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Formulae Handbook Chemistry

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Contents

1 Some Basic Concept of Chemistry

1. **Some useful conversion factors :** 1 Å = 10^{-10} m, 1 nm = 10^{-9} m, 1 pm = 10^{-12} m, 1 litre = $10^{-3}m^3$ = 1 dm^3, 1 atm = 760 mm Hg or torr = 101 325 Pa or Nm^{-2}, 1 bar = 10^5 Nm^{-2} = 10^5 Pa, 1 calorie = 4.184 J, 1 electron volt (eV) = 1.6022 × 10^{-19} J , (1 J = 10^7 ergs) 1 cal > 1 J > 1 erg > 1 eV)

2. 22.4 L of any gas at STP weigh equal to molecular mass expressed in gram . This mass is called Gram Molecular Mass and this volume is called Gram Molecular volume (G.M.V.)
Note : STP conditions are 1 atm pressure and 0° C Temperature. However if the condition taken are 1 bar and 0° C , instead of 22.4 L, we have 22.7 L (1 atm = 1.01 bar).

3. **Atomic mass :** It is the average relative mass of an atom as compared with an atom of carbon – 12 isotope taken as 12.
   - The mass of 1 atom = atomic mass (in amu)
   - The mass of 1 mole atoms = atomic mass (in g)

   eg. mass of one O atom = 16 amu
   mass of 1 mole O atom = 16 g

4. Calculation of average atomic mass. If an element exist in two isotopes having atomic masses 'm_1' and 'm_2' in the ratio x : y, then

$$\text{average atomic mass} = \frac{m_1 \times x + m_2 \times y}{x + y}$$

5. **Molecular mass :** Molecular mass of a substance is the average relative mass of its molecules as compared with an atom of C-12 isotope taken as 12.
   - The mass of 1 molecule = molecular mass (in amu)
   - The mass of 1 mole molecules = molecular mas (in g)

   eg. Mass of 1 O_2 molcules = 32 amu
   Mass of 1 mole O_2 molecules = 32 gm

6. For atom → 1 g atom = 1 mole
   For molecule → 1 g molecule = 1 mole

7. 1 amu or 1 u = $\frac{1}{12}$ th of the mass of an atom of C-12 = 1.66 × 10^{-27} kg.

8. 1 mol of $H_2O \neq$ 22400 cc of H_2O (because it is liquid). Instead , 1 mol of H_2O = 18 cc of H_2O (because density of H_2O = 1g / cc)

9. Fermi's is a unit of length used for expressing nuclear diameter (1 fermi = 10^{-13} cm = 10^{-15}m) (1 fermi = 1 femto).

10. The number of molecules in one ml of a gas at STP is known as Loschmidt number. Its value = $(6.02 \times 10^{23}) / 22400 = 2.687 \times 10^{19}$ ml^{-1}.

11. Mass of one mole of electrons = Mass of one e^- × Avogadro's No.
$= (9.11 \times 10^{-31}\text{ kg}) \times (6.02 \times 10^{23})$
$= 5.48 \times 10^{-7}$kg

12. M.W. = 2 V.D.

$$\text{V.D.} = \frac{\text{density of gas}}{d_{H_2}}$$

$$d_{H_2} = 0.000089\text{ mg / ml}$$

$$\text{number of mole (n)} = \frac{\text{wt.}}{\text{MW / At wt}}$$

$$(n) = \frac{\text{number of particles}}{N_A}$$

$$n = \frac{\text{volume at STP (in lit)}}{22.4\text{ litre}} \text{ or } \frac{\text{Volume at STP (in ml)}}{22400\text{ ml}}$$

$$n = M \times V(\text{lit})$$

13. Atomic mass × specific heat (in cal/gm) = 6.4 (Dulong and Petit's law)

14. Calculations of equivalent weight.

(i) Equivalent weight of element = $\frac{\text{Atomic weight}}{\text{Valency}}$

(ii) Equivalent weight of ions = $\frac{\text{Formula weight of ion}}{\text{Charge on ion}}$

(iii) Equivalent weight of ionic compound = equivalent weight of cation + equivalent weight of anion

(iv) Equivalent weight of acid / base = $\frac{\text{Molecular weight}}{\text{Basicity / Acidity}}$

(v) Equivalent weight of salt = $\frac{\text{Molecular weight}}{\text{Total charge on cation or anion}}$

15. Gram equivalent = NV (lit) = $\frac{W}{E}$ = number of moles × V.F.

$N_1V_1 = N_2V_2$ $\qquad$ $N_1V_1 = \frac{W}{E_2} \times V_2$

16. $\frac{W_1}{E_1} = \frac{W_2}{E_2}$

2 Solution

1. $\%\ \text{by wt.} = \dfrac{\text{Wt. of the solute (in g)}}{\text{Wt. of the solution (in g)}} \times 100$

2. $\%\ \text{by wt./vol.} = \dfrac{\text{Wt. of solute (in g)}}{\text{Vol. of solution (in cc)}} \times 100$

3. $\%\ \text{by volume} = \dfrac{\text{Vol. of solute (in cc)}}{\text{Vol. of the solution (in cc)}} \times 100$

4. $\text{Molarity} = \dfrac{\text{Moles of solute (in gm)}}{\text{Vol. of the solution (in litre)}}$

$\text{where moles} = \dfrac{\text{Mass of the solute (in g)}}{\text{Molecular mass of the solute}}$

5. $\text{Normality} = \dfrac{\text{Gram equivalents of the solute}}{\text{Vol. of the solution in cc}} \times 1000$

$\text{where gm eq.} = \dfrac{\text{Mass of the solute (in g)}}{\text{Eq. mass of the solute}}$

6. $\text{Molality} = \dfrac{\text{Moles of solute}}{\text{Mass of the solvent (in g)}} \times 1000$

7. $\text{Mole fraction of solute in solution } (x_2) = \dfrac{n_2}{n_1 + n_2} = \dfrac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2}$

$\text{Mole fraction of solvent in solution } (x_1) = \dfrac{n_1}{n_1 + n_2} = \dfrac{w_1 / M_1}{w_1 / M_1 + w_2 / M_2}$

where w_1, M_1 are mass and molecular mass of solvent and w_2, M_2 for the solute. $x_1 + x_2 = 1$. In general, for a solution containing many components (A, B, C.....), mole fraction of A

$(x_A) = \frac{n_A}{n_A + n_B + n_C + ...}$ and so on. $x_A + x_B + ... = 1.$

Strength (g/L) = N × eq. wt.

Strength (g/L) = M × mol. wt.

8. Mass fraction of component A $(x_A) = \frac{w_A}{w_A + w_B}$

Mass fraction of component B $(x_B) \setminus \frac{w_B}{w_A + w_B}$ $\quad x_A + x_B = 1.$

9. Parts per million (ppm) $= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6 \simeq \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 10^6$

10. Normality equation (for dilution of a solution or for a complete reaction between two solutions) $N_1V_1 = N_2V_2$

11. Molarity equation (for dilution of a solution) $M_1V_1 = M_2V_2$

12. If V_1 cc of a solution with normality N_1 is mixed with V_2 cc of the solution with normality N_2, then normality N_3 of the final solution can be calculated using.

$N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$.

13. Molality mole fraction and mass fraction do not change with temperature because they involve weights, Normality and molarity change with temperature because they involve volume.

14. **Demal (D)** is another unit for expressing the concentration of a solution. It is equal molar concentration at 0ºC i.e., 1D represents one mole of the solute present in one litre of the solution at 0ºC.

