A white precipitate of calcium oxalate is formed.	
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.	The $KMnO_4$ solution is decolourised.	Oxalate is confirmed

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.	A silver mirror is formed on the inner walls of the test tube.	Tartrate is confirmed.
6	**Test for phosphate :**		
	a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added.	white crystalline precipitate is formed	Phosphate is confirmed
	b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.	Light yellow precipitate is formed	
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.	A white precipitate of $BaSO_4$ which is insoluble in Conc. HCl is formed.	Sulphate is confirmed

Identification of Cations :

Preparation of original solution :

Original solution is prepared by dissolving a small quantity of the mixture in a solvent as observed in solubility test.

General Group Separation Table :

To the original solution dil Hcl is added and centrifuged.

Residue : $PbCl_2$ – white. AgCl – white Hg_2Cl_2 – White indicates the presence of I group cations.	**Centrifugate :** Added few ml of dil HCl and H_2S gas is passed and centrifuged.				
	Residue : Hg S – Black PbS – Black Bi_2S_3 – Brown Cu S – Black Cd S – Yellow As_2S_3 – Yellow Sb_2S_3 – Orange SnS – Brown SnS_2 – Yellow indicates the presence of II group cations.	**Centrifugate :** Boiled to expel H_2S gas. 3,4 drops of Conc. HNO_3 is added and boiled. Soild NH_4Cl is added in excess and NH_4OH solution is added till smell of ammonia is observed and then centrifuged. If phosphate is present, it should be eliminated before testing cations.			
		Residue : Fe $(OH)_3$ – Brown Cr $(OH)_3$ – Green Al $(OH)_3$ – White indicates the presence of III group cations.	**Centrifugate :** Few ml of NH_4OH is added. H_2S gas is passed and centrifuged.		
			Residue : Co S – Black Ni S – Black Mn S – Pale pink or flesh coloured Zn S – white indicates the presence of IV group cations.	**Centrifugate :** Boiled to expel H_2S gas. NH_4Cl ; NH_4OH and $(NH_4)_2CO_3$ are added in **excess** and then centrifuged	
				Residue : Ba CO_3 – White Sr CO_3 – White Ca CO_3 – White indicates the presence of V group cations.	**Centrifugate :** Tested for VI group cations, K+ and Mg^{2+} Ammonium ion is tested along with the anions.

Group I – separation table :

To the residue few ml of water is added , boiled and centrifuged while hot.

<table>
<tr><td colspan="2">**Residue :**
To the residue NH_4OH solution is added and centrifuged.</td><td rowspan="2">**Centrifugate :**
Contains $PbCl_2$ It is divided into two parts.
1. To the first part of solution, potassium chromate solution is added. yellow precipitate is formed.
2. To the second part, potassium iodide solution is added. Yellow precipitate is formed. It is heated and cooled suddenly. The precipitate reappered as golden yellow spangles, lead is confirmed.</td></tr>
<tr><td>**Residue :**
Black residue indicates the presence of Hg_2^{2+} . It is dissolved in Conc.HNO_3 and $SnCl_2$ solution is added. White or grey precipitate is observed. Mercurous, mecrcry is confirmed.</td><td>**Centrifugate :**
Few drops of dil. HCl is added to the centrifugate. White precipitate is formed. Silver is confirmed.</td></tr>
</table>

Separation of II group cations into II A and II B groups :

To the residue of II group, few ml of NaOH solution and few drops of yellow ammonium sulphide are added, heatead and centrifuged.

Residue :	**Centrifugate :**
Residue contains sulphides of II A group cations. Using II A group separation table II A group cations are identified.	The centrifugate is tested for II B group cations..

II A group - separation table :

The residue obtained in the separation of II group cations is boiled with dil HNO_3 and a small amount of dil H_2SO_4 is added and centrifuged.

