

CHEMISTRY HANDBOOK

For [JEE Main & JEE Advanced & NEET] Examination



MOTION CORPORATE OFFICE

Motion Education Pvt. Ltd., 394 - Rajeev Gandhi Nagar, Kota-5 (Raj.)

☎ : 1800-212-1799, 8003899588 | url : www.motion.ac.in | ✉ : info@motion.ac.in

CONTENTS

S.No.	Topic	Page No.
1.	Physical Chemistry	05 – 34
2.	Organic Chemistry	35 – 47
3.	Inorganic Chemistry	48 - 58

IIT - JEE SYLLABUS

Physical chemistry

General topics: The concept of atoms and molecules; Dalton's atomic theory; Mole concept; Chemical formulae; Balanced chemical equations; Calculations (based on mole concept) involving common oxidation-reduction, neutralisation, and displacement reactions; Concentration in terms of mole fraction, molarity, molality and normality. **Gaseous and liquid states:** Absolute scale of temperature, ideal gas equation; Deviation from ideality, van der Waals equation; Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature; Law of partial pressures; Vapour pressure; Diffusion of gases. Atomic structure and chemical bonding: Bohr model, spectrum of hydrogen atom, quantum numbers; Wave-particle duality, de Broglie hypothesis; Uncertainty principle; Quantum mechanical picture of hydrogen atom (qualitative treatment), shapes of s, p and d orbitals; Electronic configurations of elements (up to atomic number 36); Aufbau principle; Pauli's exclusion principle and Hund's rule; Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only; Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral). **Energetics:** First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity. **Chemical equilibrium:** Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure); Significance of ΔG and ΔG° in chemical equilibrium; Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts. **Electrochemistry:** Electrochemical cells and cell reactions; Electrode potentials; Nernst equation and its relation to ΔG ; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductance, Kohlrausch's law; Concentration cells. **Chemical kinetics:** Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation). **Solid state:** Classification of solids, crystalline state, seven crystal systems (cell parameters a, b, c, α , β , γ), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices; Nearest neighbours, ionic radii, simple ionic compounds, point defects. **Solutions:** Raoult's law; Molecular weight determination from lowering of vapor pressure, elevation of boiling point and depression of freezing point. **Surface chemistry:** Elementary concepts of adsorption (excluding adsorption isotherms); Colloids: types, methods of preparation and general properties; Elementary ideas of emulsions, surfactants and micelles (only definitions and examples). **Nuclear chemistry:** Radioactivity: isotopes and isobars; Properties of α , β and γ rays; Kinetics of radioactive decay (decay series excluded), carbon dating; Stability of nuclei with respect to proton-neutron ratio; Brief discussion on fission and fusion reactions.

Inorganic Chemistry

Isolation/preparation and properties of the following non-metals: Boron, silicon, nitrogen, phosphorus, oxygen, sulphur and halogens; Properties of allotropes of carbon (only diamond and graphite), phosphorus and sulphur. **Preparation and properties of the following compounds:** **Oxides, peroxides, hydroxides, carbonates, bicarbonates, chlorides and sulphates of sodium, potassium, magnesium and calcium; Boron:** diborane, boric acid and borax; Aluminium: alumina, aluminium chloride and alums; Carbon: oxides and oxyacid (carbonic acid); Silicon: silicones, silicates and silicon carbide; Nitrogen: oxides, oxyacids and ammonia; Phosphorus: oxides, oxyacids (phosphorus acid, phosphoric acid) and phosphine; Oxygen: ozone and hydrogen peroxide; Sulphur: hydrogen sulphide, oxides, sulphurous acid, sulphuric acid and sodium thiosulphate; Halogens: hydrohalic acids, oxides and oxyacids of chlorine, bleaching

powder; Xenon fluorides; Fertilizers: commercially available (common) NPK type. **Transition elements (3d series):** Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment; Coordination compounds: nomenclature of mononuclear coordination compounds, cis-trans and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral). **Preparation and properties of the following compounds:** Oxides and chlorides of tin and lead; Oxides, chlorides and sulphates of Fe^{2+} , Cu^{2+} and Zn^{2+} ; Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate. **Ores and minerals:** Commonly occurring ores and minerals of iron, copper, tin, lead, magnesium, aluminium, zinc and silver. **Extractive metallurgy:** Chemical principles and reactions only (industrial details excluded); Carbon reduction method (iron and tin); Self reduction method (copper and lead); Electrolytic reduction method (magnesium and aluminium); Cyanide process (silver and gold). **Principles of qualitative analysis:** Groups I to V (only Ag^+ , Hg^{2+} , Cu^{2+} , Pb^{2+} , Bi^{3+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Mn^{2+} and Mg^{2+}); Nitrate, halides (excluding fluoride), sulphate, sulphide and sulphite.

Organic Chemistry

Concepts: Hybridisation of carbon; Sigma and pi-bonds; Shapes of molecules; Structural and geometrical isomerism; Optical isomerism of compounds containing up to two asymmetric centers, (R,S and E,Z nomenclature excluded); IUPAC nomenclature of simple organic compounds (only hydrocarbons, mono-functional and bi-functional compounds); Conformations of ethane and butane (Newman projections); Resonance and hyperconjugation; Keto-enol tautomerism; Determination of empirical and molecular formula of simple compounds (only combustion method); Hydrogen bonds: definition and their effects on physical properties of alcohols and carboxylic acids; Inductive and resonance effects on acidity and basicity of organic acids and bases; Polarity and inductive effects in alkyl halides; Reactive intermediates produced during homolytic and heterolytic bond cleavage; Formation, structure and stability of carbocations, carbanions and free radicals. **Preparation, properties and reactions of alkanes:** Homologous series, physical properties of alkanes (melting points, boiling points and density); Combustion and halogenation of alkanes; Preparation of alkanes by Wurtz reaction and decarboxylation reactions.

Preparation, properties and reactions of alkenes and alkynes: Physical properties of alkenes and alkynes (boiling points, density and dipole moments); Acidity of alkynes; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination); Reactions of alkenes with KMnO_4 and ozone; Reduction of alkenes and alkynes; Preparation of alkenes and alkynes by elimination reactions; Electrophilic addition reactions of alkenes with X_2 , HX , HOX and H_2O ($\text{X}=\text{halogen}$); Addition reactions of alkynes; Metal acetylides. **Reactions of benzene:** Structure and aromaticity; Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes. **Phenols:** Acidity, electrophilic substitution reactions (halogenation, nitration and sulphonation); Reimer-Tieman reaction, Kolbe reaction. **Characteristic reactions of the following (including those mentioned above):** Alkyl halides: rearrangement reactions of alkyl carbocation, Grignard reactions, nucleophilic substitution reactions; Alcohols: esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, $\text{ZnCl}_2/\text{conc. HCl}$, conversion of alcohols into aldehydes and ketones; Aldehydes and Ketones: oxidation, reduction, oxime and hydrazone formation; aldol condensation, Perkin reaction; Cannizzaro reaction; haloform reaction and nucleophilic addition reactions (Grignard addition); Carboxylic acids: formation of esters, acid chlorides and amides, ester hydrolysis; Amines: basicity of substituted anilines and aliphatic amines, preparation from nitro compounds, reaction with nitrous acid, azo coupling reaction of diazonium salts of aromatic amines, Sandmeyer and related reactions of diazonium salts; carbarylamine reaction; Haloarenes: nucleophilic aromatic substitution in haloarenes and substituted haloarenes - (excluding Benzyne mechanism and Cine substitution). **Carbohydrates:** Classification; mono and di-saccharides (glucose and sucrose); Oxidation, reduction, glycoside formation and hydrolysis of sucrose. **Amino acids and peptides:** General structure (only primary structure for peptides) and physical properties. **Properties and uses of some important polymers:** Natural rubber, cellulose, nylon, teflon and PVC. **Practical organic chemistry:** Detection of elements (N, S, halogens); Detection and identification of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro; Chemical methods of separation of mono-functional organic compounds from binary mixtures.

PART-I

PHYSICAL CHEMISTRY

THE MOLE CONCEPT

One Mole = Avogadro's Number $[N_A] = 6.023 \times 10^{23}$. It is the number of atoms present in exactly 12 g of C – 12 isotope.

Atomic weight [A] : Atomic weight is the relative weight of one atom of an element with respect to a standard weight

$$A = \frac{\text{weight of one atom of an element}}{\frac{1}{12} \text{th part by weight of an atom of C - 12 isotope u (atomic mass unit) weight :}$$

$$\text{One amu} = \frac{1}{12} \text{th part by weight of an atom of C - 12 isotope} = \frac{1}{N_A} \text{ g} = 1.66 \times 10^{-24} \text{ g}$$

☞ Atomic Weight (A) \times u = Absolute atomic weight.

☞ Atomic weight is a relative weight that indicates the relative heaviness of one atom of an element with respect to amu weight.

☞ Atomic weight has no unit because it is the ratio of weights.

☞ One mol of an u = 1.00 g

Change of scale for atomic weight : If an amu is defined differently as (1/x) th party by weight of an atom of C-12 isotope rather (1/12) th part than the atomic weight (A') can be derived as :

$$A' = A \left(\frac{x}{12} \right)$$

where, A = conventional atomic weight.

Molecular weight (MW) : Like atomic weight, it is the relative weight of a molecule of a compound with respect to amu weight.

$$MW = \frac{\text{weight of one molecule of a compound}}{\frac{1}{12} \text{th part by weight of an atom of C - 12 isotope}}$$

Gram atomic, gram molecular weight (M): It is the weight of 1.0 mol (Avogadro number) of atoms, molecules or ions in gram unit.

$$M = A u \times \text{Avogadro number} = A g$$

Hence, gram molecular weight (M) is numerically equal to the atomic weight (or molecular weight) in gram unit because 1.0 mol of u is 1.0 g.

Empirical and molecular formula : Empirical formula is the simplest formula of a compound with the elements in the simple whole number ratio eg.

Molecular formula

Empirical formula

C₆H₆ (benzene)

CH

C₆H₁₂O₆ (glucose)

CH₂O

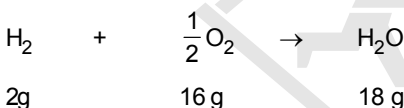
H₂O₂

HO

H₂S₂O₈

HSO₄

Laws of chemical combination: Elements combine in a fixed mass ratio, irrespective of their supplied mass ratio eg,



Here H₂ and O₂ combines in a fixed mass ratio of 1 : 8.

No matter in what ratio we mixed hydrogen and oxygen, they will always combine in 1 : 8 mass ratio

(stoichiometric mass ratio)

Limiting reactant : It is the reactant that is consumed completely during a chemical reaction. If the supplied mass ratio of reactants are not stoichiometric ratio, one of the reactant is consumed completely leaving parts of others unreacted. One that is consumed completely is known as Limiting reactant.

“Limiting Reactant determine the amount of product in a given chemical reaction.”

Concentration Units

(i) Molarity (M) : It is the moles of solute in one litre of solution.

$$M = \frac{n}{V} : n = \text{No. of solute in litre.}$$

⇒ Molarity (M) × Volume (V) = n (moles of solute)

If volume is in mL; MV = millimoles.

If d g/cc is density of a solution and it contains x% of solute of molar mass M, its

molarity can be worked out as :
$$\text{Molarity} = \frac{1000 \text{ dx}}{100 \text{ M}} = \frac{10 \text{ dx}}{\text{M}}$$

Dilution formula : If a concentrated solution is diluted following formula work:

$$M_1 V_1 = M_2 V_2$$

(M_1 and V_1 are the molarity and volumes before dilution and M_2 and V_2 are molarity and volumes after dilution)

Mixing of two or more solutions of different molarities: If two or more solutions of molarities M_1, M_2, M_3 are mixed together, molarity of the resulting solution can be worked out as:

$$M = \frac{M_1 V_1 + M_2 V_2 + M_3 V_3}{V_1 + V_2 + V_3}$$

(ii) Molality (m) : It is the number of moles of solute present in 1.0 kg of solvent :

$$m = \frac{\text{moles of solute (n)}}{\text{weight of solvent in g}} \times 1000$$

Molality is a true concentration unit. independent of temperature while molarity depends on temperature.

(iii) Normality (N) : It is the number of gram equivalents of solution in one litre of solution.

$$N = \frac{\text{gram equivalents of solute (Eq)}}{\text{volume of solutions in litre}}$$

(iv) Mole fraction (x_i) : It is the fraction of moles of a particular component in a mixture as

$$x_i = \frac{n_i}{\sum_{i=1}^n n_i}$$

(v) ppm (parts per million) Strength : It is defined as parts of solute present in 10^6 part of solution.

Equivalent Weight and Neutralization Titration

Equivalent weight of an element is that part by weight which combines with 1.0 g of hydrogen or 8.0 g of oxygen or 35.5 g of chlorine.

Equivalent weight of a salt

$$(EW) = \frac{\text{molar mass}}{\text{net positive (or negative) valency}}$$

eg, $EW : CaCl_2 = \frac{M}{2}, AlCl_3 = \frac{M}{3}, Al_2(SO_4)_3 = \frac{M}{6}$

Equivalent weights of acids and bases:

$$EW \text{ of acids} = \frac{\text{molar mass}}{\text{basicity}}$$

eg, $EW : HCl = M \text{ (basicity} = 1 \text{)} ;$

$$H_2SO_4 = \frac{M}{2} \text{ (basicity} = 2 \text{)}$$

$$H_3PO_4 = \frac{M}{3} \text{ (basicity} = 3 \text{)}$$

$$EW \text{ of bases} = \frac{\text{molar mass}}{\text{acidity}}$$

eg, $EW : NaOH = M, Ca(OH)_2 = \frac{M}{2} ; Al(OH)_3 = \frac{M}{3}$

The number of gram-equivalents (Eq) :

$$Eq = \frac{\text{weight of compound}}{\text{equivalent weight}} = \frac{w}{EW}$$

Mole equivalent relationship : In a given weight (w) of sample, no. of moles (n) and no. of equivalents (eq) are related as:

$$n = \frac{w}{M} \text{ and } Eq = \frac{w}{EW} \quad \Rightarrow \quad \frac{Eq}{n} = \frac{M}{EW} = n - \text{factor}$$

n-factor: For salt, it is valency, for acid, it is basicity and for base it is acidity.

$$N = \frac{Eq}{V \text{ (in litres)}}$$

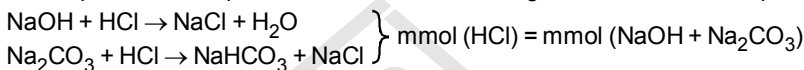
Normality/Molarity relationship :

$$N = \frac{Eq}{V} \text{ and } M = \frac{n}{V} \quad \Rightarrow \quad \frac{N}{M} = \frac{Eq}{n} = \frac{MW}{EW} = n - \text{factor}$$

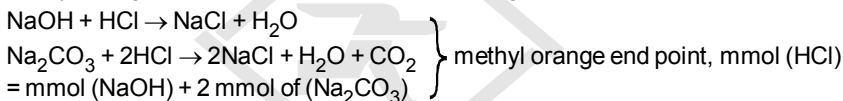
Acid base titration : In acid base titration, at the “End Point”.