15. One molar (1M) aqueous solution is more concentrated than one molal aqueous (1m) solution of the same solute.
This is because 1M solution contains 1 mole of the solute in 1000cc of the solution which includes the solute i.e., mass of solvent is less than 1000g (as density of H_2O = 1g / cc). However, in case of non aqueous solution 1M > 1m or 1M < 1m or 1M = 1m depending upon the density of the solutions

16. Alloys are solution of solids in solids.

17. According to Raoult's law, for solution containing volatile components A and B $p_A = x_A p^o_A$ and $p_B = x_B p^o_A$

$P_{Total} = p_A + p_B = x_A p^o_A + x_B p^o_B$

$= (1 - x_B) p^o_A + x_B p^o_B = (p^o_B - p^o_A) x_B + p^o_A$

18. Raoult's law for non-volaltile solute containing solution.

$$\frac{p^o - p_s}{p^o} = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \text{ (if solution is dilute i.e., < 5 \%)}$$

$$= \frac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2} \approx \frac{w_2 / M_2}{w_1 / M_1} \text{ (if solution is dilute)}$$

19. Osmotic pressure P or $\pi = C.RT$
C = molar conc. T = temp. in K, R = 0.082 L atm K^{-1} mol^{-1} (if P is in atm and vol. of solution in litres) or 8.314 JK^{-1} mol^{-1} (if P is in Nm^{-2} or Pascals and vol. in m^3)

20. Isotonic solutions have same osmotic pressure and same molar concentrations. If one solution has lower osmotic pressure, it is called hypotonic with respect to the more concentrated solution. The more concentrated solution is said to be hypertonic with respect to the dilute solution.

$\pi_1 = \pi_2$ Isotonic solution.

21. Elevation in boiling point, $\Delta T_b = K_b m$ where K_b = molal elevation constant and m = molality of the solution.

22. Depression in freezing point, $\Delta T_f = K_f m$ where K_f = molal depression constant and m = molality of the solution.

23. $K_b = \frac{RT_b^2}{1000 I_v} = \frac{M_1 RT_b^2}{1000 \Delta H_v}$

where T_0 = boiling point of the liquid (pure solvent)k
I_v = latent heat of vaporisation per g of the solvent
ΔH_v = latent heat of vaporisation per mole of the solvent
M_1 = molecular mass of the solvent
R = gas const. 8.314 JK^{-1} mol^{-1} I_v or ΔH_v is in joules or 1.987 cal K^{-1} mol^{-1} if I_v or ΔH_v is in calories.

24. $K_f = \frac{RT_f^2}{1000 I_f} = \frac{M_1 RT_f^2}{1000 \Delta H_f}$

where T_0 = freezing point of the liquid (pure solvent)
I_f = latent heat of fusion per g of the solvent
ΔH_f = latent heat of fusion per mole of the solvent

25. The lowering of vapour pressure on adding a non volatile solute to a solvent is due to converting up partially the surface of the solution by solute particles which are non - volatile.

26. Osmotic pressure method is the best method for determination of molecular masses of polymers because for polymer solutions, observed value of any other colligative property is too low to be measured accurately.

27. Van't Hoff factor (i) $= \dfrac{\text{Observed value of Colligative property}}{\text{Calculated value of colligative property}}$

$$= \frac{\text{Calculated mol. mass}}{\text{Observed mol. mass}} = \frac{M_{cal.}}{M_{obs.}}$$

$$\left(\because \text{Mol mass} \propto \frac{1}{\text{Colligative property}} \right)$$

28. For solutions undergoing dissociation / association

$$\Delta T_b = iK_b m,\ \Delta T_f = i K_f m,\ \pi = i \frac{n}{V} RT \qquad \left\{ \therefore C = \frac{n}{v} \right\}$$

29. For an electrolyte, A_xB_y undergoing dissociation with degree of dissociation α.

$$A_xB_y \rightleftharpoons xA^+ + yB^-$$

$$i = 1 - \alpha + n\alpha \ (n = x + y)$$

$$i = 1 + (n-1)\alpha \text{ or } \alpha = \frac{i-1}{n-1}$$

30. For a solute A undergoing association

$$nA \rightleftharpoons A_n$$

$$i = 1 - \alpha + \frac{\alpha}{n} \qquad \text{or } \alpha = \frac{1-i}{1-\frac{1}{n}}$$

31. Van't Hoff factor (i) > 1 for solutes undergoing dissociation and it is < 1 for solutes undergoing association.

32. Ethylene glycol is usually added to water in the rediator to lower its freezing point. It is called anti-freeze.

33. Common salt (NaCl) or anhydrous $CaCl_2$ are used to clear snow on the roads. This is because they depress the freezing point of water to such an extent it cannot freze to form ice.

34. Freezing point is same as melting point. Hence instead of depression in freezing point, depression in melting point can be determined. For this purpose camphor is used as solvent because it has high molal depression constant K_f 39.7 = 40 K/m.

35. According to Henry's law $\Rightarrow$
mass of gas dissolved $\propto$ pressure of gas above the solution
(i.e. $m \propto p$ or $m = k_H p$ where k_H is called Henry's constant)
or for a mixture of gases.
Solubility in terms of mole fraction $\propto$ partial pressure (i.e., $x_A = k_H/p_A$ where k_H is in atm^{-1} or bar^{-1} or $p_A = k_A x_A$ where k_H is in atm or bar).

36. Rosults law is a special case of Henry's law (Idea).

37. **Konowaloff's rule.** At any fixed temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase. In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.

3 Redox reactions

1. **Stock notations** Expressing the oxidation state of a metal by Roman numbers like. I ,II, III etc. within parenthesis is called stock notation e.g., $FeSO_4$ = Iron (II) sulphate; Na_2CrO_4 = Sodium chromate (VI) etc.

2. **Valency** of an element is only a number and as such there is no postive or negative sign attached to it. It can neither be zero nor fractional. Oxidation number, on the other hand, refers to charge and hence has either postive or negative sign. It can also be zero or fractional. For example oxidation state of C in CH_2Cl_2 is zero while that of Fe in Fe_3O_4 is 8/3 and of S in $Na_2S_2O_3$ is 2.0.

3. The oxidation number of metals in amalgams and metal carbonyls, i.e. $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc. is zero.

4. A substance acts only as an oxidising agent if the oxidation number of one of its element is in its highest oxidation state and as a reducing agent if the oxidation number of one of its elements is in its lowest oxidation state. However, if the oxidation number of one of the elements of a substance is in its intermediate oxidation state, it can act both as an oxidising as well as a reducing agent. For example.

   (a) The O.N. of N in HNO_3, i.e. +5 is the maximum, therefore it can act only an oxidising agent by accepting one or more electrons. For example.

   $$I_1 + 10H\overset{+5}{N}O_3 \longrightarrow 2HIO_3 + 10\overset{+4}{N}O_2 + 4H_2O$$

   Here, the O.N. of N decreases from +5 in HNO_3 to + 4 in NO_2 and hence it acts an oxidising agent.

   (b) The O.N. of S in H_2S, i.e., –2 is the minimum and hence it can act only as a reducing agent by losing one or more electrons.
   For example

   $$Br_2 + \overset{-2}{H_2}S \longrightarrow \overset{0}{S} + 2HBr$$

   Hence the O.N. of S increase from –2 in H_2S to 0 in elemental sulphur and hence it acts as a reducing agent.