Residue : The residue is boiled with ammonium acetate solution and centrifuged.		**Centrifugate :** NH_4OH solution is added till smell of ammonia is observed and centrifuged.	
Residue : The residue is boiled with Conc.HCl and 1 or 2 crystals of $KClO_3$. It is cooled, diluted and then added few drops of Sn Cl_2 solution. White silky precipitate is formed. Mercury is confirmed.	**Centrifugate :** To the centrifugate K_2CrO_4 solution is added. Yellow precipitate is formed. Lead is confirmed.	**Residue :** The residue is dissolved in few ml of hot dil HCl and divided into two parts. 1. Water is added drop wise. Turbidity is formed. Bi^{3+} is confirmed. 2. Magpie Test : $SnCl_2$ solution is added to NaoH solution till a precipitate formed is just dissolved. This solution is added to another portion. On warming black colour is observed. Bismuth is confirmed.	**Centrifugate :** 1. Blue colour indicates Cu^{2+} Acetic acid and Potassium ferro cyanide solution are added. Chacolate brown precipitate is formed. Cu^{2+} is confirmed. 2. When the solution is colourless; Cu^{2+} is absent May indicate Cd^{2+}.H_2S gas is passed Yellow precipitate is observed cadmium is confirmed.

II B group - separation table (As^{3+}, Sb^{3+}, Sn^{2+} and Sn^{4+}) :

The residue obtained in the separation of II group cations into II A and II B groups, contains $As_2 S_3$, Sb_2S_3, SnS and SnS_2 is boiled with a small quantity of Conc HCl, diluted and centrifuged.

<table>
<tr><td rowspan="2">Residue :
Residue is yellow in colour. It is boiled with dilute ammonium carbonate solution till the residue is dissolved. Acidified with dil HCl. The yellow precipitate is reappeared. Arsenic is confirmed.</td><td colspan="2">Centrifugate :
The centrifugate is boiled to expel H_2S gas. It is then cooled and excess of NaOH solution is added. Bromine water is added till the solution is yellow and centrifuged.</td></tr>
<tr><td>Residue :
The residue is dissolved in conc. HCl, diluted, boiled with iron filings and centrifuged. Mercuric chloride solution is added to the centrifugate. Gray precipitate is formed. Tin is present. Testedfor Sn^{2+} and Sn^{4+}.</td><td>Centrifugate :
The centrifugate is made alkaline with few drops of Conc.NH_4OH; added oxalic acid solution and then passed H2S gas. Orange precipitate is formed. Antimony is confirmed.</td></tr>
</table>

Group III - separation table :

The residue formed in III group is suspended in water and boiled with a little amount of Na_2O_2 to expel the oxygen gas. The solution is diluted and centrifused.

Residue :	**Centrifugate :**
Brown indicates the presence of Fe^{3+} The residue is dissolved in dil. HCl and potassium ferro cyanide solution is added. Deep blue precipitate is formed. Iron is confirmed.	Yellow colour indicates Cr^{3+}. It is divided into two parts. 1. The first part of the centrifugate is acidified with acetic acid and then lead acetate solution is added. Yellow precipitate is formed. Chromium is confirmed. 2. To the second part dil. HCl and excess. NH_4OH Solution are added White gelatinous precipitate is formed. The precipitate is dissolved in few drops of dil HNO_3 and added few drops of cobalt nitrate solution. A paper dipped in this solution is burnt. Blue ash is formed. Aluminium is confirmed.

IV group - Separation table (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}) :

The residue formed in the IV group is stirred with dil. HCl and then centrifuged.

<table>
<tr>
<td rowspan="2">Residue :
Residue is black. The residue is taken into a china dish, added conc.HCl and few crystals of $KClO_3$ and evaporated to dryness. Yellow ring on the walls of the dish indicates the presence of Nickel. The residue is dissolved in water and divided into two parts.
1. To the first part NH_4Cl ; NH_4OH and dimethyl glyoxime are added, scarlet red precipitate is formed. Nickel is confirmed.
2. To the second part solid NH_4Cl, NH_4OH and potassium ferrocyanide solution are added, brown precipitate is formed. Cobalt is confirmed.</td>
<td colspan="2">Centrifugate :
The crntrifugate id boiled to expel H_2S gas. It is cooled and added NaOH solution is excess and centrifuged.</td>
</tr>
<tr>
<td>Residue :
Flesh coloured precipitate is formed.
To the residue added conc. HNO_3 and lead peroxide and boiled. It is then diluted with water and allowed to cool. Pink coloured solution is observed. Manganese is confirmed.</td>
<td>Centrifugate :
H_2S gas is passed . A white precipitate of ZnS is formed. The precipitate is dissolved in few drops of Conc. HNO3 and added few drops of cobalt nitrate solution. A filter paper dipped in this solution is burnt. Green mass is observed.
Zinc is confirmed.</td>
</tr>
</table>