Gram equivalent of acid = Gram equivalent of base

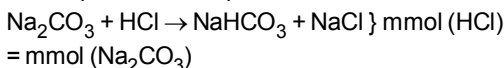
Titration of a mixture of NaOH/Na₂CO₃ : The mixture is analyzed by titrating against a standard acid in presence of phenolphthalein and methyl orange indicators. Phenolphthalein end point occur when the following neutralization is complete.



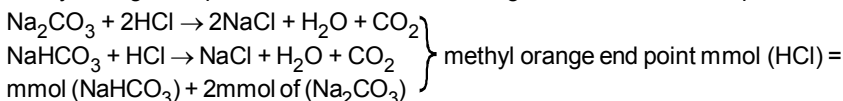
Methyl orange end point occur when the following neutralization is complete:



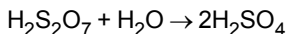
Titration of a mixture of NaHCO₃ / Na₂CO₃ : The mixture is analyzed by titrating against a standard acid in presence of phenolphthalein and methyl orange indicators. Phenolphthalein end point occur when the following neutralization is complete:



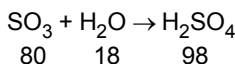
Methyl orange end point occur when the following neutralization is complete:



Percentage strength of oleum : It is the mass of H₂SO₄ obtained on hydrolysis of 100 g of oleum as :



The net reaction is :

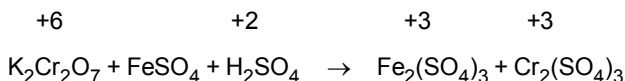


$$\Rightarrow \% \text{ of free SO}_3 \text{ in oleum} = \frac{80}{18} (\% \text{ strength} - 100)$$

REDOX REACTION AND REDOX TITRATION

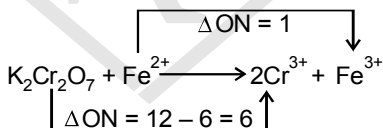
Oxidation : Loss of electrons or increase in oxidation number of oxidation.

Reduction : Gain of electrons or decrease in oxidation number is reduction.



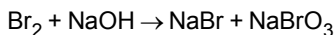
In the above redox reaction, chromium is reduced from + 6 to + 3 and iron is oxidized from + 2 to +3. Hence, $\text{K}_2\text{Cr}_2\text{O}_7$ is known as oxidizing agent (itself reduced) and FeSO_4 reducing agent (itself oxidized).

Quick balancing of a redox reaction: Cross-multiplication by net change in oxidation number per formula unit of oxidizing agent and reducing agent will balance the redox reaction in term of OA and RA as :



Hence, multiplying Fe^{2+} by 6 and $\text{K}_2\text{Cr}_2\text{O}_7$ by 1 will balance the reaction in terms of OA and RA.

Disproportionation reaction : It is a species is oxidized as well reduced eg.

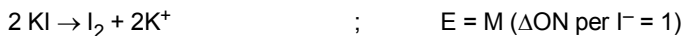
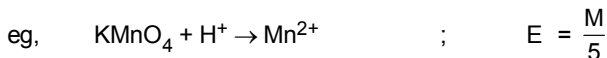


In this reaction, bromine is reduced to bromide and the same is oxidized to bromated, hence bromine is undergoing disproportionation reaction.

Equivalent weight of OA/RA:

Equivalent weight of

$$\text{OA/RA} = \frac{\text{Molar mass}}{\text{Change in ON per formula unit}}$$



n-factor and normality/molarity relationship:

$$N = \frac{\text{Eq}}{V} \text{ and } m = \frac{n}{V} \Rightarrow \frac{N}{M} = \frac{\text{Eq}}{n} = \frac{\text{MW}}{\text{EW}} = n - \text{factor}$$

n-factor = change in oxidation number per formula unit.

Redox titration : At the end point:

Gram equivalents of OA = Gram equivalent of RA.

GASEOUS STATE

$$\text{Pressure (p)} = \frac{\text{Force}}{\text{Area}} \text{ Nm}^{-2}$$

$$1.0 \text{ Nm}^{-2} = 1 \text{ Pa (Pascal)}$$

$$1.0 \text{ atmosphere} = 101325 \text{ Pa} = 10^5 \text{ Pa} = 76 \text{ cm of Hg column} = 760 \text{ mm of Hg} \\ = 760 \text{ torr} \quad (\therefore 1 \text{ mm of Hg} = 1 \text{ torr})$$

Temperature (T) : Absolute temperature

(or Kelvin temperature) = ($t^{\circ}\text{C} + 273$)K

Boyle's law: At constant temperature, for a definite amount of gas

$pV = \text{constant}$ (p vs V follow a rectangular hyperbolic path)

Charle's law: At constant pressure, for a definite amount of gas

$$V \propto T \Rightarrow \frac{V}{T} \text{ constant}$$

Avogadro's hypothesis : At same temperature and pressure:

$$V \propto n \Rightarrow \frac{V}{n} \text{ constant}$$

Combined gas law : $pV = nRT$ equation of idea gas.

$$\begin{aligned} R &= \text{Universal gas constant} \\ &= 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \\ &= 2 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Ideal gas : Gases that obey $pV = nRT$ are known as ideal gas.

Dalton's law of partial pressure : In a mixture of non-reacting gases:

$$\text{Total pressure (p)} = p_1 + p_2 + p_3 + \dots$$

where, $p_1, p_2, p_3 \dots$ etc. are the partial pressures of various components of the mixture.

$$\Rightarrow p = \sum_{i=1}^n p_i$$

Also: partial pressure of a component $p_i = x_i p$ (p = total pressure)

Here x_i = mole fraction of i th component

$$= \frac{n_i}{\sum_{i=1}^n n_i}$$

Molar volume at STP : At STP (0°C and 1.0 atm) 1.0 mol of an ideal gas occupies 22.4 L .

Effusion and Graham's law : In case of equimolar mixture of gases, ratio of their initial rate of effusion

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \text{ Graham's law}$$

(M_1 and M_2 are molar masses) If mixture contains different moles of gases then:

$$\frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$

Successive effusion : If a gaseous mixture containing n_1 mol of A and n_2 mol of B is allowed to effuse successively through a number of effusion chambers after n -step of effusion

$$\left(\frac{n_A}{n_B}\right)_{n+1} = \left(\frac{n_A}{n_B}\right)_1 \left(\frac{M_B}{M_A}\right)^{\frac{n}{2}} = \frac{n_1}{n_2} \left(\frac{M_B}{M_A}\right)^{\frac{n}{2}}$$

Kinetic theory of gases : Important postulates are For a pure gas, all its molecules are identical in shape, size and mass. Volume of gas molecules are negligible in comparison to volume of container. Collision among the gas molecules are perfectly elastic in nature. Average kinetic energy is directly proportional to absolute temperature.

Kinetic gas equation:

$$pV = \frac{1}{3} mNC^2 \quad (\overline{C^2} \text{ is mean square speed})$$

Average translational kinetic energy $E = \frac{3}{2} K_b T$

(K_b = Boltzmann's constant = 1.38×10^{-23})

For 1.0 mol : $E_{\text{trans}} = \frac{3}{2} RT$

Maxwell's law : $dN_u = 4\pi N \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}} u^2 du$

Here dN_u is the number of molecules having speeds between 'u' and $u + du$.

rms (root mean square speed) = $\sqrt{\frac{3RT}{M}}$

mps (most probable speed) = $\sqrt{\frac{2RT}{M}}$

Average speed = $\sqrt{\frac{8RT}{\pi M}}$

Real gas : Gases that do not obey $pV = nRT$ equation of state.

Compression (compressibility) factor (Z)

$$= \frac{V}{V_{\text{ideal}}} = \frac{pV_m}{RT}$$

For ideal gas, $Z = 1$ and for non-ideal gas $Z \neq 1$.

If $Z < 1$, net-intermolecular attraction exist and if $Z > 1$, net intermolecular repulsion exist.

van der Waals' equation:

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

"a" and "b" are van der Waals' constants and they are characteristic of a gas.

As $V \rightarrow \infty$, $Z \rightarrow 1$, ie, At very high temperature and very low pressure, a non-ideal gas becomes an ideal gas.

Virial equation :

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \quad B = b - \frac{a}{RT}$$

Boyle's temperature : $T_B = \frac{a}{Rb}$ (At Boyle temperature, a non-ideal gas becomes an ideal gas)

Critical points : Critical volume (V_c) = $3b$

Critical temperature (T_c) = $\frac{8a}{27Rb}$ (temperature above which only gaseous state exist)

$$\text{Critical pressure (} p_c \text{)} = \frac{a}{27b^2}$$

$$\text{At critical point } Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8}$$

ATOMIC STRUCTURE

Rutherford's nuclear model of atom: Through α -particle (He^{2+}) scattering experiment.

Rutherford presented that :

- (i) Atom is mostly empty.
- (ii) Atom possess a highly dense, positively charged centre called "Nucleus".
- (iii) Entire mass of atom is concentrated inside the nucleus.
- (iv) Later Rutherford model was abandoned due to its failure to comply with classical theory of electromagnetic radiation. Also the theory failed to explain the line spectrum of H-atom.

Plank's equation:

$$E = h\nu = \frac{hc}{\lambda}; h = 6.625 \times 10^{-34} \text{ Js}$$

Bohr's model : Angular momentum (mvr) = $\frac{nh}{2\pi}$,

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

Centrifugal force of orbiting electrons = Coulombic attraction by nucleus.

$$\Rightarrow \frac{mv^2}{4} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

Bohr's radius : $r_n = a_0 \frac{n^2}{A}$ where, a_0 = First Bohr's radius of H-atom. = 0.529 Å

Energy of electrons in nth Bohr's orbit (E_n):

$$E_n = -13.6 \times \frac{Z^2}{n^2} \text{ eV}$$

$$KE = -TE = \frac{-PE}{2}$$

Speed of electron in nth Bohr's orbit

$$(v_n) = \frac{2.18 \times 10^6 Z}{n} \text{ ms}^{-1}$$

No. of revolution made by an electron in nth Bohr's orbit = $\frac{v_n}{2\pi r}$ per sec.

Emission spectrum of H-atom: The frequency or wavelength or wavenumber of any spectral line in any of the series of H-atom can be calculated using the following Rydberg's equation:

$$\bar{\nu} = \frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]; R_H = 1.09678 \times 10^7 \text{ m}^{-1}$$

- (i) For Lyman series : $n_1 = 1, n_2 > 1$ (2,3,4,.....)
- (ii) For Balmer series : $n_1 = 2, n_2 > 2$ (3, 4, 5,)
- (iii) For Paschen series : $n_1 = 3, n_2 > 3$ (4, 5, 6,.....)
- (iv) For Brackett series : $n_1 = 4, n_2 > 4$ (5, 6, 7,)
- (v) For Pfund series : $n_1 = 5, n_2 > 5$ (6, 7, 8,)

Wave-Particle Duality (de-Broglie relationship)

$$\lambda = \frac{h}{p}, p = \text{momentum (mv)}$$

If an electron at rest is accelerated by a potential difference of 'V' volt then the de-Broglie wavelength:

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Heisenberg's uncertainty principle : According to this principle, simultaneous and accurate measurement of both position and momentum of an electron in an atom is impossible:

$$\Rightarrow \Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Here Δx is uncertainty in position and Δp is the uncertainty in momentum.

Quantum number: To describe an electron completely inside the atom, four sets of a quantum numbers are required. They are :

(i) Principal quantum number (n) : This specifies position and energy of an electron in the atom. Possible values of n are 1, 2, 3, 4 ∞ (positive integers).

(ii) Azimuthal (or even subsidiary) quantum number (ℓ): This is used to specify subshell (orbital). Possible values of ' ℓ ' are 0, 1, 2,($n - 1$). Orbitals with different ' ℓ ' values are denoted as : $\ell = 0$, s-orbital, $\ell = 1$, p-orbital, $\ell = 2$, d-orbital, $\ell = 3$, f-orbital etc. ' ℓ ' also determines shape of orbitals as:

$\ell = 0$, s-orbital, spherical shape.

$\ell = 1$, p-orbital, dumb-bell shape

$\ell = 2$, d-orbital, double dumb-bell shape.

It determines the orbital angular momentum (L) as:

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

It also determine magnitude of magnetic moment as:

$$\mu_L = \frac{h}{4\pi mC} \sqrt{l(l+1)} \quad \text{where, } \frac{3h}{4\pi mC} = 3.27 \times 10^{-14} \text{ J}$$

(iii) Magnetic quantum number (m) : It determine the preferred orientation of orbitals in three dimensional space. Its possible values are:

$$m = -l, \dots, 0, \dots, +l$$



Total values of $m = (2l + 1) = \text{no. of orbitals in a given orbital.}$



Spilliting of spectral lines occurs when placed in a magnetic field (Zeeman effect) or in an electric field (Stark effect). Total lines from a single line in the normal spectrum $= (2l + 1)$



The total number of orbitals in nth orbit $= n^2$



The total number of electrons in nth orbit $= 2n^2$

(iv) Spin quantum number(s) : Electrons spin on its own axis like a top, in clockwise and anticlockwise directions. The two directions of spinning are denoted by spin quantum number as:

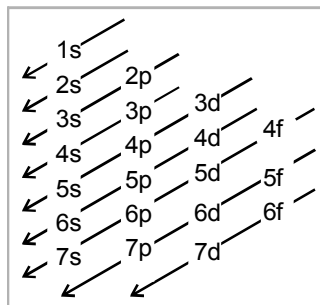
$$s = +\frac{1}{2} \text{ and } -\frac{1}{2}$$

Spin quantum number are also denoted by up-half arrow (\uparrow) and down-half arrow

(\downarrow) but neither the $+\frac{1}{2}$ and $-\frac{1}{2}$ nor the \uparrow or \downarrow are specific for and direction, they just represent the two opposite directions of spinning of electrons.