   (c) The O.N. of N in HNO_2 i.e., +3 is neither maximum (i.e., +5) nor minimum (i.e–3), therefore it can act both as an oxidising as well as a reducing agent. For example.

(i) $2KMnO_4 + 3H_2SO_4 + 5H\overset{+3}{N}O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 5H\overset{+5}{N}O_3 + 3H_2O$

(ii) $2HNO_2 + 2HI \longrightarrow 2NO + 2H_2O + I_2$

In equation (i), The O.N. of N increases from +3 in HNO_2 to +5 in HNO_3, therefore it acts as a reducing agent.

In equation (ii), the O.N. of N decreases from +3 in HNO2 to +2 in NO, therefore it acts as an oxidising agent.

5. Redox reaction are also called electron - transfer reactions since electron are transferred from the reductant to the oxidant.

6. Oxidation is also called de-electronation while reduction is called electronation.

7. If a compound contains two or more atoms of the same element, all of them may not have same oxidation number e.g.

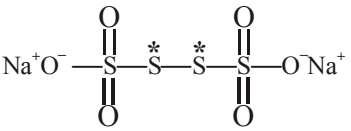
(i) In $Na_2S_2O_3$, one S-atom has oxidation number = –2 while the other has oxidation number = +6

(ii) In $CaOCl_2$ i.e., Ca(OCl) Cl (bleaching powder), oxidation number of one Cl = –1 while oxidation number of the other Cl = +1.

(iii) In Fe_3O_4 i.e., FeO. Fe_2O_3 oxidation number of one Fe = +2 while that of each other two = +3.

(iv) In NH_4NO_3, oxidation no. of N of NH_4^+ = –3 while that of N in NO_3^- = +5.

(v) In $N_2S_4O_6$ (sodium tetrathionate) having the structure



The oxidation number of both S* is equal to 0 (pure covalent nature) and other two sulphur atoms have O. No = +5.

4 Electrochemistry

1. **Specific conductivity** [K] :- Conductivity is the reciprocal of specific resistance i.e., $K = \frac{1}{\rho}$

   Hence from $R = \rho.\frac{\ell}{a}.\frac{1}{C} = \frac{1}{K}.\frac{\ell}{a}$ or $K = C \times \frac{\ell}{a}$

   Where $\frac{\ell}{a}$ = cell constant

   If ℓ = 1cm and a = 1 cm^2, K = C, Hence conductivity is the conductance of 1 cm^3 of the conductor. Units of K = $ohm^{-1}\ cm^{-1}$ or in SI units, these are $\Omega^{-1}m^{-1}$ or Sm^{-1} ($1\ Scm^{-1} = 100\ Sm^{-1}$)

2. **Relationship between Equivalent conductivity $(\wedge_{eq})$ and Specific conductivity (K).**

$$\wedge_{eq} = K \times \frac{1000}{C_{eq}} = K \times \frac{1000}{\text{Normality}}$$

   C_{eq} represents the concentration of the solution in gram equivalents per litre (i.e. normality of the solution).

3. **Units of equivalent conductivity =** $ohm^{-1}\ cm^2\ eq^{-1}$ or in SI units, these are $S\ m^2\ eq^{-1}$ ($1\ S\ m^2\ eq^{-1} = 10^4\ S\ cm^2\ eq^{-1}$ or $S\ cm^2\ eq^{-1} = 10^{-4}\ S\ m^2\ eq^{-1}$).

4. **Relationship between molar conductivity $(\wedge_m)$ and Specific conductivity (K)**

$$\wedge_m = K \times V = K \times \frac{1000}{C_m} = K \times \frac{1000}{\text{Molarity}}$$

   Where V is volume of solution in cm^3 containing one mole of the electrolyte and C_m is molar concentration (moles L^{-1})

5. **Units of molar conductivity =** $ohm^{-1}\ cm^2\ mol^{-1}$ or in SI units, these are $S\ m^2\ mol^{-1}$ ($1\ S\ m^2\ mol^{-1} = 10^4\ S\ cm^2\ mol^{-1}$ or $1\ S\ cm^2\ mol^{-1} = 10^{-4}\ S\ m^2\ mol^{-1}$)

6. **Effect of dilution :** Conductance increases, specific conductivity decreases, equivalent and molar conductivity increase with dilution.

7. **Kohlrausch's law :** The law states that at infinite dilution where dissociation of all electrolytes is complete and all interionic effects disappear, each ion migrates independently of its co-ion and contributes to the total molar conductivities of an electrolyte a definate shape, which depends on its own nature and not at all on the ions with which it is associated.

General formula : For molar conductance $\wedge_m^{\infty} = m\lambda_c^{\infty} + n\lambda_a^{\infty}$

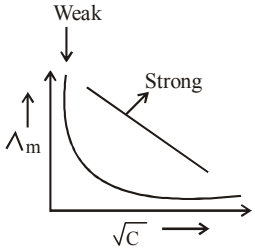
where m and n = moles of cation and anion λ_c^{∞} and λ_a^{∞} = ionic conductance at inifinite dilution for cation & anion

For equivalent conductance

$$\wedge_{eq}^{\infty} = \frac{1}{Z^+}\lambda_c^{\infty} + \frac{1}{Z^-}\lambda_a^{\infty}$$

Relation between in $\wedge_m$ and $\wedge_{eq}$

$$\boxed{\wedge_{eq} = \frac{\wedge_m}{\text{v.f.}}}$$



8. **Absolute value of electrode potential cannot be determined** because oxidation or reduction half reaction cannot occur alone. Moreover, a reference electrode is required.

9. A negative value of standard reduction potential means that oxidation takes place on this electrode with reference to standard hydrogen electrode. The standard electrode potential of hydrogen electrode is taken as zero.

10. **(a)** Greater the reduction potential of a substance, stronger is the oxidizing agent.
(b) A more reactive metal with greater oxidation potential (lower reduction potential) displaces the less reactive metal (higher reduction potential) from its aqueous solution.

11. **An electrochemical cell or galvanic cell or voltaic cell** is a device used to convert chemical energy produced in a redox reaction into electrical energy.
LOAN $\rightarrow$ Left oxidation anode negative.

12. In electrochemical cell, the electrode on which oxidation takes place is called anode or negative pole (because it is rich in electrons) and the electrode on which reduction takes place is called the cathode or **positive pole (being deficient in electrons)**

13. **Difference between Electrochemical and Electrolytic cell** lies is the fact that the former is used convert chemical energy produced in the spontaneous redox reaction into electrical energy whereas in the latter, electrical energy is passed to bring about the redox reaction (electrolysis) which is otherwise non spontaneous.

14. In a salt brige the electrolytes commonly used are KCl or KNO_3 or NH_4NO_3. This is because their cations and anions move almost at the same speed and hence have almost the same transport number.

15. KCl / NaCl/NH_4Cl etc. cannot be used in the salt bridge of a cell containing silver as one of the electrodes because they react to form a precipiate of AgCl.

$$E_{cell} = E^{o}_{O.P.(Anode)} - E^{o}_{O.P.(Cathode)}$$

16. $E_{cell} = E^{o}_{Red}$ (R.H.S. electrode) – E^{o}_{Red} (L.H.S. electrode)

$E_{cell} = E^{o}_{R.P.(Cathode)} + E^{o}_{O.P.(Anode)}$

$E_{cell} = E^{o}_{R.P.(Cathode)} - E^{o}_{R.P.(Anode)}$

17. $E^{o}_{R.P.} = E^{o}_{O.P.}$ (For a same electrode)

18. In balancing of half cell reactions to get overall reaction, the equations may be multiplied by suitable integers but electrode potential are fixed quatities and are not multiplied with that integer.