V group Separation table (Ba^{2+}, Sr^{2+}, and Ca^{2+}) :

The V group residue is dissolved in hot dilute acetic acid and centrifuged. A small par tof the centrifugate is treated with K_2CrO_4 solution. If an yellow precipitate is formed, Barium is present. If yellow precipitate is formed, K_2CrO_4 solution is added to the entirre centrifugate and again centrifuged.

<table>
<tr>
<td rowspan="2">Residue :
Yellow residue indicates barium. The residue is tested for flame colouration. Apple green flame is formed. Barium is present.</td>
<td colspan="2">Centrifugate :
The centrifugate is divided into two parts.
To the first part calcium sulphate solution is added, boiled and centrifuged.</td>
</tr>
<tr>
<td>Residue :
White precipitate is formed.
Strontium is present. The precipitate is tested for flame colouration. Crimson red flame is observed. Strontium is present.</td>
<td>Centrifugate :
(If strontium is present) To the second part added $(NH_4)_2SO_4$ solution, boiled and centrifuged. Rejected the residue. The centrifugate is treated with NH_4OH solution and then added ammonium oxalate solution. White precipitate is formed. Calcium is present. The precipitate is tested for flame colouration. Brick red flame is observed. Calcium is present.</td>
</tr>
</table>

VI group Separation table (K^+,Mg^{2+}, and NH_4^+) :

To the centrifugate from V group few drops of ammonium oxalate and ammonium sulphate are added, boiled and centrifuged. The residue is rejected. The centrifugate is evaporated to dryness and the residue is dissolved in water and divided into three parts.

Residue :	**Centrifugate :**
1) To the first part solid NH_4Cl, excess of NH_4OH solution and then sodium phosphate solution are added. White precipitate is formed . Magnesium is present.	a) To the second part saturated solution of tartaric acid is added and scratched the sides of the test tube with a glass rod. White crystalline precipitate is formed. Potassium is present. b) To the third part picric acid is added and scratched the sides of the test tube with a glass rod. Yellow precipitate is formed. Potassium is confirmed.

Systematic semi micro qualitative analysis of the given mixture - I :

	EXPERIMENT	OBSERVATION	INFERENCE
1.	Colour		
2	State		
3	Odour		
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.		
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.		

	EXPERIMENT	OBSERVATION	INFERENCE
6	**Flame test :** A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame.		
7	**Charcoal test :**		
a)	A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.		
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.		
8	**Action of dil. HCl :** A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.		

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4		
	Action of Conc. H_2SO_4 : in hot condition : The above contents are heated.		
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.		
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc. H_2SO_4 and copper turnings.		

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.		
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4		
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water		
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.		
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.		
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.		

	EXPERIMENT	OBSERVATION	INFERENCE
18	**Boron Trifluoride test** : To a small quantity of the mixture, few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.		
19	**Test for phosphate** : To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated		
20	**Test for tartrate** : To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.		
21	**Test for Chomate** : To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.		
22	**Test for Ammonium radical (NH_4^+)** : To a small quantity of the mixture, NaOH solution is added and heated.		
23	**Test with Nessler's reagent** : A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.		

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.		
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.		
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.		
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.		
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.		

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.		
6	**Test for phosphate :** a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added. b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.		
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.		

GENERAL GROUP SEPARATION TABLE :

GROUP SEPARATION TABLE:

GROUP SEPARATION TABLE:

Report :

a) Anion : ....

b) Cations : ....

Systematic semi micro qualitative analysis of the given mixture - II :

	EXPERIMENT	OBSERVATION	INFERENCE
1	Colour		
2	State		
3	Odour		
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.		
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.		

	EXPERIMENT	OBSERVATION	INFERENCE
6	**Flame test :** A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame.		
7 a)	**Charcoal test :** A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.		
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.		
8	**Action of dil. HCl :** A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.		