Electronic configuration:

Electrons are filled in atomic orbitals in increasing order of their energy according to Aufbau principle. During filling-up of electrons Pauli's exclusion principle is obeyed, ie, no two electrons in an orbital can have all four quantum numbers same (an orbital can have a maximum of $2e^-$).



Hund's rule of maximum multiplicity of obeyed, ie, orbitals of same energies are first singly occupied then pairing starts, Exception occurs in case of Cr (24) and Cu(29) as:

Cr : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ (not $3d^4 4s^2$)

Cu : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ (not $3d^9 4s^2$)

Quantum mechanical model of atom (Schrodinger's equation)

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

"Schrodinger's" Equation

Some normalized wave-functions:

$$1s : \quad \psi_{1s} = 2 \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

$$2s : \quad \psi_{2s} = \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}}$$

$$3p_x : \quad \psi_{2p_x} = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}}$$

Radial wave function (ψ) and no. of nodes : As ψ is plotted against distance from nucleus (r), $(n - l - 1)$ radial nodes are obtained. at nodes, the function ψ changes its sign.

Probability density (ψ^2) and radial distribution function $|R_{n,l}|^2 r^2$; For s and orbital, probability density (ψ^2) is maximum at nucleus but $|R_{n,l}|^2 r^2$ is minimum at nucleus. Also when any of these two functions are plotted against ' r ' $(n - l - 1)$ nodes are observed.

THERMOCHEMISTRY

Standard molar enthalpy of formation ($\Delta H^\circ_{\text{fm}}$) : It is the enthalpy change associated with the formation of one mole of a substance in the standard state from the constituent elements in their standard state. It can be either positive or negative.

Standard molar enthalpy of combustion ($\Delta H^\circ_{\text{comb}}$) : It is the heat evolved when one mole of a substance in the standard state is oxidized completely. $\Delta H^\circ_{\text{comb}}$ is always negative.

Standard enthalpy of a reaction ($\Delta H^\circ_{\text{rxn}}$) : It is the net enthalpy change associated with a reaction. It is determined with the help of ΔH°_f of reactants and products or from $\Delta H^\circ_{\text{comb}}$ of reactants and products

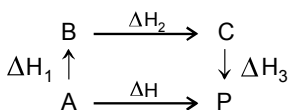
$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_f (\text{products}) - \sum \Delta H^\circ_f (\text{reactants})$$

or
$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{comb}} (\text{reactants}) - \sum \Delta H^\circ_{\text{comb}} (\text{products})$$

Also, ΔH°_f of a pure element in its standard state is zero.

Some properties of enthalpy change:

- (i) It is an extensive property ie, when a reaction is multiplied by a constant factor, enthalpy is also multiplied by the same factor.
- (ii) It is a state function, ie, it does not depend on path it depends on initial and final state of system.
- (iii) reversing a chemical reaction reverse the sign of enthalpy change.
- (iv) Hess's law of constant heat of summation:



According to Hess's law : $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Calorimetry : If a reaction is carried out in a calorimeter, the enthalpy change of reaction can be determined as:

$$q = ms\Delta T$$

Where, m = mass of calorimeter content

s = specific heat of calorimeter content

ΔT = change in temperature of calorimeter

Bond dissociation energy and bond-enthalpy:

Bond dissociation energy is the average energy required to break a specific type of bond in a molecule.

Bond enthalpy of a compound: It is the total energy required to convert one mole of a gaseous substance into their constituent atoms. In term of bond -enthalpy, $\Delta H^\circ_{\text{rxn}}$ can be determined as:

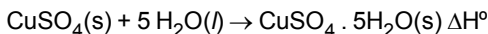
$$\Delta H^\circ_{\text{rxn}} = \sum \text{BE}(\text{reactants}) - \sum \text{BE}(\text{products})$$

Resonance energy : It is the difference in enthalpy change (ΔH) between one determined experimentally (calorimetrically) and other calculated theoretically.

$$\Rightarrow \Delta H_{\text{R.E.}} = \Delta H_{(\text{exp})} - \Delta H_{(\text{theoretical})}$$

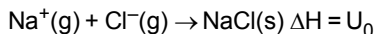
Enthalpy of neutralization : It is the heat liberated when one gram equivalent of an strong acid or base is neutralized completely. Hence, all neutralization reactions are exothermic in nature.

Enthalpy of hydration ($\Delta H^\circ_{\text{hyd}}$) : It is the heat evolved when one mole of a substance is hydrated to a certain specific degree of hydration eg.



Hence, ΔH° above is enthalpy of hydration of anhydrous $\text{CuSO}_4(\text{s})$ to its pentahydrate.

Lattice energy (U_0) : It is the heat liberated when one mole of an ionic compound in its standard state is formed from the constituent ions in their gaseous state eg,



THERMODYNAMICS

System and surrounding : System is that part of universe to which we focus our attention for studying the effect of applied change, ie, test tube, beaker, flask etc. Rest part of universe other than system is known as surrounding.

Types of system

(i) Open system : Exchange of both matter and energy with surroundings is allowed ie, $\Delta m \neq 0$, $\Delta E \neq 0$.

(ii) Closed system : Exchange of energy with surrounding is allowed but not the matter ie, $\Delta m = 0$, $\Delta E \neq 0$.

(iii) Isolated system : Exchange of neither matter nor energy with surrounding is allowed ie, $\Delta m = 0$, $\Delta E = 0$.

Thermodynamic processes : On the basis of condition of change, processes are classified into four types

(i) Isothermal process : Occur at constant temperature; $\Delta T = 0$.

(ii) Adiabatic process : Occur without exchange of heat with surrounding, $q = 0$.

(iii) Isobaric process : Occur at constant volume $\Delta V = 0$.

Reversible and irreversible processes

(i) Reversible process : Processes in which system always remains in equilibrium with surrounding, occur due to infinitesimal difference in conditions between system and surroundings.

(ii) Irreversible process: Process that occur against a constant external force (pressure). In this process system attain equilibrium only at the final state of change, ie, system does not remain in equilibrium with surroundings during the change.

Intensive and extensive properties

Intensive properties are those property which do not depend on the mass of sample, eg, temperature density concentration etc.

Extensive properties are those properties which depends on mass of the sample eg, mass, volume, heat capacity, energy etc.

State function : Those functions which do not depend on the path followed during the change. It depends only on the initial and the final state of system eg, internal energy, enthalpy, entropy Gibb's free energy, standard state emf etc. Properties

like heat, work etc depends on path and they are non-state (path) functions.

Sign convention : In thermodynamics, anythings given to the system are taken as positive eg, heat given to the system, $q_{\text{sys}} > 0$, work done on the system, $w_{\text{sys}} > 0$ etc. Anything given by the system are taken as negative eg, heat given by the system, $q_{\text{sys}} < 0$, work done by the system, $w_{\text{sys}} < 0$ etc. First law of thermodynamics deals with conservation of energy. If q amount of heat is given according to first law:

$$q = \Delta E + (-W) \Rightarrow \Delta E = q + W$$

where, ΔE = Change in internal energy.

Also, $\Delta E = q_v = nC_v\Delta T$

In irreversible isothermal expansion:

$$q = -W = p_{\text{ext}} \Delta V \quad (\Delta E = 0)$$

In reversible isothermal expansion:

$$q = -W = nRT \ln \frac{V_2}{V_1}$$

In adiabatic process:

$$-W = -\Delta E = -nC_v\Delta T = nC_v(T_1 - T_2)$$

Also in reversible process : $pV^\gamma = \text{constant}$, where $\gamma = \frac{C_p}{C_v}$

$$TV^{\gamma-1} = \text{constant} \quad \text{and} \quad p^{1-\gamma} T^\gamma = \text{constant}$$

In irreversible adiabatic process : If gas is expanded against a constant external pressure p_{ext}

$$T_f = \left[\frac{C_v + (P_{\text{ext}} / p_1)R}{C_v + (p_{\text{ext}} / p_2)R} \right] T_i$$

where, T_i = initial temperature,

If $p_{\text{ext}} = p_2$ then

$$T_f = \left[\frac{C_v + (P_2 / p_1)R}{C_v + R} \right] T_i = \left[\frac{C_v + (P_2 / p_1)R}{C_p} \right] T_i$$

Enthalpy : $H = E + pV$

$$\Rightarrow dH = dE + pdV + Vdp$$

At constant pressure : $dH = dE + pdV = Q_p = C_p dT$

$$\Rightarrow \Delta H = \Delta E + p\Delta V = C_p \Delta T$$

Entropy : $S = \frac{q_{rev}}{T}$

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right)$$

$$= nC_p \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{p_1}{p_2} \right)$$

Gibb's free energy (G) :

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

Also

$$dG = Vdp - SdT$$

At constant temperature : $\Delta G = nRT \ln \left(\frac{p_1}{p_2} \right)$

Criteria for spontaneity : For a spontaneous process, entropy of universe must increase ie,

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 \text{ or } \Delta G_{sys} < 0$$

(i) If $\Delta H < 0$, $\Delta S > 0$, ΔG is always negative, always spontaneous.

(ii) If $\Delta H > 0$ and $\Delta S < 0$, ΔG is always positive, always non-spontaneous.

(iii) If $\Delta H > 0$ and $\Delta S > 0$, process will be spontaneous at high temperature only.

(iv) If $\Delta H < 0$, $\Delta S < 0$, process will be spontaneous only at lower temperature.

CHEMICAL EQUILIBRIUM

Law of mass-action : According to law of mass action, rate of a reaction is proportional to the active masses of reacting species raised to the power stoichiometric coefficients.



Rate of forward reaction

$$(R_f) \propto [A]^a[B]^b \Rightarrow R_f = k_f [A]^a[B]^b$$

Rate of back ward reaction

$$(R_b) \propto [D]^d[E]^e \Rightarrow R_b = k_b [D]^d[E]^e$$

Active mass : For solution, active mass is the mean molar concentration. For gases, active mass is partial pressure. For solids and pure liquids, active mass is unity.

At equilibrium: Rate of forward reaction = Rate of backward reaction.

$$\Rightarrow \frac{k_f}{k_b} = \frac{[D]^d[E]^e}{[A]^a[B]^b} = K_C$$

(Equilibrium constant expressed in terms of concentration). If the reactants and products are in gaseous state :

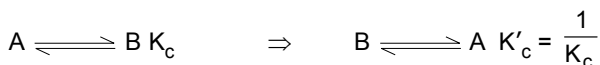
$$K_p = \frac{p_D^d p_E^e}{p_A^a p_B^b}$$

Properties of equilibrium constants:

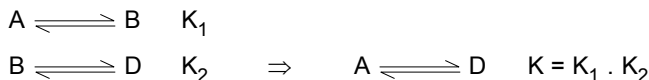
- (i) Equilibrium constant (K_c or K_p) is a characteristic constant for a given reaction.
- (ii) Equilibrium constant of a reaction does not depend on concentration, pressure, volume, catalyst.
- (iii) Equilibrium constant depends only on temperature.
- (iv) If a reversible reaction is multiplied by a constant factor, equilibrium constant changes as follows:



(v) If a reversible reaction reversed, equilibrium constant is inversed as



(iv) If reversible reactions are added, equilibrium constants are multiplied:

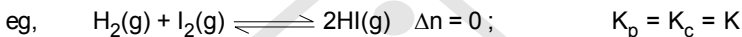


Reversible reaction where $\Delta n = 0$: In this type of reversible reactions, $K_p = K_c = K$ (a dimensionless equilibrium constant)

$$K_p = K_c (RT)^{\Delta n}$$

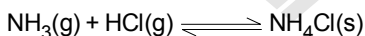
where,

Δn = (stoichiometric coefficients of products – {stoichiometric coefficients of reactants})



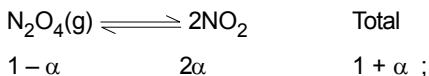
$$K_p = K_c = K$$

Important: In determining Δn ; species whose active masses are unity, are not considered eg,



$$\Delta n = 0 - 2 = -2$$

Reversible reactions where $\Delta n \neq 0$: Such type of reactions require extra attention when manipulating at equilibrium. In this case, K_p and K_c are never same



α = degree of dissociation

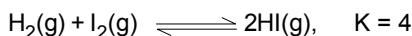
$$\text{Mole - fractions : } \frac{1 - \alpha}{1 + \alpha} \quad \frac{2\alpha}{1 + \alpha}$$

$$\text{Partial pressure : } \frac{1 - \alpha}{1 + \alpha} p \quad \frac{2\alpha p}{1 + \alpha} ;$$

p = Equilibrium total pressure, not the initial pressure p_0 ,

$$\Rightarrow K_p = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{1-\alpha p}{1+\alpha}\right)} = \frac{4\alpha^2}{1-\alpha^2}$$

Reaction Quotient (Q) : It is the law of mass action expression but at non-equilibrium position. It helps in determining the spontaneous direction of change that occur from the given initial position eg,



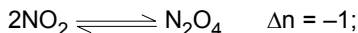
If one mol of each H_2 , I_2 and HI are mixed then

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 1$$

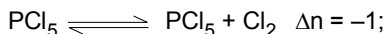
\therefore $Q < K$, reaction will proceed in forward direction to attain the equilibrium. Similarly if $Q > K$, reaction will proceed in backward direction to restore equilibrium.

Le-Chatelier's principle: When a stress is applied to the system at equilibrium, system adjust itself (by moving in forward or backward direction) in order to nullify the effect of applied stress.

(i) Effect of pressure and volume at constant temperature : If for a fixed amount of equilibrium system, pressure is increased at constant temperature, reaction proceed from more crowded to less crowded side to restore equilibrium.

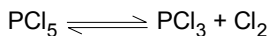


increase in pressure, forward shift.



Increase in pressure, backward shift. Reverse is true for decrease in pressure.

(ii) Effect of adding/removing reactant/product: If an addition is done at equilibrium (whether reactant or product), reaction proceeds in a direction opposite to the side where addition is done. If a removal is done at equilibrium (whether reactant or product), reaction proceed to the side from where removal is done eg.



Add PCl_5 - Forward shift

Add PCl_3 or Cl_2 - Backward shift

Remove PCl_5 - Backward shift

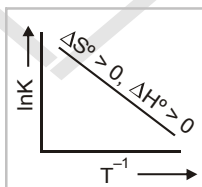
Remove PCl_3 or Cl_2 - Forward shift

(iii) Effect of adding “Inert Gas”: If an inert gas is added at constant volume, it does not affect equilibrium composition anyway. If an inert gas is added at constant pressure, it has the same effect as of increasing volume i.e., reaction proceeds towards more crowded side.