19. For a given reaction to be spontaneous , E_{cell} must be postive.

20. When the cell reaction attains equailibrim , $E_{cell} = 0$.

21. The EMF of a cell (complete redox reaction) is found by adding the oxidation potential and reduction potential of the half-cell reaction. But the electrode potential of the half-cell form two other half-cells cannot be found by simply adding their electrode potentials.

For example, suppose we have to calculate standard electrode potential for Cu^{+}/Cu half-cell from known value for Cu^{2+}/Cu and Cu^{2+}/Cu^{+} (which are 0.337 V and 0.153 V respectively) ie.,

Given : (i) $Cu^{2+} + 2\,e^{-} \longrightarrow Cu$, $E^{o} = 0.337$ V

(ii) $Cu^{2+} + e^{-} \longrightarrow Cu^{+}$, $E^{o} = 0.153$ V

Aim : $Cu+ + e^{-} \longrightarrow Cu$, $E^{o} = ?$

Substracting equation. (ii) from equation (i) will not give the required result. We have to calculate their free energy changes. Let the free energy changes of the above three reaction be ΔG^{o}_{1}, ΔG^{o}_{2} and ΔG^{o}_{3} respectively.

Then $\Delta G^{o}_{3} = \Delta G^{o}_{1} - \Delta G^{o}_{2}$.

i.e., $-1 \times F \times E^{o}_{Cu+/Cu} = (-2 \times F \times 0.337) - (-1 \times F \times 0.153)$

($\Delta G^{o} = -nFE^{o}$)

The gives $E^{o}_{Cu+/Cu} = 0.521$V.

22. According to Faraday's first law of electrolysis, $\boxed{\frac{W}{E} = \frac{Q}{F}}$

Weight of substance liberated $\propto$ Quantity of electricity passed.

$W \propto Q$ or $W = ZQ = Z \times i \times t$ (Z = electrochemical equaivalent)

23. Z = Equivalent wt. of the substance / 96500 or $Z = \frac{E}{F}$

24. According to Faraday's second law of electrolysis for the same quantity of electricity passed through solutions of different electrolysis , (e.g, $CuSO_4$ and $AgNO_3$)

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equivalent wt. of Cu}}{\text{Equivalent wt. of Ag}} \qquad \boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2}}$$

25. In an aqueous solution of SO_4^{2-} and NO_3^-, at the anode these ions are not oxidised but H_2O is oxidized to give O_2 gas ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$).

26. For metals to be deposited on the cathode during electrolysis, the volage required is almost the same as the standard electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called over voltage or bubble voltage.

27. **Primary cell** are those which cannot be recharged ie., dry cell and mercury cell.
Secondary cells are those which can be recharged ie., lead storage battery and Ni – Cd cell.
Fuel cells are those in which energy produced from the combustion of fuels can be coverted into electrical energy e.g., H_2–O_2 fuel cell.

28. **Main features of different cell.**

	Name of the cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite	MnO_2 + C black (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode)
(ii)	Mercury cell	Zinc	Graphite	HgO + KOH (moist)
(iii)	Lead storage battery	Lead	Lead dioxide	H_2SO_4 (38% sol.)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH sol.
(v)	H_2–O_2 fuel cell	Porous carbon cont. catalysts H_2 passed)	Porous carbon cont. catalyst (O_2 passed)	Conc. aq. KOH sol.

29. A dry cell does not have a long life because the acidic NH_4Cl corrodes the zinc container even when the cell is not in use.

30. Mercury cell gives a constant voltage (1.35 V) throughout its life and is used in hearing aids and watches.

31. **Reactions ocurring in lead storage battery** (a) Reactions occurring during discharge.

At anode : $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode : $PbO_2 + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

The complete reaction may be written as

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

As H_2SO_4 is consumed, the voltage of the battery drops.

32. In the Apollo moon flights, the source of electric energy and that of drinkiing water was the H_2— O_2 fuel cell.

33. Corrosion is the process of change of metal surface into salts like oxides, sulphides, carbonates etc. due to attack of atmospheric gases.

34. Rust is hydrate ferric oxide, $Fe_2O_3.xH_2O$

35. **Factors which enhance corrosion are**

(i) Presence of impurities in the metal (pure metals do not corrode).

(ii) Presence of moisture (e.g., in rainy season)

(iii) Presence of electrolytes (e.g., saline water)

36. **Corrosion can be prevanted** by the following methods.

(i) Barrier protection by oil/grease layer, paints or electroplating.

(ii) Sacrificial protection by coating the metal with more electropositive metal (e.g. Zn called galvanisation).

(iii) Electrical protection by connecting the iron pipe to a more electropositive metal with a wire. (Cathodic protection)

37. Corrrosion takes place faster in saline water than in pure water.

38. According to Nernst equation,

(i) For the reaction half reduction (electrode reaction)

$Mn^+ + ne^- \longrightarrow M$

$$E_{R.P.} = E^0_{R.P.} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]} = E^0_{Red} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \text{ at } 298\text{ K}$$

(ii) For the cell reaction $a\,A + b\,B \rightleftharpoons x\,X + y\,Y$

$$E_{Cell} = E^0_{Cell} - \frac{RT}{nF}\ln\frac{[X]^x[Y]^y}{[A]^a[B]^b} = E^0_{Cell} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b} \text{ at } 298\text{ K}$$

For a pure solid, pure liquid at 1 atm. put molar conc. 1.

e.g. for $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$.

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = E^0_{Cell} - \frac{0.0591}{n}\log\frac{[Product]}{[Reactant]}$$

39. $$E_{Cell} = \frac{RT}{nF}\ln K = \frac{2.303}{nF}\log K = \frac{0.0591}{n}\log K \text{ at } 298\text{ K}$$

(K = Equilibrium constant of the cell reaction).

40. Thermodynamic efficiency of a fuel cell $(\eta) = \dfrac{\Delta G}{\Delta H} = \dfrac{-nFE}{\Delta H}$

41. **Calculation of ΔG and ΔS for cell reactions.**

(i) $\Delta G = -n\,FE_{cell}$

(ii) $\Delta S = nF\left(\dfrac{\partial E}{\partial T}\right)_P$

where $\left(\dfrac{\partial E}{\partial T}\right)_P$ = temperature coefficient of e.m.f = $\dfrac{E_2 - E_1}{T_2 - T_1}$ at constant pressure

(iii) $\Delta G = \Delta H - T\Delta S$.