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4		
	Action of Conc. H_2SO_4 : in hot condition : The above contents are heated.		
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.		
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc.H_2SO_4 and copper turnings.		

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.		
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4		
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water		
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.		
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.		
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.		

	EXPERIMENT	OBSERVATION	INFERENCE
18	**Boron Trifluoride test** : To a small quantity of the mixture; few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.		
19	**Test for phosphate :** To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated		
20	**Test for tartrate :** To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.		
21	**Test for Chomate :** To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.		
22	**Test for Ammonium radical (NH_4^+) :** To a small quantity of the mixture, NaOH solution is added and heated.		
23	**Test with Nessler's reagent :** A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.		

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.		
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.		
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.		
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.		
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.		

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.		
6	**Test for phosphate :** a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added.. b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.		
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.		

GENERAL GROUP SEPARATION TABLE :

GROUP SEPARATION TABLE:

GROUP SEPARATION TABLE:

Report :

a) Anion : ....

b) Cations : ....

Systematic semi micro qualitative analysis of the given mixture - III :

	EXPERIMENT	OBSERVATION	INFERENCE
1.	Colour		
2	State		
3	Odour		
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.		
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.		

	EXPERIMENT	OBSERVATION	INFERENCE
6	**Flame test :** A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame.		
7 a)	**Charcoal test :** A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.		
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.		
8	**Action of dil. HCl :** A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.		

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4		
	Action of Conc. H_2SO_4 : in hot condition : The above contents are heated.		
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.		
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc. H_2SO_4 and copper turnings.		

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.		
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4		
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water		
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.		
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.		
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.		

	EXPERIMENT	OBSERVATION	INFERENCE
18	**Boron Trifluoride test** : To a small quantity of the mixture; few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.		
19	**Test for phosphate :** To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated		
20	**Test for tartrate :** To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.		
21	**Test for Chomate :** To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.		
22	**Test for Ammonium radical (NH_4^+) :** To a small quantity of the mixture, NaOH solution is added and heated.		
23	**Test with Nessler's reagent :** A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.		

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.		
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.		
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.		
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.		
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.		

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.		
6	**Test for phosphate :** a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added. b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.		
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.		

GENERAL GROUP SEPARATION TABLE :

GROUP SEPARATION TABLE:

GROUP SEPARATION TABLE:

Report :

a) Anion : ....

b) Cations : ....

Systematic semi micro qualitative analysis of the given mixture - IV :

	EXPERIMENT	OBSERVATION	INFERENCE
1	Colour		
2	State		
3	Odour		
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.		
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.		

	EXPERIMENT	OBSERVATION	INFERENCE
6	**Flame test :** A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame.		
7	**Charcoal test :**		
a)	A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.		
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.		
8	**Action of dil. HCl :** A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.		

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4		
	Action of Conc. H_2SO_4 : **in hot condition :** The above contents are heated.		
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.		
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc.H_2SO_4 and copper turnings.		

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.		
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4		
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water		
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.		
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.		
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.		

	EXPERIMENT	OBSERVATION	INFERENCE
18	**Boron Trifluoride test** : To a small quantity of the mixture; few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.		
19	**Test for phosphate :** To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated		
20	**Test for tartrate :** To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.		
21	**Test for Chomate :** To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.		
22	**Test for Ammonium radical (NH_4^+) :** To a small quantity of the mixture, NaOH solution is added and heated.		
23	**Test with Nessler's reagent :** A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.		

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.		
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.		
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.		
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.		
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.		

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.		
6	**Test for phosphate :** a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added. b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.		
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.		

GENERAL GROUP SEPARATION TABLE :

GROUP SEPARATION TABLE:

GROUP SEPARATION TABLE:

Report :

a) Anion : ....

b) Cations : ....

Systematic semi micro qualitative analysis of the given mixture - V :

	EXPERIMENT	OBSERVATION	INFERENCE
1	Colour		
2	State		
3	Odour		
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.		
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.		

	EXPERIMENT	OBSERVATION	INFERENCE
6	**Flame test :** A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame.		
7	**Charcoal test :**		
a)	A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.		
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.		
8	**Action of dil. HCl :** A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.		