(iv) Effect of catalyst: A catalyst has no effect on equilibrium however it speeds up both forward and backward reaction and reduces the time required to attain equilibrium.

(v) Effect of temperature : Increasing temperature increases the equilibrium constant (K) of an endothermic reaction i.e., forward reaction is favoured. Decreasing temperature increases equilibrium constant (K) of an exothermic reaction and forward reaction is favoured.

Equilibrium and Thermodynamics:



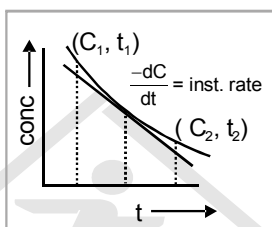
$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T \Delta S^\circ$$

$$\Rightarrow \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

CHEMICAL KINETICS

Average and instantaneous rate : Average rate of reaction is the rate measured between a finite time intervals, Instantaneous rate of reaction is the rate measured at a given instant.

$$\text{Avg. rate} = \frac{C_2 - C_1}{t_2 - t_1}$$



Rate law : $aA + bB \rightarrow dD + eE$

Inst - Rate

$$= \frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = \frac{1}{e} \frac{d[E]}{dt} = k[A]^m[B]^n$$

Rate constant $[k]$, characteristic of a given reaction, independent of pressure, volume or amount. k is independent on temperature and it changes on addition of a catalyst.

(i) 'm' and 'n' are the partial orders with respect to A and B and $(m + n)$ is the overall order of a reaction. Order of a reaction is a permanent constant, independent of any physical or chemical parameters.

First order reaction : $A \rightarrow P$

$$\frac{-d[A]}{dt} = k[A] \Rightarrow [A] = [A]_0 e^{-kt}$$

Half-life ($t_{1/2}$) = $\frac{\ln 2}{k}$ independent of initial amount of reactant.

(ii) Both concentration '[A]' and rate decreases exponentially with time.

(iii) Reaction complete in infinite time.

(iv) All radioactive process are first order.

n^{th} order reaction : $A \rightarrow P$

$$\frac{-d[A]}{dt} = k[A]^n \quad \Rightarrow \quad kt = \frac{1}{(n-1)} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

$$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1} - 1}{[A]_0^{n-1}} \right]$$

Effect of temperature on rate : increasing temperature increases the rate of reaction. Rate constant is related to temperature by arrhenius equation as

$$k = Ae^{-\frac{E_a}{RT}} \text{ or } \ln k = \ln A - \frac{E_a}{RT}$$

E_a = Activation energy

A = pre-exponential factor or frequency factor Temperature coefficient : It is the factor by which rate of reaction increases on increasing temperature by 10° . For most of the reaction it ranges between 2 and 3.

Effect of catalyst: A catalyst lowers the activation energy, hence increases the rate of reaction.

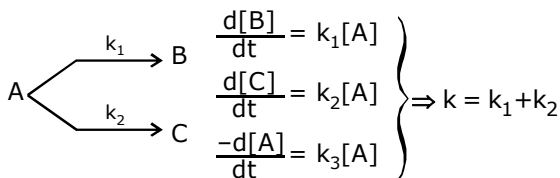
$$\ln \left(\frac{k_c}{k_{uc}} \right) = \frac{E_{uc} - E_c}{RT}$$

k_c = rate constant for catalyzed path

k_{uc} = rate constant for uncatalyzed, path

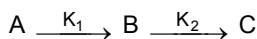
E_{uc} and E_c are activation energies of uncatalyzed and catalyzed paths.

Parallel first order reaction:



At any instant : $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

Consecutive first order reaction:

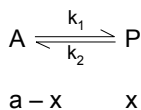


$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

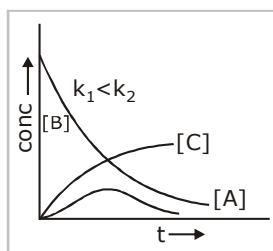
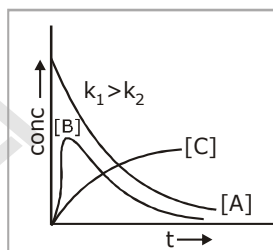
$$t_{\max} = \frac{1}{k_2 - k_1} \ln \left(\frac{k_2}{k_1} \right)$$

$$[B]_{\max} = [A]_0 \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{k_1 - k_2}}$$



$$\frac{dx}{dt} = k_1(a - x) - k_2x$$

$$\Rightarrow t = \frac{1}{k_1 + k_2} \ln \left[\frac{k_1 a}{k_1 a - (k_1 + k_2)x} \right]$$

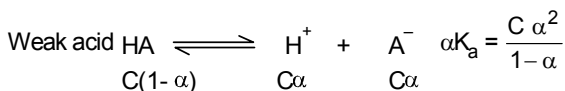


IONIC EQUILIBRIUM

pH and pOH of acids and bases

$\text{pH} = -\log [\text{H}^+]$ and $\text{pOH} = -\log [\text{OH}^-]$

for any solution ; $\text{pH} + \text{pOH} = 14$ at 25°C



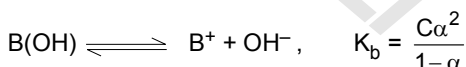
If α is very small $1 - \alpha \approx 1$, $K_a = C\alpha^2$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad \text{Ostwald's law}$$

According to the Ostwald's law, degree of ionization of weak electrolyte increases with dilution. As $C \rightarrow 0$, $\alpha \rightarrow 1$

$$\text{If } 1 - \alpha \approx 1, K_a = \frac{[\text{H}^+]^2}{C} \Rightarrow [\text{H}^+] = \sqrt{K_a C}$$

In case of weak base:

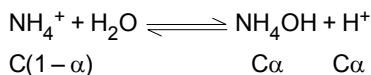


$$(C - \alpha) \qquad C\alpha \quad C\alpha$$

$$K_h = \frac{K_w}{K_a} = \frac{C\alpha^2}{1 - \alpha}$$

If " α " is small, $[\text{OH}^-] = \sqrt{K_h C}$

(iii) Salt of strong acid and weak base eg, NH_4Cl - acidic salt.



$$K_h = \frac{K_w}{K_b} = \frac{C\alpha^2}{1 - \alpha}$$

If α is very small, $[H^+] = \sqrt{K_h C}$

(iv) Salt of weak acid and weak base eg, CH_3COONH_4 : Nature of salt depends on K_a and K_b values, if $K_a > K_b$ – acidic and if $K_a < K_b$, basic salt

$$[H^+] = \sqrt{\frac{K_w K_a}{K_b}}$$

(Independent of salt concentration)

Buffer solution : A solution that maintain almost constant pH. If small amount of strong acid or strong base is added to buffer solution, pH of solution remains almost invariable.

Acid buffer : Formed by mixing weak acid with salt of its conjugate base eg, CH_3COOH and CH_3COONa , HCN & $NaCN$, HF and CaF_2 etc.

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Basic buffer : Formed by mixing weak base and salt of its conjugate acid eg, $(NH_3 + NH_4Cl)$ etc. For basic buffer

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

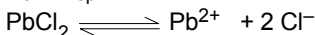
Solubility and solubility product: Solubility (s) is the moles of salt dissolved to obtain one litre of its saturated solution eg,



Solubility:



$$K_c = K_{sp} = [Ag^+] [Cl^-] = S^2$$



$$K_{sp} = [Pb^{2+}] [Cl^-]^2 = S[2S]^2 = 4S^3$$



$$K_{sp} = (xS)^x (yS)^y = x^x y^y (S)^{x+y}$$

SOLID STATE

Radius ratio : In a given coordination number, radius ratio has fixed value in the limiting case.

C.N.	3	4(T_d)	4(sp)	6	8
r_+/r_-	0.155	0.225	0.414	0.414	0.732

Packing fraction : In atomic solid, the greatest fraction of unit cell that can be occupied by atoms are

SC	BCC	FCC	HCP
0.53	0.68	0.74	0.74

Relationship between radius and side-length of unit cell in closest packing

SC	BCC	FCC	HCP
$a = 2r$	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	$a = 2r$ $h = \left(4\sqrt{\frac{2}{3}}\right)r$

Seven crystal system and cell parameters

System	Parameters	Interaxial angles
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$

System	Parameters	Interaxial angles
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

Density of solid : If there are N particles per unit cell and M is the molar mass then density can be calculated as

$$\text{density (f)} = \frac{NM}{N_A \cdot V} \quad \left. \vphantom{\frac{NM}{N_A \cdot V}} \right\} N_A = \text{Avogadro's number, } V = \text{volume of unit cell.}$$

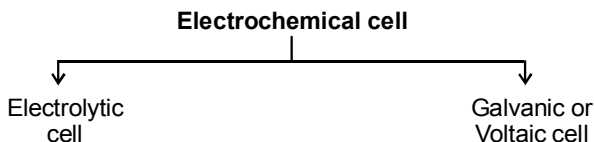
Tetrahedral and octahedral voids : If there are N particles per unit cell then there will be “ $2N$ ” tetrahedral voids and “ N ” octahedral voids.

Point defect:

Schottky Defect : A pair of ions remaining absent from their normal lattice positions, found in ionic solids in which cation and anion have comparable size.

Frenkel Defect : An ion remaining absent from its normal lattice point, but occupying interstitial voids, found in ionic solid in which cation is much smaller than anions.

ELECTROCHEMISTRY



Faraday's Law of electrolysis:

(i) The amount of electrolyte discharged at an electrode is directly proportional to the quantity of electricity passed eg,

$W \propto Q$, where, $Q = It$, I = current strength

$\Rightarrow W = zIt$ where, 'Z' is constant of proportionality, known as electrochemical equivalence (ECE).

ECE : It is the amount of electrolyte discharged on passing one coulomb of electricity.

Faraday's constant 'F' : It is the charge possessed by 1.0 mol of electrons and it is equal to 96500 C (approx). In term of Faraday's constant, the number of gram equivalent of electrolyte discharged at an electrode is equal to number of faradays passed.

$$\Rightarrow W = E \left(\frac{Q}{96500} \right) \quad \text{where, } E = \text{equivalent weight}$$

(ii) If same quantity of electricity is passed through different cells connected in series, same number of gram equivalent of electrolytes are discharged at each of the electrodes.

\Rightarrow If same quantity of electricity is passed through different cells connected in series, same number of gram equivalent of electrolytes are discharged at each of the electrodes.

$$\Rightarrow \frac{W_1}{W_2} = \frac{E_1}{E_2} \quad W_1 \text{ and } W_2 \text{ are weight of electrolytes discharged at two different}$$

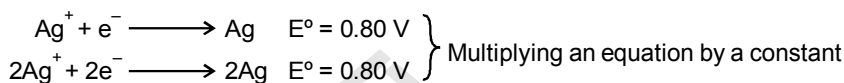
electrodes in two different cells connected in series and E_1 and E_2 are their respective equivalent weights.

Galvanic cell

EMF: It is the potential difference across the electrodes.

Standard state emf of a cell (E°): It is the emf of a cell when all the species have unit active mass.

(i) E° is an intensive properties ie, it does not depend on amount eg,



factor do not change E° .

(ii) In a galvanic cell ; $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

(iii) Half-cell with smaller E° constitute anode and half-cell with larger E°

constitute cathode eg, in Daniell cell, $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ and $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34$

V. Hence, Zn electrode is anode and Cu electrode is cathode and E°_{Cell} is 1.10 V.

(iv) Smaller the value of E° stronger is the reducing agent and larger the value of E° , stronger the oxidising agent.

Gibbs Free Energy and 'E' : $\Delta G = -nEF$

In standard state, $\Delta G = -nE^\circ F$

The Nernst's equation:

$$E = E^\circ - \frac{0.059}{n} \log Q \text{ at } 25^\circ\text{C}.$$

COLLIGATIVE PROPERTIES OF DILUTE SOLUTION

Raoult's law and vapour pressure of solution: According to Raoult's law, addition of a non-volatile solute to a volatile solvent ($V. P = p_0$) decreases vapour pressure of solution.

$p = p_0 x_1$ where, $p = V. P.$ of solution and x_1 is mole fraction of solvent.

Relative lowering of V.P. = $\frac{-\Delta p}{p_0} = \frac{p_0 - p}{p_0} = x_2$ (a colligative property)

Elevation of boiling point (Ebullioscopy) : Addition of a non-volatile solute to a volatile solvent increases the boiling point of solution and

$$\Delta T_b = K_b \cdot m$$

$\Delta T_b = T_b - T_b^\circ$; T_b = boiling point of solution, T_b° is boiling point of pure solvent, m = molality of solution.

K_b = molal elevation constant (ebullioscopic constant), a characteristic of solvent and determined as

$$K_b = \frac{M_1 R (T_b^\circ)^2}{\Delta H_{M_v}} \quad M_1 = \text{Molar mass of solvent}$$

T_b° = Boiling point of solvent

ΔH_{M_v} = Molar enthalpy of vaporization of solvent.

Depression in freezing point (Cryoscopy): Addition of a non-volatile solute to a volatile solvent lowers the freezing point of solution as

$$-\Delta T_f = T_f^\circ - T_f = K_f m$$

T_f° = freezing point of pure solvent, T_f = freezing point of solution, m = molality of solution and K_f = molal depression (cryoscopic) constant, characteristic of solvent.

$K_f = \frac{M_1 R (T_f^\circ)^2}{\Delta H_{mf}} \quad M_1 = \text{molar mass of solvent} \quad \Delta H_{mf} = \text{molar enthalpy of fusion of solvent.}$

Osmosis and osmotic pressure (π) :

$$\pi = CRT = hfg$$

C = concentration T = experimental temperature, h = height of liquid raised in capillary attached to solution chamber of osmometer, f = density of solution and g is acceleration due to gravity.

Binary solution : When two volatile solvents A and B with their vapour pressures p_A° and p_B° are mixed, the resulting solution is known as binary mixed, the resulting solution is known as binary solution whose vapour pressure lies between p_A° and p_B° and determined as

$$p = p_A + p_B = x_A p_A^\circ + x_B p_B^\circ \dots\dots\dots(a)$$

Where, x_A and x_B are mole fractions of A and B in solution. The mole fractions of A and B in the vapour phase are y_A and y_B then

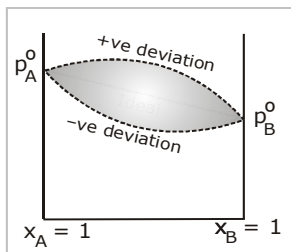
$$y_A = \frac{p_A}{p} = \frac{x_A p_A^\circ}{x_A p_A^\circ + x_B p_B^\circ}$$

and
$$y_B = 1 - y_A = \frac{p_B}{p} = \frac{x_B p_B^\circ}{x_A p_A^\circ + x_B p_B^\circ}$$

Ideal and non-ideal solution : If the solution obeys Raoult's law i.e., equation a, it is called ideal binary solution otherwise non-ideal binary solution.