5 Behvaiour of Gases

1. Gas law

(i) Boyle's law :

$$V \propto \frac{1}{P}(n, T = \text{const.})$$

$$\boxed{P_1V_1 = P_2V_2}$$

(ii) Charle's law

$$V \propto T(n, P = \text{const.})$$

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$

(iii) Gay lussac's law :

$$P \propto T(n, V = \text{const.})$$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1}$$

(iv) Avogadro's law :

$V \propto$ moles $\propto$ number of molecules $(P, T = \text{const.})$

Ideal gas equations $PV = nRT$

$R = 0.082$ lit atm mol^{-1} K^{-1}

$R = 8.314$ JK^{-1} mol^{-1} or 8.314 $N \times m$ K^{-1} mol^{-1}

$R = 2$ cal K^{-1} mol^{-1}

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

2. Graham's diffusion law :

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}$$

$$r \propto \frac{1}{\sqrt{VD}}$$

$$r \propto \frac{1}{\sqrt{Mw}} \quad (P, T = \text{const.})$$

$$VD = \frac{d_{gas}}{dH_2} = \frac{Mw}{2}$$

rate of diffusion $r = \frac{\ell_{\text{diffused gas}}}{t_{\text{time take}}}$

(Where, ℓ = distance travelled by differed gas)

$$r = \frac{V_{\text{diffused gas}}}{t_{\text{time taken}}}$$

$$r = \frac{n_{\text{diffused gas}}}{t_{\text{time taken}}}$$

3. Dalton's law of partial pressure

$$P_{mixture} = \underbrace{P_1 + P_2 + P_3}_{\text{Partial pressure}} \ldots\ldots\ldots\ldots\ldots (T \& V \text{const})$$

$$P_1 = P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapours}}$$

It is applicable for non reacting gases.

Methods of determination of partial pressure

(P_A & P_B are partial pressure)

(i) From ideal gas equation

$$P_A V = n_A RT \text{ and } P_B V = n_B RT$$

(ii) In the form of mole fraction.

$$P_A = X_A P_T = \frac{n_A}{n_1} P_T \qquad P_B = X_B P_T = \frac{n_B}{n_1} P_T \qquad X_A + X_B = 1$$

P_T = sum of partial pressure of all gases

(iii) In the form of volume fraction

$$P_A = \frac{V_A}{V} P_T \text{ and } P_B = \frac{V_B}{V} P_T$$

(iv) If individual pressure and individual volume are given

$$P_A = \frac{V_A}{V} P_1 \text{ and } P_B = \frac{V_B}{V} P_2$$

P_1, P_2 = pressure of gases before mixing

P_A, P_B = pressure of gases after mixing

4. Kinetic gas equation

$$PV = \frac{1}{3}mNV_{rms}^2$$

5. Average KE (KEav)

$$KEav = \frac{3}{2}nRT \quad \text{(n moles)}$$

$$KEav = \frac{3}{2}RT \quad \text{(1 mol or NA molecular)}$$

$$KEav = \frac{3}{2}KT \quad \text{(1 molecule)}$$

$K = 1.38 \times 10^{-23}\ JK^{-1}$

6.

$V_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + ...v_n^2}{N}}$	$V_{avs} = \frac{v_1 + v_2 + v_3 .... v_n}{N}$	$V_{mps} = \sqrt{\frac{2RT}{Mw}}$
$V_{rms} = \sqrt{\frac{3RT}{Mw}}$	$V_{avs} = \sqrt{\frac{8RT}{\pi Mw}}$	$V_{mps} = \sqrt{\frac{2PV}{Mw}}$
$V_{rms} = \sqrt{\frac{3PV}{Mw}}$	$V_{avs} = \sqrt{\frac{8PV}{\pi Mw}}$	$V_{mps} = \sqrt{\frac{2P}{d}}$
$V_{rms} = \sqrt{\frac{3P}{d}}$	$V_{avs} = \sqrt{\frac{8P}{\pi d}}$	

Vrms	:	Vavs	:	Vmps
$\sqrt{3}$	:	$\sqrt{\frac{8}{\pi}}$	:	$\sqrt{2}$
1.732	:	1.596	:	1.414
1.224	:	1.128	:	1

7. Compressibility factor (z) $= \frac{(V_m)obs}{RT} = \frac{P(V_m)obs}{RT}$

If z = 1. the gas show ideal gas behaviour
If z > 1, the gas show positive deviation
If z < 1, the gas show negative deviation

8. Vanderwaal's equation

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

$$P_I = P_R + \frac{an^2}{V^2} \quad \Rightarrow \quad P_I > P_R$$

a↑ force of attraction ↑ liquification↑
b↑ effective size of molecule ↑
incompressible vol↑, compressible vol↓

(i) At high pressure, Vanderwaal's equation is $\boxed{PV_m - Pb = RT}$

(ii) At high pressure, Vander waal's equation is $\boxed{PV_m + \frac{a}{V_m} = RT}$

6 Atomic Structure

- The word "atom" was given by Ostawald.

DISCOVERY & THEIR DISCOVERES

Name of Particles	Scienteist	Mass	Charge
Electron	J.J. Thomson	9.1×10^{-31} kg	-1.6×10^{-19} cb
Proton	Goldstein	1.673×10^{-27} kg	$+1.6 \times 10^{-19}$ cb
Neutron	Chadwick	1.675×10^{-27} kg	Zero
Positron	C.D. Anderson	(same as electron)	same as proton
Anti Proton	Sugrie	(same as proton)	electron
Neutrino	Pauli	Negligible	Zero
Meson	Yukawa	(200 times the electron)	(+, –, zero)
Isotopes	Soddy		
Isobar	Aston		
Cathode Ray	William Crooke's		
Anode Ray	GoldStein		
Neucleus	Rutherford		
Atomic No.	Moseley		
Nomenclature of e^-	Stoney		
Charge of e^-	Millikan		
Specific charge on e^- (e/m)	J.J. Thomson		

- **Important Definations :**

(i) Atomic number (Z) = no. of protons

- Mosley's relation $\Rightarrow \sqrt{\nu} = a(z-b)$

(ii) Mass no. (A) = number of (n + p)

(iii) Isotopes = Same Z + Different A

(iv) Average Atomic wt.

$$= \frac{m_1x_1 + m_2x_2 + m_3x_3 + ...}{x_1 + x_2 + x_3 + ...}$$

where m_1, m_2, m_3 are mass of isotopes

x_1, x_2, x_3 are their percentage aboundance or relative ratio.

(v) Isobar = Same A + Different Z

(vi) Isotones / Isoneutronic / Isotonic = same no. of neutrons

(vii) Isodiaphers = Same (n–p)

(viii) Isosters = Molecules with same no. of atoms and electrons.

(ix) Isoelectronic = Same no. of e^-s.

Electromagnetic radiations

- The electric & magnetic components of wave have same wavelength, frequency speed and amplitude but they vibrate in two mutually perpendicular planes.
- EM waves do not need any medium for propagation and all EM waves travel with same velocity ($3 \times 10^8\ ms^{-1}$).
- Relation between frequency (v), wavelength (λ), wave number $\left(\bar{\nu}\right)$ and time period (T).
  - $c = \nu\lambda$
  - $\vec{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$ $\qquad \boxed{1\ cm^{-1} = 100\ m^{-1}}$
  - $T = \frac{1}{\nu} = \frac{\lambda}{c}$

Electromagnetic Spectrum

The arrangment of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequency is known as electromagnetic spectrum.