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4		
	Action of Conc. H_2SO_4 : in hot condition : The above contents are heated.		
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.		
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc.H_2SO_4 and copper turnings.		

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.		
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4		
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water		
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.		
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.		
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.		

	EXPERIMENT	OBSERVATION	INFERENCE
18	**Boron Trifluoride test** : To a small quantity of the mixture, few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.		
19	**Test for phosphate :** To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated		
20	**Test for tartrate :** To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.		
21	**Test for Chomate :** To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.		
22	**Test for Ammonium radical (NH_4^+) :** To a small quantity of the mixture, NaOH solution is added and heated.		
23	**Test with Nessler's reagent :** A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.		

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.		
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.		
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.		
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.		
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.		

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.		
6	**Test for phosphate :** a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added. b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.		
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.		

GENERAL GROUP SEPARATION TABLE :

GROUP SEPARATION TABLE:

GROUP SEPARATION TABLE:

Report :

a) Anion : ....

b) Cations : ....

Systematic semi micro qualitative analysis of the given mixture - VI :

	EXPERIMENT	OBSERVATION	INFERENCE
1	Colour		
2	State		
3	Odour		
4	Solubility : A small quantity of the mixture is taken in a test tube and solubility is tested in the following order.		
5	Action of heat : A small quantity of the mixture is taken in a dry test tube and heated.		

	EXPERIMENT	OBSERVATION	INFERENCE
6	**Flame test :** A small quantity of the mixture is made into a paste with Conc. HCl in a watch glass. A small amount of the paste is taken on the end of a glass rod and is introduced into the non luminous flame.		
7 a)	**Charcoal test :** A small quantity of the mixture is mixed with anhydrons Na_2CO_3 in the ratio 1:2 and one or two drops of water is added. The moist mass is heated on the cavity of a charcoal using blow pipe.		
b)	Few drops of cobalt nitrate solution is added and heating the mass is continued.		
8	**Action of dil. HCl :** A small quantity of the mixture is treated with dil. HCl in cold and hot conditions.		

	EXPERIMENT	OBSERVATION	INFERENCE
9	**Action of Conc. H_2SO_4 in cold condition :** A small quantity of the mixture is treated with Conc. H_2SO_4		
	Action of Conc. H_2SO_4 : in hot condition : The above contents are heated.		
10	**Action of Conc. H_2SO_4 and MnO_2 :** To the mixture, conc H_2SO_4 and solid MnO_2 are added and heated.		
11	**Action of Conc. H_2SO_4 and copper turnings :** A small quantity of the mixture is heated with conc.H_2SO_4 and copper turnings.		

	EXPERIMENT	OBSERVATION	INFERENCE
12	**Chromyl chloride test :** A small quantity of the mixture is heated with few drops of Conc. H_2SO_4 and few crystals of potassium dichromate.		
13	**Action of dil H_2SO_4 and MnO_2:** A small amount of the mixture is treated with MnO_2 and dil. H_2SO_4		
14	**Test for acetate :** A small quantity of the mixture is rubbed with oxalic acid and few drops of water		
15	**Ethyl acetate test :** A small quantity of the mixture is heated with Conc. H_2SO_4 and few drops of ethyl alcohol and is poured into a beaker full of water.		
16	**Amyl acetate test :** A small quantity of the mixture is warmed with Conc. H_2SO_4 and few drops of amyl alcohol and is poured into a beaker full of water.		
17	**Ethyl borate test :** To a small quantity of the mixture; few drops of Conc. H_2SO_4 and ethyl alcohol are added and heated. The vapours are then exposed to flame.		

	EXPERIMENT,	OBSERVATION	INFERENCE
18	**Boron Trifluoride test** : To a small quantity of the mixture; few drops of Conc. H_2SO_4 and calcium fluoride are added and made into a paste. The paste is then introduced in the non luminous flame with the help of a glass rod.		
19	**Test for phosphate** : To a small quantity of the mixture, few drops Conc. HNO_3 and excess of ammonium molybdate are added and heated		
20	**Test for tartrate :** To the mixture, few drops of aqueous resorcinol solution and few drops of conc. H_2SO_4 are added and warmed.		
21	**Test for Chomate** : To a small quantity of the mixture, equal amount of solid NaCl and few drops of conc. H_2SO_4 are added and warmed.		
22	**Test for Ammonium radical (NH_4^+) :** To a small quantity of the mixture, NaOH solution is added and heated.		
23	**Test with Nessler's reagent** : A small quantity of the mixture, is dissolved in water, added excess of Nessler's reagent and few ml of NaOH solution.		