(i) If observed vapour pressure is greater than the ideal vapour pressure, it is known as positive (+) deviation.

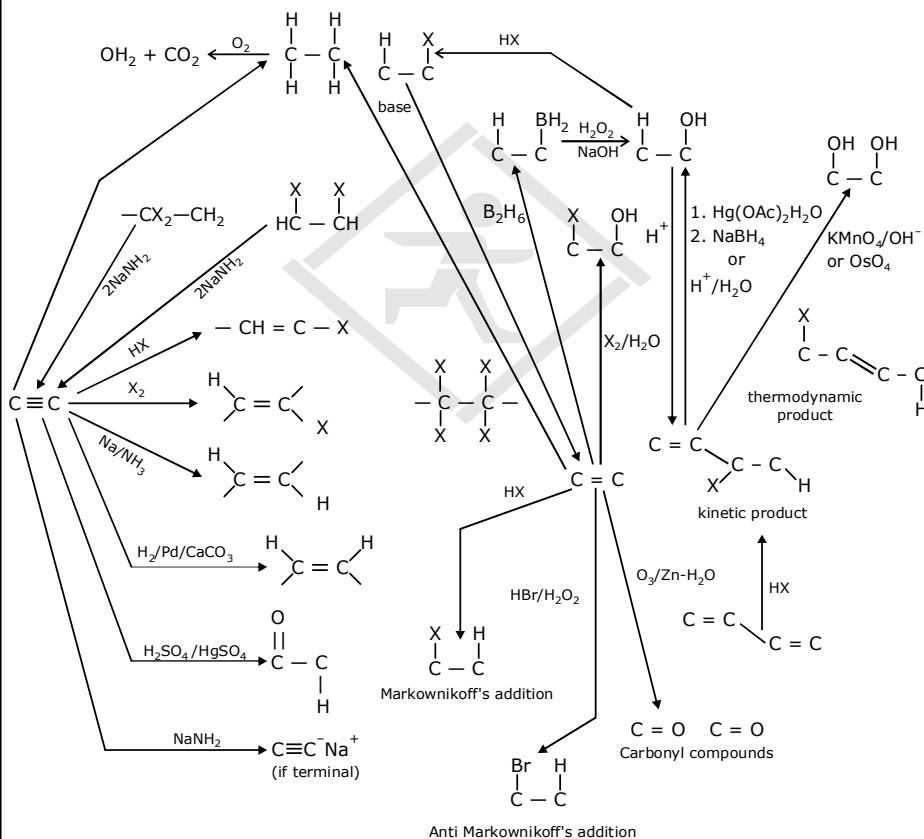
(ii) If the observed vapour pressure approaches to ideal curve on dilution hence dilution decreases the extent of deviation.



PART-II ORGANIC CHEMISTRY

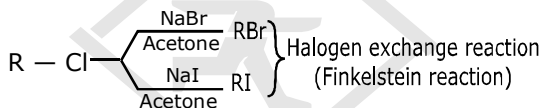
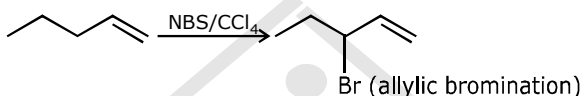
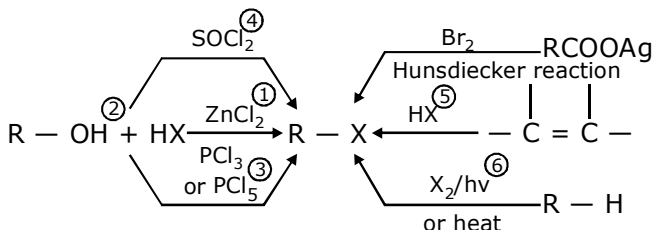
REACTION SUMMARY

HYDROCARBONS



ALKYL HALIDES

Preparation

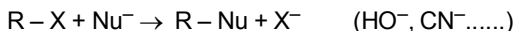


- (i) Tertiary alcohol react even in absence of a Lewis catalyst.
- (ii) Reaction proceeds via carbocation intermediate, rearrangement may accompany.
- (iii) Primary alcohol react without undergoing rearrangement.
- (iv) Primary alcohol give un-rearranged product, not suitable with 2° or 3° alcohols.
- (v) Addition proceeds through carbocation intermediate, rearrangement may accompany.
- (vi) Free radical halogenation, not suitable for fluorination or direct iodination. Iodination can be achieved using an oxidising agent with I_2 .

Properties : A polar, covalent compound, undergo substitution and elimination reactions.

Substitution Reaction

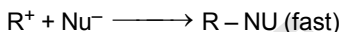
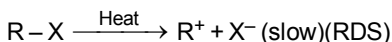
S_N2 reaction :



Salient features of S_N2 reaction :

- (i) The reaction is an elementary, bimolecular in nature.
- (ii) No reactive intermediate and only one transition state is involved.
- (iii) Reaction usually require a strong nucleophile.
- (iv) The order of leaving ability is $F^- < Cl^- < Br^- < I^-$
- (v) The reactivity of different alkyl halides is : $3^\circ < 2^\circ < 1^\circ$.
- (vi) There occur inversion of configuration at α -carbon.
- (vii) Polar, protic solvents like H_2O , ROH slow down the reaction.
- (viii) Polar, aprotic solvents like DMSO, DMF, THF etc. favour reaction.
- (ix) Vinyl and aryl halides are usually inert in this reaction.

S_N1 Reaction :

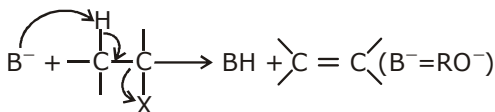


Salient features of S_N1 reaction:

- (i) It is a two step process as shown above first order in alkyl halide and first order overall.
- (ii) Carbocation may undergo rearrangement.
- (iii) The order of leaving ability is $F^- < Cl^- < Br^- < I^-$
- (iv) Reactivity of alkyl group:
 $1^\circ < 2^\circ < 3^\circ < \text{allylic} < \text{benzylic}$.
- (v) Reaction occur at elevated temperature.
- (vi) Strength of nucleophile is unimportant because it is involved in non-rate determining step.
- (vii) Polar solvents favour reaction. Presence of Lewis acid catalyst speed-up reaction.

Elimination Reaction

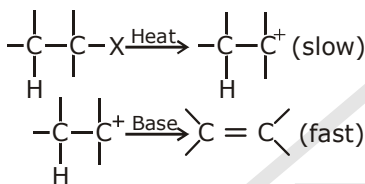
Bimolecular (E-2) elimination:



Salient Features of E-2 reaction:

- (i) It is single step, bimolecular, concerted reaction, with order of reaction equal to 2.
- (ii) Presence of a β -hydrogen anti to leaving group is essential.
- (iii) In case of more than one type of β -H, elimination occurs to produce most substituted, most stable product as major product.
- (iv) The order of leaving ability is $F^- < Cl^- < Br^- < I^-$
- (v) The order of reactivity is : $1^\circ < 2^\circ < 3^\circ$.
- (vi) Polar protic solvent slow down the reaction.
- (vii) Presence of a strong base is essential.

● **Unimolecular Elimination (E-1)**

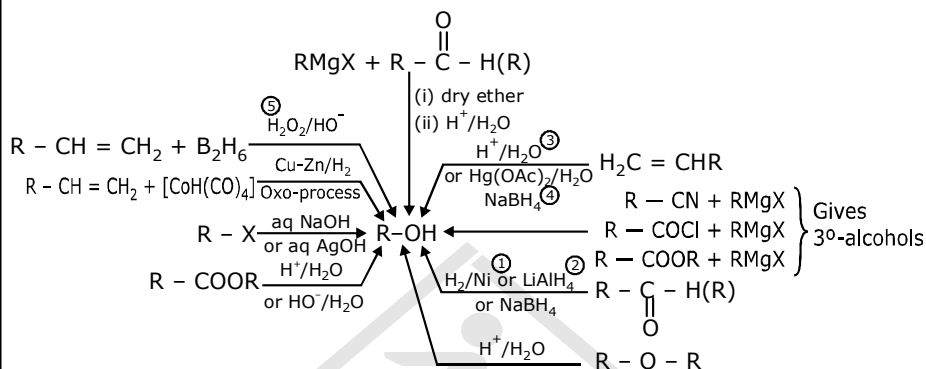


Salient features of E-1 reactions:

- (i) It is a two step reaction, proceed via carbocation intermediate. Therefore, carbocation may undergo rearrangement.
- (ii) The order of leaving ability is $F^- < Cl^- < Br^- < I^-$
- (iii) The order of reactivity is : $1^\circ < 2^\circ < 3^\circ$ (same as S_N1).
- (iv) Reaction complete with S_N1 , high temperature favour E-1.
- (v) Strength of base is unimportant.
- (vi) Polar solvent or Lewis acid catalyst favours reaction.

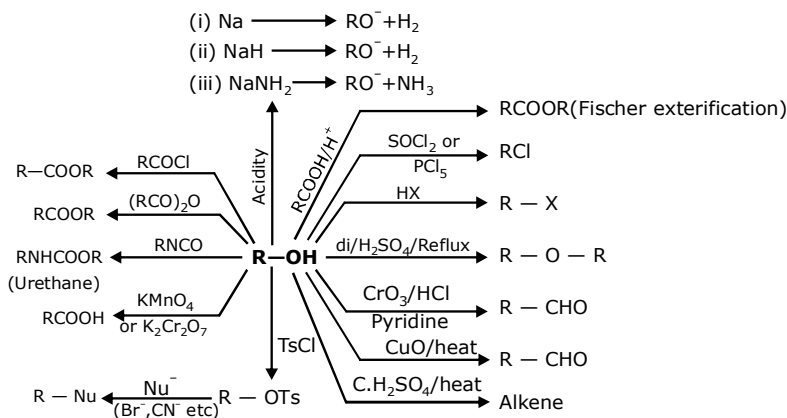
ALCOHOLS, ETHERS AND EPOXIDES

Alcohol Preparation



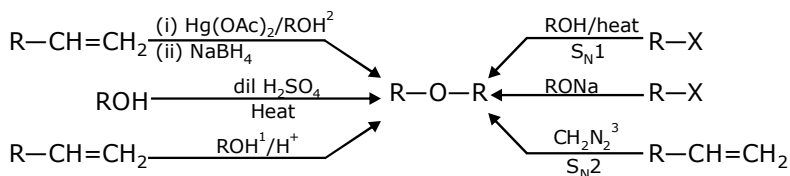
- (i) H_2/Ni reduces all reducible groups including olefinic bonds.
- (ii) LiAlH_4 does not reduce olefinic bonds.
- (iii) Reaction proceeds via carbocation, rearrangement may accompany.
- (iv) Avoid rearrangement
- (v) Anti-Markownikoff's hydration takes place.

Properties



Ethers

Preparation

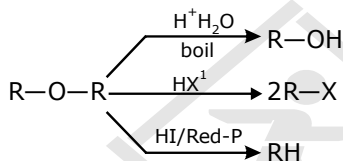


(i) Proceed via carbocation intermediate, rearrangement may take place.

(ii) Do not proceed via carbocation intermediate, rearrangement is avoided.

(iii) Gives methyl ether ($\text{RCH}_2\text{CH}_2\text{OCH}_3$)

Properties: Ethers are one of the most inert organic compound, not attacked by base, used as inert solvent in most of the organic synthesis.

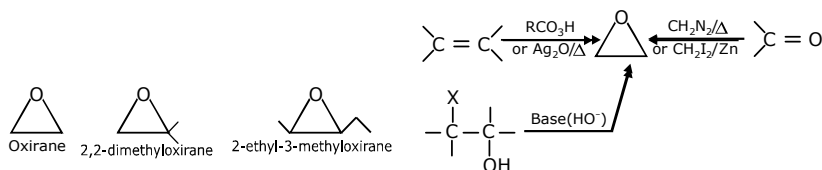


In case of phenyl ether, one product is phenol:

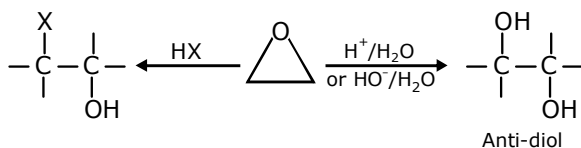


Epoxides : The cyclic ether

Preparation :

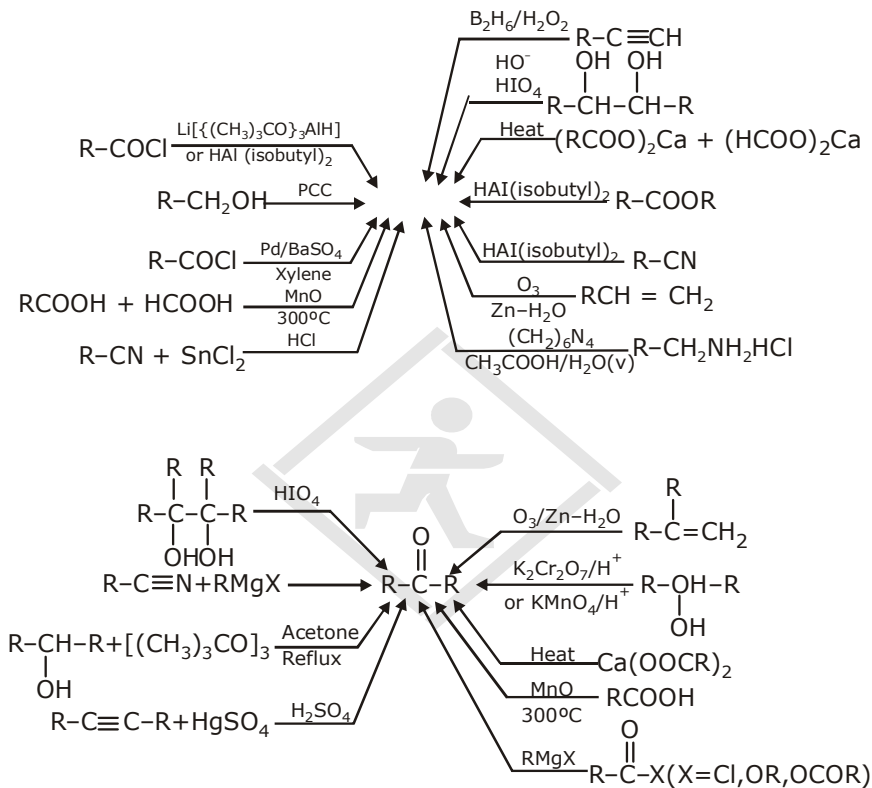


Properties:



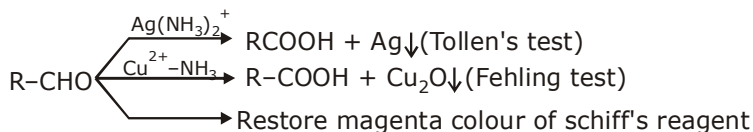
ALDEHYDE AND KETONE

Preparation :



Properties:

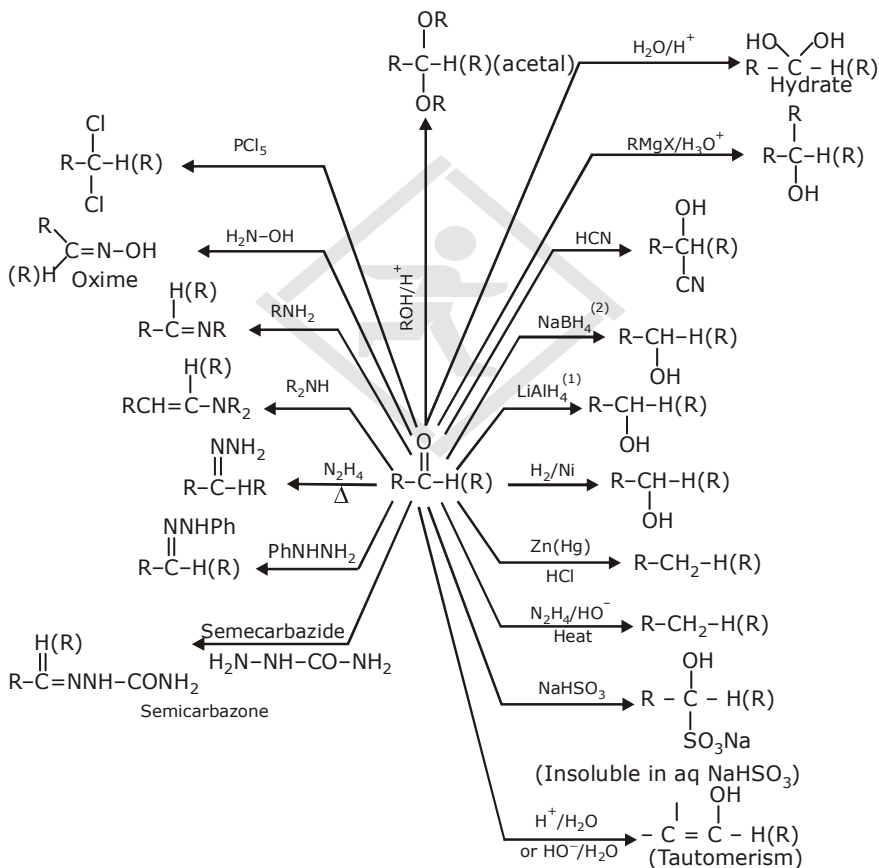
Reactions given by Aldehyde only:



- (i) Ketones do not restore magenta colour of Schiff's reagent
- (ii) Ketones are not oxidized by Tollen's reagent or Fehling solution.



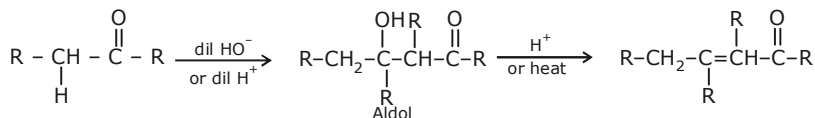
Reactions common to aldehydes and ketones



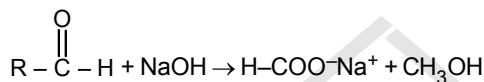
(i) Do not reduce olefinic bonds but reduces acid and its derivatives.

(ii) Do not reduce olefinic or acids or acid derivatives.

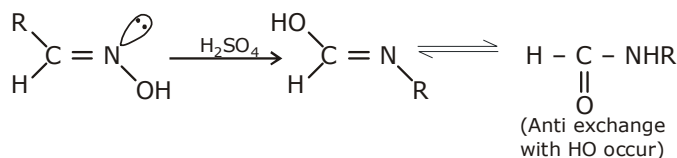
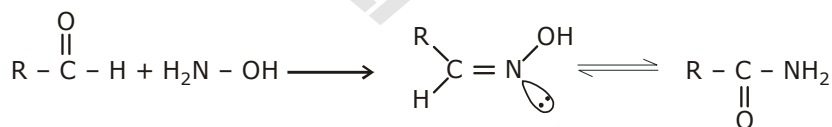
Aldol condensation : Aldehydes or ketones containing at least α -hydrogen on treatment with dilute alkali or dilute acid undergo condensation to produce β -hydroxy aldehyde or β -hydroxy ketone:



Cannizzaro reaction : Aldehydes lacking α -hydrogen, when treated with concentrated solution of strong base, undergo mutual oxidation reaction as:



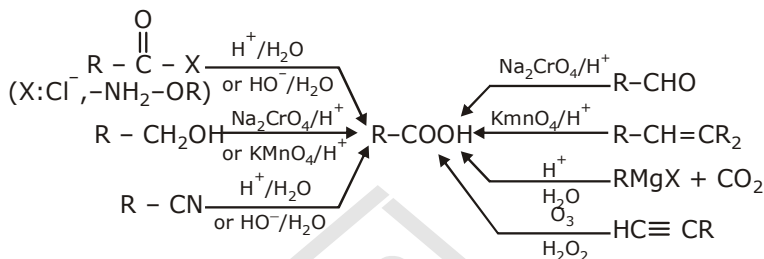
Beckmann's rearrangement : Aldehydes or ketones on treatment with hydroxylamine give oximes. Oximes on further treatment with conc. H_2SO_4 or PCl_5 undergoes rearrangement as:



CARBOXYLIC ACIDS AND DERIVATIVES

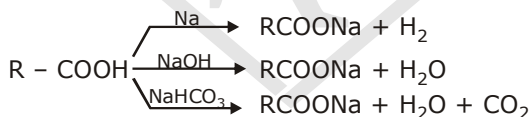
Carboxylic acid

Preparation

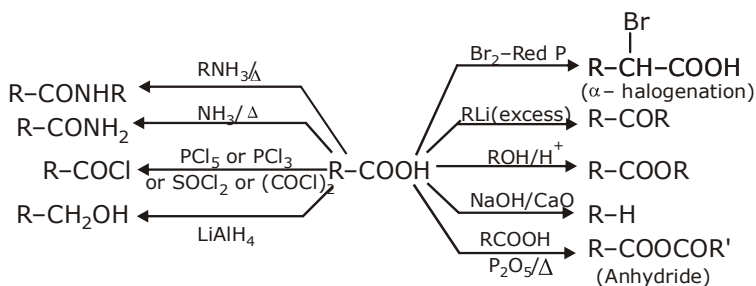


Properties:

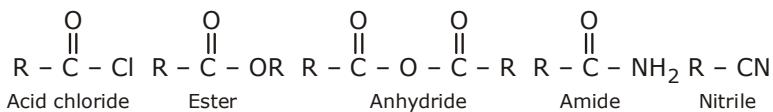
Acidity



NaHCO_3 can be used to distinguish a carboxylic acid from aliphatic and aromatic alcohols.

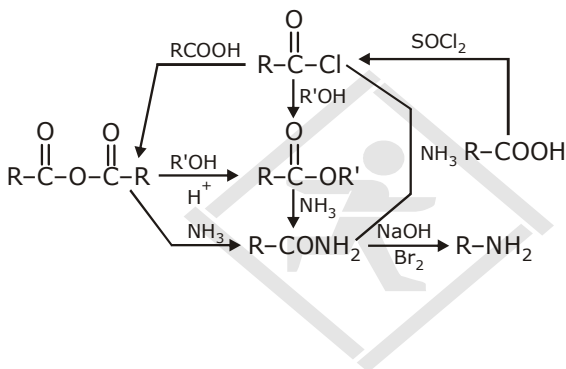


Acid derivatives : Derived from acids



Interconversion of acid derivatives : A more reactive acid derivative is spontaneously converted into a more stable acid derivative. The order of reactivity is

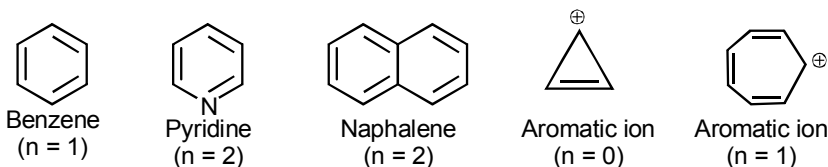
Acid -chloride > Anhydride > Ester > Amide



AROMATIC COMPOUNDS

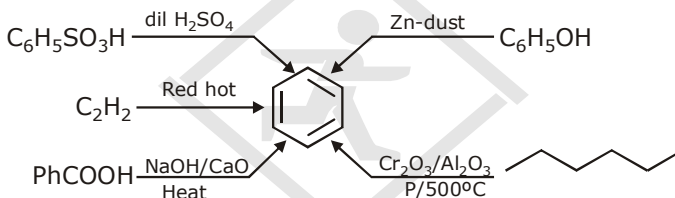
Aromaticity The “Huckel Rule” : Factors required for aromaticity are:

- A planar (or near planar) cycle of sp^2 hybridized atoms, the p-orbitals of which are oriented parallel to each others. These overlapping p-orbitals generate an array of π -molecular orbitals.
- These π -orbitals are occupied by $(4n + 2)$ electrons (where, n is an integer or zero) eg,

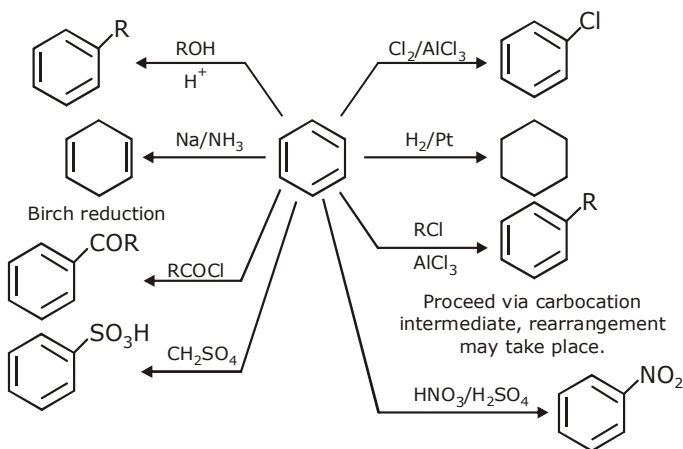


Benzene

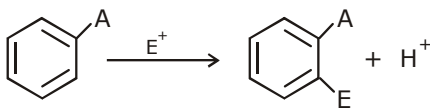
Preparation



Preparation



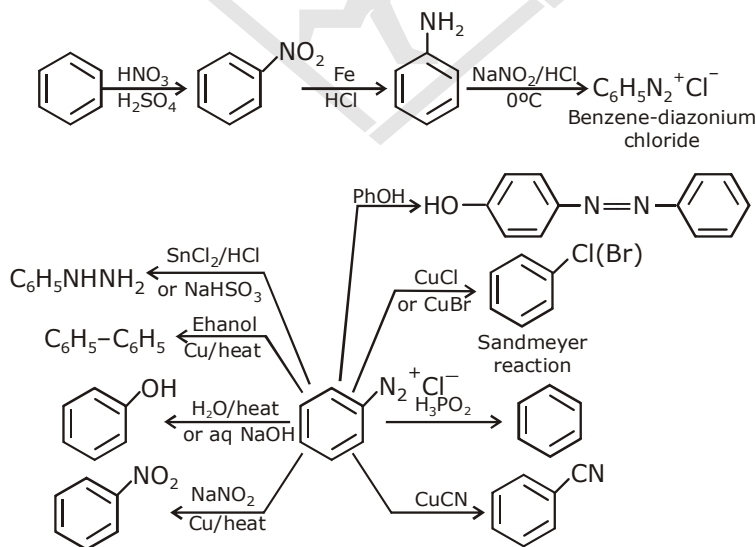
Aromatic electrophilic substitution "Reactivity and Orientation".



Reactivity : Electron donating A activate the ring towards substitution and electron withdrawing A deactivate the ring towards substitution reaction.

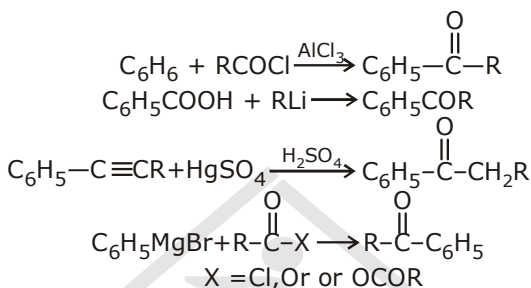
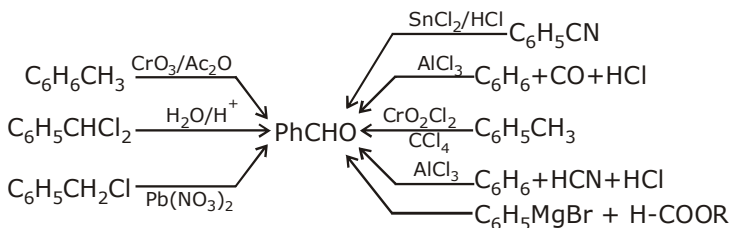
Activating groups	Deactivating groups
R, OR, - OH - OCOR, - NH ₂ , - NR ₂ - NHR, - NHCOCH ₃ - R, - C ₆ H ₅	- NO ₂ , - N ⁺ R ₃ , - SO ₃ H - COOH, - COOR, - CONH ₂ - CHO, - COR, - CN - CH = CH - NO ₂

Diazonium synthesis



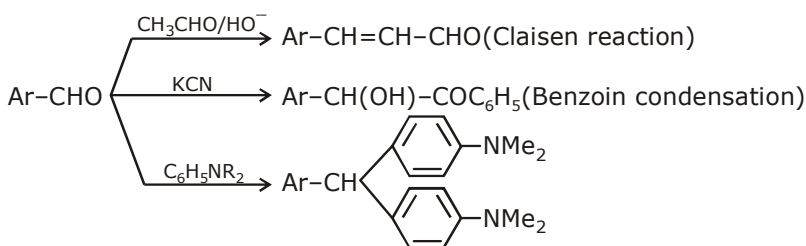
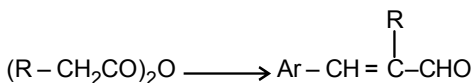
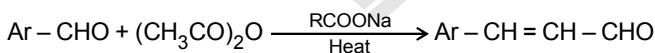
Aromatic Aldehydes and Ketones

Preparation



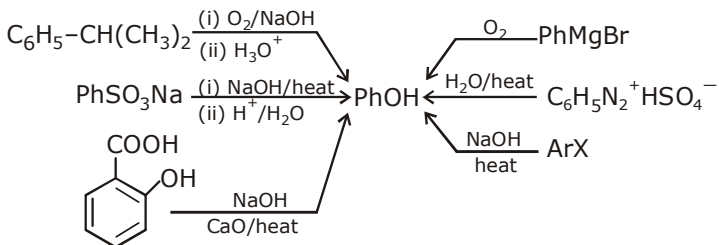
Properties: Aromatic aldehydes do not give Fehling solution test. This reaction distinguishes it from aliphatic aldehyde.