Radition	Wavelength (λ)	Frequency (Hz)
Gamma rays	0.01 to 0.1	3×10^{19} to 3×10^{20}
X-rays	0.1 to 150	2×10^{16} to 3×10^{19}
UV radiations	150 to 3800	7.9×10^{14} to 2×10^{16}
Visible rays	3800 to 7600	3.95×10^{14} to 7.9×10^{14}
Microwaves	6×10^{6} to 3×10^{9}	1×10^{5} to 1×10^{9}

Photoelectric effect

E_{photon} = Thereshold Energy (work function) + KE

$E_{photon} = hv_0 + KE$

$$hv = hv_0 + KE$$

$$hv = hv_o + \frac{1}{2} m_e v^2$$

or $$KE = h(v - v_0)$$

Plancks Quantum theory (Importatant Formulae)

- $E = hv$ (E = Energy of one photon)

or $$E = hv = \frac{hc}{\lambda} = hc\bar{v}$$

- Total energy transfered = N × Energy of one photon.

$$E_r = N \times hv = N \times \frac{hc}{\lambda} = N \times hc\bar{v}$$

Where h = planck constant $= 6.626 \times 10^{-34}$ Js
$= 6.626 \times 10^{-27}$ erg s

Bohr's Model

Applicable for single e^- species only like H, He^+, Li^{+2}, Be^{+3}, Na^{+10} etc.
Related with particle nature of electron.
Based on Plancks Quantum theory.

Important Formula :

Angular momentum in an orbit is quantized.

$$mvr = n \times \frac{h}{2\pi}$$

Radius of bohr orbit = $r = \frac{n^2h^2}{4\pi^2 mKZe^2}$

On solving $r = 0.529 \times \frac{n^2}{Z}$ Å

where 0.529 Å = a_0 is called atomic unit of length (Bohr)

Velcoity of electron in Bohr orbit.

$$v = \frac{2\pi KZe^2}{nh} \text{ (MKS)}$$

On solving $v = 2.18 \times 10^6 \frac{Z}{n}$ m/s

$$v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/s}$$

Energy of electron in Bohr orbit

Potential energy (PE) $= -\frac{KZe^2}{r}$ i.e., At $r = \infty$, PE = 0

Kinetic energy (KE) $= \frac{1}{2}\frac{KZe^2}{r}$ i.e., At $r = \infty$, KE = 0

Total energy (TE) $= -\frac{2\pi^2 mK^2 z^2 e^4}{n^2 h^2}$

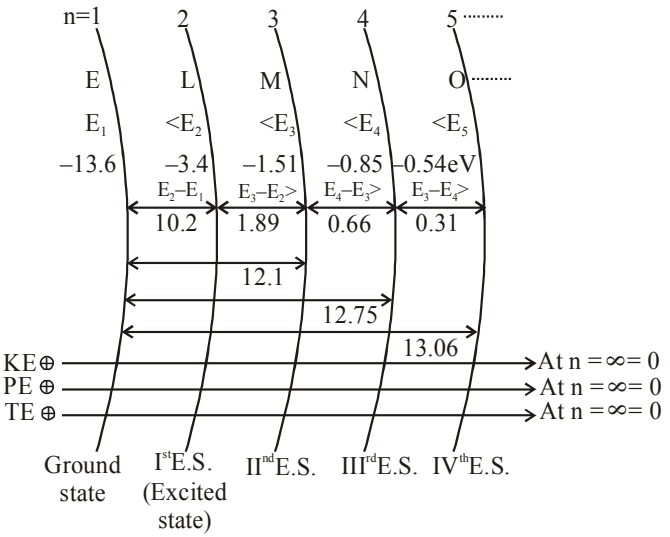
On solving TE $= -2.18 \times 10^{-18} \frac{z^2}{n^2}$ J/atom

$$= -13.6 \times \frac{z^2}{n^2} \text{ eV/atom}$$

$$= -313.6 \times \frac{z^2}{n^2} \text{ Kcal/mol}$$

$$= -1313{,}6 \times \frac{z^2}{n^2} \text{ KJ/mol}$$

Relation between TE, PE and KE = PE = 2 × TE
= TE = –KE
= PE = –2KE



Important Shortcuts

T.E. of any H-like species = TE or Hydrogen × Z^2
(For same orbit)

ΔE for H like species = ΔE (For hydrogen) × Z^2
(For same transition)

Energy in n^{th} orbital for H like species = $\frac{E_1}{n_1}$ [For same atom]

(I.E.) Ionisation Energy $\Rightarrow$ n = 1 $\longrightarrow$ n = ∞

(S.E) Separation Energy n = 2, 3, 4..... $\longrightarrow$ n = ∞
Ist S.E
2nd S.E.

(E.E.) Excitation Energy - n = 1 $\longrightarrow$ n = 2, 3, 4
Ist E.E
2nd E.E.

Spectrum (Important points)

Continous emission spectrum is given by incandescent sources.
Emission line spectrum is given by atoms.

Emission band spectrum is given by molecules.
Angle of deviation $\propto$ frequency of radiation
More lines are observed in emission spectrum than absorption specturm.

Hydrogen Spectrum (n_2)		**(n_1)**
Lyman	⟶ Any higher orbit ⟶	1 [Found in U.V. region]
Balmer	⟶ Any higher orbit ⟶	2 [Found in Visible region]
Paschen	⟶ Any higher orbit ⟶	3 [Found in I.R. region]
Bracket	⟶ Any higher orbit ⟶	4 [Found in I.R. region]
P fund	⟶ Any higher orbit ⟶	5 [Found in I.R. region]

Rydberg Equation :

$$\bar{v} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

[Where C = velocity of electromag netic waves]

$$v = R_H C Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$E = R_H Ch Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where R_H = Rydberg constant $= 109678\ cm^{-1}$
$= 10967800\ m^{-1}$

$\boxed{\frac{1}{R_H} = 912 Å}$

$R_H Ch$ = Energy of Ist orbit of hydrogen
$R_H Ch\ Z^2$ = Energy of Ist orbit of any hydrogen like species.

Important Point :

α line / First line/starting line/Initial line (First line of any series)
Last line/limitting line/ marginal line (Last line of any series)
Total number of lines in emission spectrum (For $n_2 \rightarrow n_1$)

(T.E.L.) Total Emission lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

But for $(n \rightarrow 1)$, T.E.L. $= \frac{n(n-1)}{2}$

De-Broglie Equation (Important Formulae)

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$

Where h = Planck's constant
m = mass

$\boxed{\because P = mv}$

$$\lambda = \frac{h}{\sqrt{2mKE}}$$ v = velocity

KE = Kinetic Energy

$$\lambda = \frac{h}{\sqrt{2mqv}}$$ (for e^- if solved) than $\lambda = \sqrt{\frac{150}{V}}$ Å

Important Points :

When an e^- revolves in orbit then no. of waves made by e^- = orbit number (n).

Frequency of matter waves.

$$v = \frac{v}{\lambda} = \frac{vP}{h} = \frac{mv^2}{h} = \frac{2KE}{h} [v = \text{frequency}]$$

Electron microscope is on the basis of the wave nature of electron.

de-Broglie on the basis of Milikan's oil drop experiment (which showed partical nature) and diffraction study (which showed wave nature) suggested the dual nature of electron.

Heisenberg uncertainity principle.

$$\Delta x \times \Delta P \geq \frac{h}{4\pi}$$

or $$\Delta x \times \Delta V \geq \frac{h}{4\pi m}$$

where Δx = Uncertainity in position

Δv = Uncertainity in velocity

ΔP = Uncertainity in momentum

m = Mass of particles

$\frac{h}{4\pi} = 5.27 \times 10^{-35}$ Js (In SI unit)

Quantum number

In an atom each shell, subshell, orbital and electron are designated by a set of 1, 2, 3, 4 quantum numbers respectively .

1. Principal Quantum number (By Bohr)

Indicates Size and energy of the orbit, distance of e^- from nucleus

Values in = 1,2,3,4,5.....