Wet Tests :

Preparation of sodium carbonate extract :

To a small quantity of the given mixture, thrice its amount of anhydrous sodium carbonate and few ml of distilled water are added, boiled and centrifuged. The centrifugate is known as sodium carbonate extract.

	EXPERIMENT	OBSERVATION	INFERENCE
1	**Test for halides :** A small portion of the sodium carbonate extract is acidified with dil HNO_3 and $AgNO_3$ solution is added.		
2	**Test for Nitrate - Brown ring test:** A small portion of the extract is acidified with dil. H_2SO_4 and freshly prepared ferrous sulphate solution is added. Then Conc. H_2SO_4 is added drop wise by keeping the test tube in an inclined position.		
3	**Test for acetate :** A small portion of the extract is acidified with dil HCl and the excess of acid is neutralised by adding few drops of ammonia. Excess of ammonia is removed by heating and then, neutral ferric chloride solution is added.		
4	**Test for oxalate :** a) A small portion of the extract is acidified with dil CH_3COOH and few drops of $CaCl_2$ solution is added.		
	b) To the above precipitate, few drops of dil H_2SO_4 is added, warmed and then few drops of dilute $KMnO_4$ solution is added.		

5	**Test for Tartrate - Silver mirror test :** In a clean test tube, few drops of $AgNO_3$ solution is taken. Then a very dilute solution of ammonia is added drop wise, till the precipitate of silver oxide formed is nearly dissolved but not completely. Now few drops of the sodium carbonate extract is added and then the test tube is heated by placing in a beaker of hot water.		
6	**Test for phosphate :** a) A small portion of the extract is acidified with dil. H_2SO_4 and the excess of acid is neutralised by adding ammonia solution and then solution of magnesia mixture is added. b) A small portion of the extract is neutralised with acetic acid and neutral ferric chloride solution is added.		
7	**Test for sulphate :** A small portion of the extract is acidified with dil.HCl and few drops of $BaCl_2$ solution is added.		

GENERAL GROUP SEPARATION TABLE :

GROUP SEPARATION TABLE:

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Report :

a) Anion : ....

b) Cations : ....

Preparation of Ammonium chloride

Ammonium chloride known as salt ammonia can be prepared by boiling the solution of ammonium sulphate with sodium chloride.

$$(NH_4)_2SO_4 + 2NaCl \rightarrow 2NH_4Cl + Na_2SO_4$$

Preparation :

5 gms of sodium chloride is dissolved in 50 ml of distilled water and the solution is concentrated by heating.

6 gms of ammonium sulphate is dissolved in 50 ml of distilled water and the solution is concentrated by heating.

Then the above two solutions are mixed slowly with constant stirring and then heated on a water bath for 30 minutes. On cooling, the least soluble Na_2SO_4 is crystallised. The mixture is filtered and the solution is concentrated by heating in a china dish. Then, a glass rod is dipped in the solution and exposed to air. When crystals are formed on the glass rod, the heating is stopped and the china dish is cooled to room temperature. The crystals of ammonium chloride containing Na_2SO_4 impurity is taken into a dry china dish and 3 funnel is inverted over it. The tip of the funnel is closed with cotton and the china dish is heated on a tripad stand. Ammonium chloride sublimed and collected on the inner walls of the funnel. It is then collected into a watch glass.

Preparation of Potash Alum

Potash alum (K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$) is a double salt of potassium sulphate and aluminium sulphate with 24 molecules of water as water of crystallisation.

Potash alum is prepared in the laboratory by mixing hot saturated solutions of K_2SO_4 and $Al_2(SO_4)_3$ and concentrating the solution.

Preparation :

5 gms of K_2SO_4 is dissolved in 50 ml of distilled water and then concentrated the solution in a china dish by heating. 20 gms of $Al_2(SO_4)_3$ is dissolved in 50 ml of distilled water and 5ml of dil. H_2SO_4 is added to prevent hydrolysis of the salt. The solution is concentrated by heating in a china dish.