Perkin's reaction : Reaction of aromatic aldehydes with aliphatic anhydride containing α -hydrogen



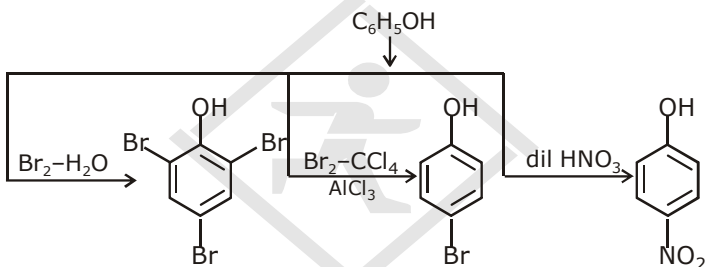
Phenol

Preparation

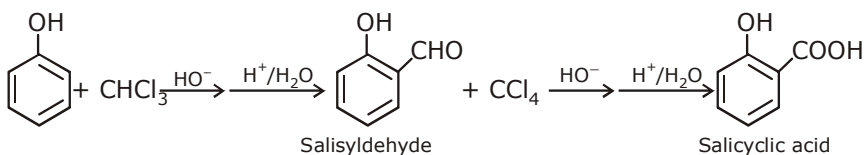


Properties:

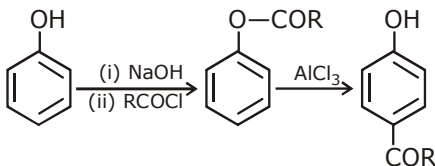
- (i) **Acidity** stronger acid than aliphatic alcohols and water but weaker acid than a carboxylic acid.
- (ii) Highly reactive in aromatic electrophilic substitution reaction if occur in aqueous medium.



Reimer Tiemann's reaction



Fries rearrangement



PART-III

INORGANIC CHEMISTRY

CHEMICAL BONDING

- Summary of molecular geometry and hybridization

Total no. of independent electron pairs	No. of independent bonding electron pair	No. of Nonbonding electron pair	Orbital geometry	Molecular geometry	Distortion?	Hybridization	Bond angles	Examples
2	2	0	linear	linear	never	sp	180°	CO ₂ , BeCl ₂
3	3	0	trigonal planer	trigonal planar	possible	sp ³	120°	HgCl ₂ , ZnI ₂ , CS ₂
3	2	1	trigonal planer	bent	always	sp ²	120°	NO ₂ , SO ₂ , SnCl ₂
4	4	0	tetrahedral	tetrahedral	possible*	sp ³	109.5°	CH ₄ , SO ₄ ²⁻
4	3	1	tetrahedral	trigonal pyramidal	always	sp ³	109.5°	NH ₃ , SO ₄ ²⁻
4	2	2	tetrahedral	bent	always	sp ³	109.5°	H ₂ O, NH ₂ ⁺ , SeCl ₂
5	5	0	trigonal bipyramidal	trigonal bipyramidal	possible*	sp ³ d	90° and 120°	PF ₅
5	4	1	trigonal bipyramidal	distorted square pyramidal (see-saw)	always	sp ³ d	90° and 120°	SF ₄ , TeCl ₄
5	3	2	trigonal bipyramidal	T-shaped	always	sp ³ d	90°	IF ₃
5	2	3	trigonal bipyramidal	linear	never	sp ³ d	180°	I ₃ , ICl ₄ ⁻
6	6	0	octahedral (square bipyramidal)	octahedral	possible*	sp ³ d ²	90°	SF ₆ , PF ₆ ⁻
6	5	1	octahedral (square bipyramidal)	square pyramidal	always	sp ³ d ²	90°	IF ₅ , BrF ₅
6	4	2	octahedral (square bipyramidal)	square planar	possible**	sp ³ d ²	90°	XeF ₄ , ICl ₄ , BrF ₄ ⁻

Note: Under distortion, “possible” means that the bond angles will be distorted when the outer atoms are not identical eg, tetrahedral CH₄ (all outer atoms are H) has no distortion (all bond angles are exactly 109.5°). but in tetrahedral CH₃F (three H and one F) the bond angles are slightly distorted from 109.5°.

**For square planar molecules, distortion will occur if the outer four atoms are not symmetrically distributed. this needs to be considered on a case-by-case basis.

Note on molecular polarity: The following types of molecules are nonpolar; linear AB₂, trigonal planar AB₃, tetrahedral AB₄, trigonal bipyramidal AB₅, octahedral AB₆, square planar AB₄, and symmetric square planar AB₂C₂. Any other molecule having

a single “central atom” will be polar, as long as the electronegativities of the elements that make it up are not equal. This includes molecules that have the above geometries but which have dissimilar outer atoms (such as tetrahedral CH_3F and linear $\text{O} = \text{C} = \text{S}$).

Molecular Orbital Theory (MOT)

Energy	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
	σ_{2p}^*	σ_{2p}^*	σ_{2p}^*	σ_{2p}^*	σ_{2p}^*	σ_{2p}^*	σ_{2p}^*	σ_{2p}^*
	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*	π_{2p}^* π_{2p}^*
	σ_{2p}	σ_{2p}	σ_{2p}	σ_{2p}	σ_{2p}	π_{2p} π_{2p}	σ_{2p}	σ_{2p}
	π_{2p} π_{2p}	π_{2p} π_{2p}	π_{2p} π_{2p}	π_{2p} π_{2p}	π_{2p} π_{2p}	σ_{2p}	σ_{2p}	σ_{2p}
	π_{2s}^*	σ_{2s}^*	σ_{2p}^*	\square_{2s}^*	σ_{2s}^*	σ_{2s}^*	σ_{2s}^*	σ_{2s}^*
	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	σ_{2s}	σ_{2p}	σ_{2s}^*	σ_{2s}	σ_{2s}	σ_{2s}	σ_{2s}	σ_{2p}

Bond order : Determines the number and nature of bonds as:

$$\text{Bond order} = \frac{\text{No. of bonding electrons} - \text{No. of antibonding electrons}}{2}$$

eg, N_2 : Bond order = $\frac{8 - 2}{2}$ (one sigma and two pi bonds)

(i) **Molecular orbitals (MOs)** : Are mathematical equations that describe the regions in a molecule where there is a **high probability of finding electrons**.

(ii) Molecular orbitals (MOs) are essentially combinations of atomic orbitals - two types exist, **bonding** and **antibonding** orbitals.

(iii) Molecular orbitals (MOs) are built up (Aufbau principle) in the same way as atomic orbitals.

(iv) Electron filling in MOs of second-period homonuclear diatomic molecules:

Highlights of MOT

(i) Higher the bond order, greater the bond energy and smaller the bond length.

(ii) Zero bond order indicated nonexistence of molecule or ion.

(iii) If there is any unpaired electron in MO, the system will be paramagnetic with s

in only magnetic moment (μ_s) = $\sqrt{n(n+2)}$ BM where, 'n' is the number of unpaired electrons.

PERIODIC TABLE

Main feature of Modern Periodic Table

- (i) The modern Periodic table is divided into two main categories: (i) Vertical columns called groups and (ii) Horizontal columns called Periods.
- (ii) There are 18 vertical columns or groups. These are further sub-divided into A and B (groups I to VII), VIII group and zero group.
- (iii) Member of the same group have similar electronic configuration of the valence shell and thus show same valency.
- (iv) Elements of groups IA to VIIA are called groups of typical elements, representative elements or normal elements.
- (v) Groups IA and IIA are strongly metallic and are called group of 'alkali metals and alkaline earth metals'.
- (vi) Groups IB to VIIB and VIII lie in the middle to the table between IIA and IIIA groups and are called groups of transition elements. They consist of metals
- (vii) The zero group consists of 'Noble gasses'.
- (viii) There are 7 horizontal rows in the Periodic Table. These are called the periods.
- (ix) In a period, the number of valence shell remains the same for all elements. However, the number of electrons in the valence shell increases from left to right.

Atomic size and atomic radius

(i) The distance from the centre of the nucleus to the outermost shell of an atom is called the atomic radius of that atom. Electrons in the same period progressively increase from left to right, as the atomic number increases, eg, in the 3rd period, from sodium (Z = 11) to chlorine (Z = 17). It would be expected that as the number of protons, electrons and neutrons increase, the size of the atom increases. Contrary to expectations, inspite of the increased atomic number, the size of the atom gradually decreases from left to right.

Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
----------	----------	----------	----------	---------	---------	----------	----------

(ii) The distance from the nucleus to the outermost shell depends on the electrostatic attraction (nuclear charge) that the nucleus exerts on the electrons of the outer shell. More the nuclear charge closer are the shell and electrons, hence smaller is the atomic radius of an atom.

(iii) With the increase in the atomic number (increased number of protons, electrons and neutrons) in the 3rd period, the net positive charge of the nucleus gradually increases. This increased positive charge exerts a greater attraction on the shells and attract the electrons in the shells a little close to the nucleus. Hence, sodium has the largest atom and chlorine the smallest. This is true of other periods as well.

(iv) Conversely, elements in the same group increase in size downward, eg, in group IA, starting from lithium to sodium, potassium, rubidium and cesium, the atomic size increases because there is a gradual increase in the number of shells.

Ionization Potential

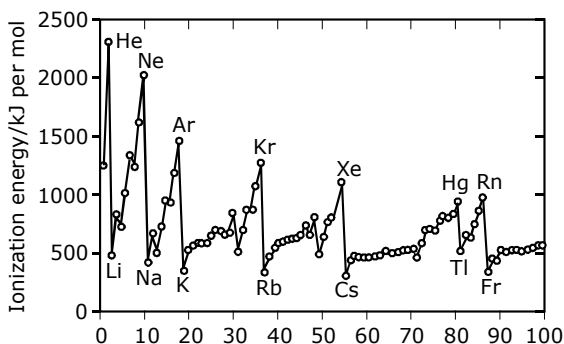
Ionization potential (or ionization energy) is the amount of energy required to remove one or more electrons from the outermost shell of an isolated atom in the gaseous state. Ionization energy is also called as ionization potential because it is measured as the minimum potential required to remove the most loosely held electron from the rest of the atom. It is measured in the units of electron volts (eV) per atom or kilo joules per mole of atoms [kJ mol^{-1}], Thus, the ionization energy gives the ease with which the electron can be removed from an atom. The smaller the value of the ionization energy, the easier it is to remove the electron from the atom. In referring to the Periodic Table of ionization potentials (in electron volts) shown, the following conclusions may be arrived at

(i) Metals usually have low ionization potential whereas non-metals have high ionization potential. Metalloids have intermediate ionization potential.

(ii) The inert gases have very high ionization potential, due to the stability of the outer shell. Helium has the highest ionization potential.

(iii) Within a group, the ionization potential generally decreases with increasing atomic number.

Increasing atomic number results in increasing atomic radii. Thus, the electrons of the outer shell are further away than those of the previous element and can be removed easily.



Atomic number

(iv) Ionization potential does not necessarily vary uniformly from one element to another. But it is a periodic property. It increases from group I to group VIII. But the increase is not very regular.

(v) Ionization potential increases across the period because of increase in nuclear charge due to which the atomic size decrease. Thus, more energy is required to pull away the electron from outermost shell of the atom of smaller size.

(vi) Ionization potential decreases down the group because of increase in the number shells. The effective nuclear charge decreases as atomic size increases. Thus it is easier to pull one electron from the outermost shell of the atom.

Electron Affinity

(i) Electron affinity is the amount of energy released with an electron is added to an isolated gaseous atom

(ii) Electron affinity depends on

(a) Extent of nuclear charge, (b) Size of the atom, (c) Electronic configuration.

As a result of the gain in electrons, the atom gains one negative charge. In the case of halogens, all the element have a high electron affinity, as they need one electron to complete the octet of their outermost shell.

(iii) If the electron affinity is low, the electron is weakly bond: if the electron affinity is high, the electron is strongly bonded, eg, electron affinity of chlorine is 3.79 which is higher than that of iodine ie, 3.28. Hence chlorine accepts the electrons more easily than iodine.

(iv) Electron affinity increases from left to right across the period because of increase in nuclear charge and decrease in atomic size. This causes the incoming electron to experience a greater pull of the nucleus thus giving a higher electron affinity.

(v) Electron affinity decreases down the group because the number of shells increases ie, the atomic size increases and the effective nuclear charge decreases. This causes the incoming electron not to experience much attraction of the nucleus thus giving a lower electron affinity.

(vi) The electron affinity of completely filled atoms is almost zero. An atom does not accept an electron in its outermost shell if it already has a stable configuration ie, a duplet or octet, as in the case of inert gases.