Angular momentum = $n \times \frac{h}{2\pi}$

Total number of e^-s in an orbit = $2n^2$

Total number of orbitals in an orbit = n^2

Total number of subshell in an orbit = n

2. Azimuthal / Secondary/Subsidiary/Angular momentum Q.No. (l)

$\Rightarrow$ Given by = Sommerfiel

$\Rightarrow$ Indicates = Subshells/sub orbit/sub level

$\Rightarrow$ Value $\Rightarrow$ 0,1.....(n–1)

$\Rightarrow$ Indicates shape of orbital/Subshell

Values of n	Values of l [Shape]	Initial from word
e.g. If n = 4	1 = 0 (s) [Spherical]	Sharp
	1 [p [Dumb bell]	Principal
	2 [d] [Double dumb bell]	Diffused
	3 [f] [Complex]	Fundamental

Total number of e^-s in a sub-orbit = $2(2\ell+1)$

Total number of orbitals in a sub - orbit = $(2\ell+1)$

Orbital angular momentum = $\sqrt{\ell(\ell+1)}\,\frac{h}{2\pi} = \cancel{h}\sqrt{\ell(\ell+1)}h$

h = Plank's cosntant

For H & H-like species all the subshell of a shell have same energy

i.e., 2s = 2p

3s = 3p = 3d

3. Magnetic Quantum number (m)

Given by linde

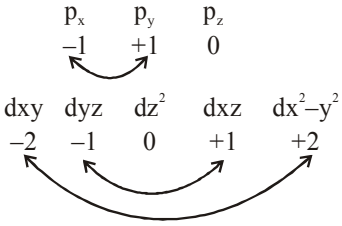
Indicates orientation of orbitals ie., direction of e^- density

value of m = $-\ell$.....0.....$+\ell$

Maximum no of e's in an orbital = 2 (with opposite spin)

m for p sub shell =

m for d sub shell =



4. Spin Quantum no. (m_s or s)

Given by Uhlenbeck & Goldsmit

Value of s = $\pm\frac{1}{2}$

Total values of spin in an atom = $\pm\frac{1}{2}$ × number of unpaired e^-

Spin Angular momentum = $\sqrt{s(s+1)}\,\frac{h}{2\pi}$

Rules for filling of orbits :

1. **Aufbau principle :** The electron are filled up in increasing order of the energy in subshells.
   $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$
2. **(n + ℓ) rule :** The subshell with lowest (n + ℓ) values is filled up first, but when two or more subshell have same (n + ℓ) value then the subshell with lowest values of n is filled up first.
3. **Pauli exclusion principle :** Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
4. **Hund's rule of maximum multiplicity :** Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.

7 Chemical Kinetics

1. Rate of reaction :

$n_1A + n_2B \longrightarrow m_1C + m_2D$

$$ROR = \frac{1}{n_1}.\frac{-d[A]}{dt} = \frac{1}{n_2}.\frac{-d[B]}{dt} = \frac{1}{m_1}.\frac{+d[C]}{dt} = \frac{1}{m_2}.\frac{+d[D]}{dt}$$

Rate of disappearance of A $= -\frac{d[A]}{dt}$

Rate of disappearance of B $= -\frac{d[B]}{dt}$

Rate of appearance of C $= \frac{d[C]}{dt}$

Rate of appearance of D $= \frac{d[D]}{dt}$

Order of reaction :

R is defined as "the total number of reacting molecules whose concentration determines the rate of reaction or the total number of reacting molecules whose concentration changes during the chemical change.

In general order of a reaction is defined as, "the sum of the powers to which the concentration terms of reactant must be raised in order to determine the reaction rate."

For a reaction, $mA + nD \longrightarrow C$

Rate equation is $\frac{dx}{dt} = K[A]^x[D]^y$

Order of reaction with respect to A = x

Order of reaction with respect to B = y

Total order of reaction = x + y

Here K is a rate constant and value depend on

(1) Temperature

(2) Catalyst

(3) Nature of reactant

Zero order reaction

Eg. decomposition of gases on metal surface

Eg. Photochemical reaction

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\upsilon} 2HCl_{(g)}$$

Integrated rate equation

$[A]_t = [A]_0 - kt$ .....(1)

$x = kt$ .....(2)

$$\text{Half life } t_{1/2} = \frac{[A]_o}{2k} \Rightarrow t_{100\%} = \frac{a}{k} \Rightarrow t_{100\%} = 2 \times t_{1/2}$$

$$\text{Rate equation : } \frac{-d[A]}{dt} = k[A]^0$$

First order reaction

Eg. All radio active disintegration

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Hydrolysis of ester in acidic medium

$$CH_3COOC_2H_6 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Inversion of cane sugar in acidic medium

$$C_{12}H_{22}O_{12} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\text{Rate equation : } \frac{-d[A]}{dt} = K[A]^1$$

First order rate expression :

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{Half - life } (t_{1/2}) = \frac{0.693}{k}$$

$t_{75\%} = 2 \times t_{1/2}$, $t_{87.5\%} = 3 \times t_{1/2}$, $t_{93.75\%} = 4 \times t_{1/2}$, $t_{100\%} = \infty$

Integrated rate equation for n^{th} order reaction :

$$Kt = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} \frac{1}{a^{n-1}}\right]$$

$$t_{1/2} = \frac{1}{(n-1)}\left[\frac{2^{n-1}-1}{a^{n-1}}\right]_k \qquad \Rightarrow \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

$$\boxed{\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}}$$

half life method to determine order of reaction.

Activation Energy :

- Only those collisions, in which the colliding molecules possess certain minimum energy called threshold energy result in a chemical reaction.
- The excess energy that is supplied to the reactant molecules in order to raise them to the level of threshold energy is called activation energy.
- Arrhenius gave a relationship between the temp. and rate constant of a reaction called Arrhenius equation.

  Where, k_1 = rate constant at temp. T_1

  k_2 = rate constant at temp. T_2

- Temperature coefficient $\mu = \frac{k_{T+10}}{k_T}$

  range of $\mu = 2 \le \mu \le 3$

  $\mu^{\Delta T/10} = \frac{k_2}{k_1} = \frac{r_2}{r_1}$ at any two different temperatures.

Factors which affecting activation energy

(1) Catalyst

(2) Nature of reactant

(1) Factors affecting rate of reaction

(i) Nature of reactant.

(a) Physical state (b) Physical Nature (c) Chemical nature

(ii) Concentration of reactant

(iii) Pressure

(iv) Temperature

(v) Catalyst

(vi) Exposure to radiation

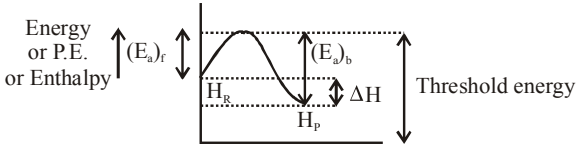
2. Collision theory - Arrhenius

Two conditions must be satisfied at a line for effective collision.

(i) Reacting molecules must posses a minimum amount of energy. which is equal to threshold energy.

(ii) Proper orientation of collision.

- Threshold energy = Potential energy of reactant + activation energy.