25 ml of K_2SO_4 and 25 ml of $Al_2(SO_4)_3$ solutions are mixed in a china dish and then heated on a water bath for 30 minutes. A glass rod is dipped in the solution and exposed to air. When crystals are formed, heating is stopped and the solution is cooled. The solution is filtered and the crystals of alum are dried first with dry fitter paper and finally dried in hot air over at 100°c. Alum loses water of crystallisation at 200°c.

Preparation of Copper - ammonia complex

Preparation of Cupric ammine sulphate :

When ammonia is added to a cupric salt solution, a pale blue precipitate of cupric hydroxide first forms which then dissolves in excess of ammonium hydroxide to give an intense blue coloured solution of a complex cupric ammine sulphate.

$$CuSO_4 + 2NH_4OH \rightleftharpoons Cu(OH)_2 + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 4NH_3 \rightleftharpoons [Cu(NH_3)_4](OH)_2$$

The cupric ammine sulphate or tetra amine cupric sulphate which is insoluble in alcohol can be crystallised by changing the solvent from water to alcohol.

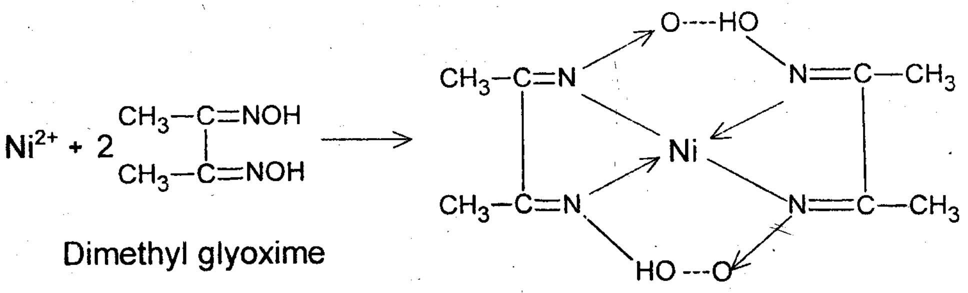
Preparation :

5 gms of hydrated copper sulphate ($CuSO_4 . 5H_2O$) crystals are dissolved in few ml of water in a beaker. About 5 ml of dil. H_2SO_4 is added to prevent the hydrolysis of $CuSO_4$. Now 1:1 ammonia solution is added drop wise with constant stirring until the pale blue precipitate formed just dissolves to give a deep blue solution. Then few drops of ammonia are added in excess to the blue solution. Now ethanol is added drop wise with constant stirring. This solution is now taken in a china dish and heated on a water bath and reduced the volume to half. A glass rod dipped in the solution and exposed to air. When the needle like crystals are formed. heating is stopped and the solution is filtered using a Gooch crucible and then the crystals are washed with alcohol.

Nickel - DMG complex

Preparation of Nickel Dimethyl Glyoxime :

Dimethyl glyoxime reacts with a solution of nickel salt in neutral or alkaline medium to give a bright red precipitate of nickel dimethyl glyoxime.



Dimethyl glyoxime

Nickel Dimethyl glyoxime

(కత్తిరించి పంపవలెను)

అధ్యాపకుల, విద్యార్థుల సలహాలు, సూచనలు :

అధ్యాపకులు, విద్యార్థులు ఈ స్టడీ మెటీరియల్‌కు సంబంధించిన సలహాలు, సూచనలు, ముద్రణ దోషాలు తెలియపరచినచో, పునర్ముద్రణలో తగు చర్యలు తీసుకొనగలము. తెలియపరచవలసిన చిరునామా : **డిప్యూటీ డైరెక్టర్, దూరవిద్యా కేంద్రం, ఆచార్య నాగార్జున విశ్వవిద్యాలయం, నాగార్జున నగర్ - 522 510.**

Course	Year	Paper No. & Title
B.Sc., Chemistry	2nd Year	Paper - II : Chemistry

(కత్తిరించి పంపవలెను)

(కత్తిరించి పంపవలెను)

(కత్తిరించి పంపవలెను)