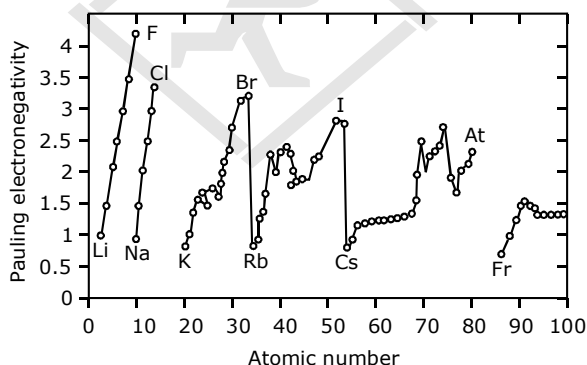
Electronegativity

(i) Electronegativity is the tendency of an atom to attract electrons towards itself in a molecule of a compound. The value of electronegativity of an element describes the ability of its atom to compete for electrons with the other atom to which it is bonded. Electronegativity is however not the property of an isolated atom.

(ii) Electronegativity-increases from left to right in each period ending at group VII.

(iii) In the 3rd period, electronegativity increases from sodium to chlorine ie, chlorine can accept electrons most easily in that period followed backwards y sulphur, phosphorus, silicon, sluminium, magnesium and sodium. All the atoms of the above mentioned elements have three shells but chlorine has the smallest atomic radii. Hence, chlorine experiences more positive charge from the nucleus that all other atoms in that period. So, if one electron is available, chlorine can attract it most easily.

(iv) Fluorine is the most electronegative element.



COORDINATION COMPOUNDS

IUPAC Nomenclature : Following rules are obeyed in systematic naming of coordination compounds:

- (i) The positive ion is named first followed by negative ion.
- (ii) When writing the name of a complex, the ligands are written in alphabetical order, regardless of their charge followed by metal.

- (a) The name of negative ligands ends in $-o$ eg,

F^- = fluoro H^- = hydrido

HS^- = mercapto Cl^- = chloro

HO^- = hydroxo S^{2-} = thio

Br^- = bromo O^{2-} = oxo

CN^- = cyano I^- = iodo

O_2^{2-} = peroxo NO_2^- = nitro

- (b) Neutral groups have no special ending eg, NH_3 – ammie, H_2O - aqua, CO- carbonyl, NO-nitrosyl. Organic ligands are usually given their common name eg, phenyl, methyl ethylenediamine, pyridine. Positive groups end in ium eg, $N_2H_5^+$ - hydrazinium, NO^+ - nitrosonium, NO_2^+ - nitronium.

- (iii) the oxidation state of the central metal is shown by Roman numerals in brackets immediately following its name eg, iron (III).

- (iv) Complex positive ions and neutral molecules have no special ending.

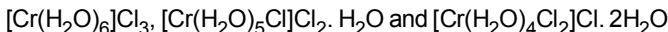
- (v) If complex ion is negative, metal name ends in ate (with original name of metal eg, ferrate, argentate, aurate, plumbate etc.)

Complex cation	Name
$[CO(NH_3)_6]Cl_3$	Hexaammine cobalt (III) chloride
$[CO(NO_2)_2(NH_3)_4]Cl$	Tetraamminedinitro cobalt(III) chloride
$[Cu(NH_3)_4]SO_4$	Tetraammine copper(II)
$[Cr(en)_3]Cl_3$	Tris (ethylenediammine) cobalt (III) chloride
Complex Anion	
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
$K_2[Cr(CN)_2O_2(O_2)NH_3]$	Potassium amminedicyanodioxoperoxo chromate (VI)
$Li[AlH_4]$	Lithium tetrahydrido aluminate (III)
$[Ni(NH_3)_4][Ni(CN)_4]$	Tetraammine nickel(II) tetracyanonickelate(II)

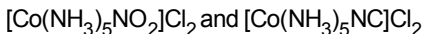
Isomerism in Complexes

(i) **Ionization isomerism** : Complexes having same molecular formula but giving different ions in solution are known as ionization isomers. This type of isomerism arises due to exchange of groups between the complex ion and the ions outside it.

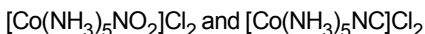
(ii) **Hydrate isomerism** : Complexes with same molecular formula but different number of water molecules of crystallization are known as hydrate isomer eg,



(iii) **Linkage isomers** : Ambident ligands (ligands that contain more than one donor atoms) like NO_2^- , CN^- , SCN^- etc forms linkage isomers eg,

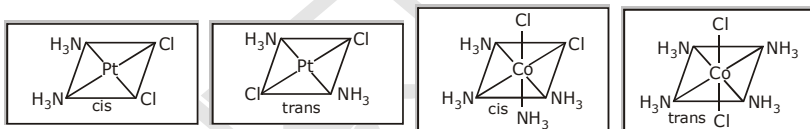


are linkage isomers.



are linkage isomers

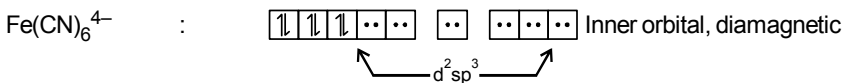
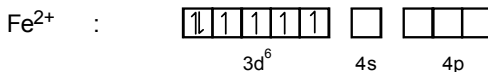
(iv) **Geometric isomers**:



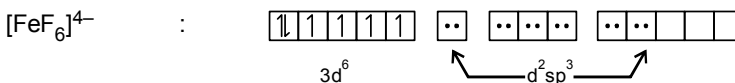
Structure and Bonding in Complexes

The “Valence Bond Theory”: According to valence bond theory, a strong ligand field forces the d-electrons of central metal to pair up against Hund's rule. The strong ligands which cause this are, CO, NO, CN^- , NO_2^- , NH_3 , en (ethylene diamine) and some common weak ligands are H_2O , X^- , NO_3^- , ROH etc.

Example : $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{FeF}_6]$ both have iron in +2 state.



complex, octahedral in shape

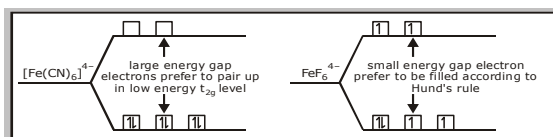


An outer orbital complex, paramagnetic, octahedral in shape

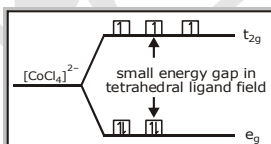
Spin only magnetic moment (μ_s) = $\sqrt{n(n+2)}\text{BM}$ n = no of unpaired "e". Spin only magnetic moment of $\text{K}_4[\text{Fe}(\text{CN})_6]$ is zero because it has no unpaired electron while the same for $\text{K}_4[\text{FeF}_6]$ is $\sqrt{24}\text{ BM}$.

The crystal field theory : It is more appropriate theory than VBT. According to CFT, under the influence of ligand field, degeneracy of the d-orbital is destroyed and it splits into two or more energy level. The extent of splitting depends on the strength of ligand. A strong ligand causes greater splitting while a weak ligand causes smaller splitting.

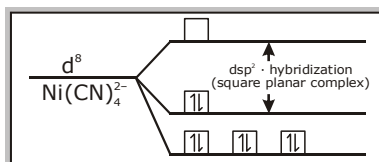
In octahedral ligand field:



In tetrahedral ligand field, the splitting pattern is reversed. Also, in tetrahedral ligand field, no ligands approaches exactly along the lobes of d-orbital, energy gap is always smaller than in octahedral complex and



Square planar complex: When the d-orbitals are unsymmetrically occupied, it gives rise to square planar complex eg, $\text{Na}_2[\text{Ni}(\text{CN})_4]$



Au Cu(II) 'd⁹' complex are square planar eg, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Cu}(\text{CN})_4]^{2-}$ or $[\text{CuCl}_4]^{2-}$

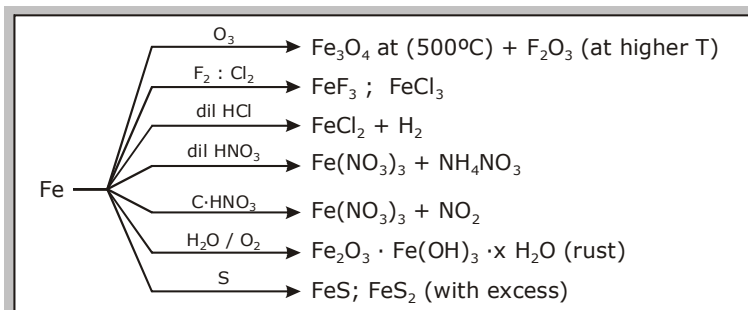
METALLURGY

Extraction of Metals

Metals	Important Ores	Extraction Method	Reactions Involved in Extraction
Fe	Fe_2O_3 , Fe_3O_4 , FeS , CuFeS_2 , FeCO_3	Carbon-reduction method	$\text{C} + \text{O}_2 \xrightarrow[\text{Furnace}]{\text{Blast}} \text{CO}$ $3\text{CO} + \text{Fe}_2\text{O}_3 \longrightarrow 2\text{Fe} + 3\text{CO}_2$
Sn	SnO_2	Carbon-reduction method	$\text{C} + \text{O}_2 \xrightarrow[\text{Furnace}]{\text{Blast}} \text{CO}$ $2\text{CO} + \text{SnO}_2 \longrightarrow \text{Sn} + 2\text{CO}_2$
Gu	CuFeS_2 , CuS , CuO , Cu_2O	Self-reduction method	$\text{CuS} + \text{O}_2 \xrightarrow{\text{Partial}} \text{CuO} + \text{SO}_2$ $\text{CuS} + 2\text{CuO} \longrightarrow 3\text{Cu} + \text{SO}_2$
Pb	PbS (Galena) PbO , Pb_3O_4	Self-reduction method	$\text{PbS} + \text{O}_2 \xrightarrow{\text{Partial}} \text{PbO} + \text{SO}_2$ $\text{PbS} + 2\text{PbO} \longrightarrow 3\text{Pb} + \text{SO}_2$
Mg	Sea water, MgCl_2 , KCl , $6\text{H}_2\text{O}$ $\text{MgCO}_3 \cdot \text{CaCO}_3$	Electrolytic reduction	$\text{MgCl}_2 \xrightarrow{\text{Melt}} \text{Mg}^{2+} + 2\text{Cl}^-$ $\text{Mg}^{2+} + 2\text{e}^- \xrightarrow{\text{Electrolysis}} \text{Mg}$
Al	Al_2O_3 (bauxite)	Electrolytic reduction	$\text{Al}_2\text{O}_3 \xrightarrow{\text{Melt}} \text{Al}^{3+}$ $\text{Al}^{3+} \xrightarrow{\text{Electrolysis}} \text{Al}$
Ag	Ag_2S (argentite)	Cyanide Process	$\text{Ag}_2\text{S} + 2\text{NaCN} \longrightarrow 2\text{AgCN} + \text{Na}_2\text{S}$ $\text{AgCN} + \text{NaCN} \longrightarrow \text{Na}[\text{Ag}(\text{CN})_2]$
Au	Exist in free state	Cyanide process	$[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Ag} + \text{Na}_2[\text{Zn}(\text{CN})_4]$ $\text{Au} + \text{NaCN} \longrightarrow \text{Na}[\text{Au}(\text{CN})_2]$ $[\text{Au}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Au} + \text{Na}_2[\text{Zn}(\text{CN})_4]$

Important Reactions

(i) Iron

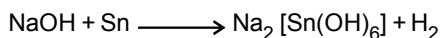


(ii) Tin

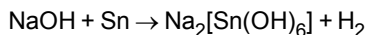
- Stable to water and air at ordinary temperature.
- Does not react with dil HCl or dil H_2SO_4 but reacts with dil HNO_3 .



- With hot conc. HCl, SnCl_2 is formed while with hot concentrated H_2SO_4 , SnSO_4 is formed evolving SO_2 .



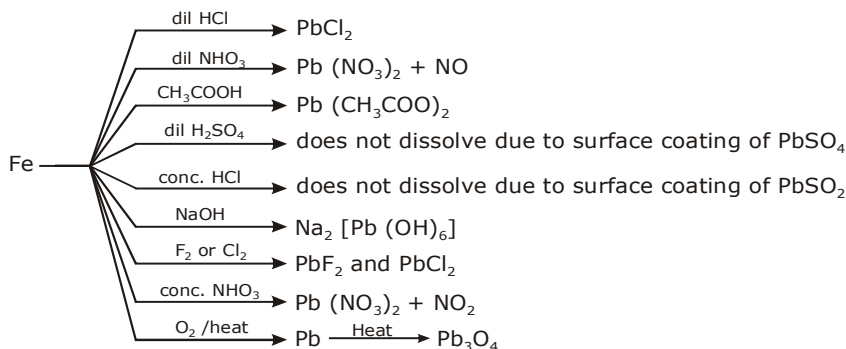
- With hot conc. HCl, SnCl_2 is formed while with hot concentrated H_2SO_4 , SnSO_4 is formed evolving SO_2 .



- Sn reacts with Cl_2 and Br_2 in cold forming SnCl_4 and SnBr_4 . F_2 and I_2 reacts on warming.
- With hot concentrated HNO_3 , metastannic acid H_2SnO_3 is formed.



(iv) Lead



(v) Magnesium

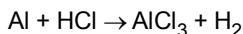
- A highly electropositive metal, displace H^+ from dilute acid.



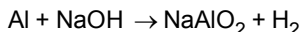
- Reacts with N_2 forming Mg_3N_2 .
- Reacts with halogens forming MgX_2
- A strong reducing metal, displaces less active metal from solution.

(vi) Aluminium:

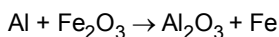
- A strong electropositive metal, liberate H_2 from solution of dilute acid.



- concentrated HNO_3 render Al passive due to formation of Al_2O_3 on surface.
- With halogens, AlX_3 is formed.

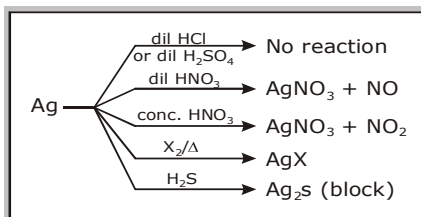


- Thermite welding



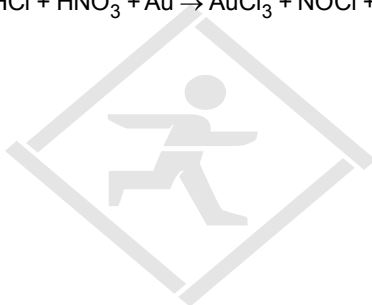
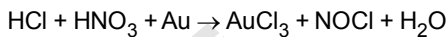
- Reduces intrates and nitrites in basic medium to NH_3 .

(vii) Silver



(viii) **Gold** : Highly inert metal, has very high malleability and ductility.

- Reacts with aqua regia



Important Notes