$\Delta H = H_P - H_R = (E_a)_f - (E_a)_b$

8 Theromdynamics

Work

Mechanical work = force × displacement = F × d

Electrical work = pot. diff. × quantity of current = E × Q

Gravitational work = gravitational force × height = mg × h

Mechanical Work = pressure × change in volume $P \times \Delta V$

For expanssion W = –ve ($\because V_2 > V_1$)

For compression W = +ve ($\because V_2 > V_1$)

Units of work 1 cal = 4.184×10^7 erg = 4.184 J

Enthalpy :

Enthalpy (H) is defined as the total heat contant of the system at constant pressure,

$H = E + PV$

$\Delta H = \Delta E + \Delta(PV)$

or $\Delta H = \Delta E + (P_2V_2 - P_1V_1)$

$\Delta H = \Delta E + P\Delta V + V\Delta P$

at constant pressure $\Delta H = \Delta E + P\Delta V$

so $\Delta H = \Delta E + \Delta n_g RT$ (for chemical reaction)

First law of thermodynamic

Mathematically

$q = \Delta E - w$

or $\Delta E = q + w$

q = heat absorted or evolved (+ve if absorbed and –ve if evolved)

For isothermal process

$\Delta T = 0 \because \Delta E = 0\ q = -W$

i.e., heat absorved is used in word done by the system.

For Adiabatic process

$\because q = 0 \ \therefore \ \Delta E = W$

i.e., Internal energy is used up in work done by the system. If work is done on the system. Its internal energy will increase or if work is done by the system process work behaves as state function.

In adiabatic process work behave as state function.

For isobaric process

$\because \quad \Delta P = 0 \qquad q_P = \Delta H$

Work done

(1) For irreversible process

$$W = -P_{ext} \times \Delta V$$

(2) For reversible process -

$$W = -\int_{v_1}^{v_2} PdV$$

(3) For reversible isothermal process -

$$W = -2.303\, nRT \log_{10} \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

(4) In adiabatic process $-W = \Delta E$

For an ideal gas $W = nC_v(T_2 - T_1)$

or $$W = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$$

(5) When an ideal gas is freely expand in vacuum then the obtained work done is zero because $P_{ext.} = 0$

(6) Reversible expansion process are more efficient than the irrvesible expansion process.

Entropy

Entropy of a system is a measure of the degree of randomness or disorderness of the system and is denoted by S.

(1) ΔS for reversible isothermal process -

$$\Delta S = \frac{q_{rev.}}{T} = \frac{-W_{rev.}}{T} = \frac{2.303 nRT \log \frac{V_2}{V_1}}{T}$$

$$\Delta S = 2.303\, nR \log \frac{V_2}{V_1} = 2.303\, nR \log \frac{P_1}{P_2}$$

(q_{rev} = heat supplied to a system at temp. TK in a reversible manner)

(2) $\Delta S = S_{products} - S_{reactants}$

(3) $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

$$\Delta S_{total} = \frac{+q}{T_{system}} + \frac{-q}{T_{surroudings}}$$

If $T_{system} < T_{surroundings}$ heat flows a hot region to cold one ΔS_{total} is +ve and heat flow is spontaneous.

If ΔS_{total} is –ve the change is non spontaneous.

(4) ΔS for reversible adiabatic process

$$\Delta S = \frac{q_{rev.}}{T} = O$$

(5) ΔS for reversible isobaric process

$$= 2.303 n C_P \log \frac{T_2}{T_1}$$

(6) ΔS for reversible isochoric process

$$= 2.303 n C_V \log \frac{T_2}{T_1}$$

(7) ΔS for phase transition

$$q_{rev} = \Delta H_{rev} \qquad \Rightarrow \quad \Delta S = \frac{\Delta H_{rev}}{T}$$

- Entropy change of fusion , $\Delta S_f = \frac{\Delta H_f}{T}$

  (T = freezing point or melting point)

- Entropy change of vapourization, $\Delta S_v = \frac{\Delta H_v}{T}$ (T = boiling point)

(8) Standard entropy (S°) = entropy of one mole of substance at 1 atm and 25°C

Free energy

Free energy (G) is a measure of maximum useful work done.

$$G = H - TS,$$

At constant T & P

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Gibbs - Helmholtz equation)}$$

$$\Delta G = G_{products} - G_{reactants}$$

(i) $\Delta G^\circ = \Delta G^\circ_{f\ products} - \Delta G^\circ_{i\ reactants}$

(ii) ΔG° for the element = 0

(iii) $\Delta G^\circ = -2.303\ RT \log K$ (K = equilibrium constant)

If ΔG° is –ve, $K > 1$

$\Delta G^\circ = 0, K = 0$
ΔG° is +ve , $K < 1$

Condition for spontaneity of a chemical reaction is ΔG = –ve

ΔH	ΔS	$\Delta H - T\Delta S$	Behaviour
$-ve$	$+ve$	$\therefore \Delta G = -ve$	Spontaneous at all temperatures
$+ve$	$-ve$	$\therefore \Delta G = +ve$	Non -spontaneous at all temperatures
$+ve$	$+ve$	$\Delta G = -ve(\text{if } \Delta H < T\Delta S)$ $\Delta G = +ve(\text{if } \Delta H > T\Delta S)$	Spontaneous Non-spontaneous
$-ve$	$-ve$	$\Delta G = -ve(\text{if } \Delta H > T\Delta S)$ $\Delta G = +ve(\text{if } \Delta H < T\Delta S)$	Spontaneous Non-spontaneous

9 Energetics

1. Thermochemical reaction :

The balanced chemical reaction which give information about the physical states of reactant and product and heat change is called as thermo chemical reaction.

e.g., $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$; $\Delta H = +X$ cal.

Thermochemical reactions are of two types :

(i) Endothermic reaction : The reaction which absorb heat.

$\Delta H = H_P - H_R = +Ve$

Ex. Dessociation , Fusion, Vapourization, Sublimation, Photosynthsis reaction.

(ii) Exothermic reaction : The reaction which evolve heat.

$\Delta H = H_P - H_R = -Ve$

Ex. Combustion , Neutralisation, Hydration, Respiration reaction.

2. Heat of reaction OR Enthalpy of reaction OR ΔH_R :

The amount of heat evolved or absorbed when number of moles of the reactant indicated in the chemical reaction had completely reacted is called as heat of reaction.

Factor effecting the heat of reaction :

(i) Quantity of reactants and products.

(ii) Physical state of products and reactants

(iii) Allotropic form

(iv) Temperature

(v) Reaction is carried out at constant volume or at constant pressure.

3. Types of heat of reaction :

(I) Heat of formation (ΔH_i or $\Delta_f H$) :

Amount of heat absorbed or evolved when 1 mole of substance is formed from its constituent elements which are in their standard state called as heat of formation.

For a chemical reaction.

$$\Delta H = \left(\sum \Delta H_f\right)_{Product} = \left(\sum \Delta H_f\right)_{reactant}$$

(II) Heat of combustion ($\Delta H_{comb.}$) :

Amount of heat evolved when 1 mole of substance is completely burnt in excess of oxygen.

For a chemical reaction $\Delta H = \left(\sum \Delta H_{comb.}\right)_{Reactant} - \left(\sum \Delta H_{comb.}\right)_{Product}$

Note : Calorific value $= \dfrac{\Delta H_{comb.}}{\text{Molecular Weight}}$ kcal / gm or kJ / gm.

(III) Heat of neutralisation ($\Delta H_{neutralisation}$) :

If one of the acid or base or both are weak, then the heat of neutralisation is usually less than –13.7 kcal eq^{-1} or –57.3 kJ eq^{-1}.

The heat evolved when one equivalent of acid is completely neutralise by one equivalent of base in dilute solution. Its value is –13.7 kcal/equivalent or –57.3 kJ / equivalent for the neutralisation of strong acid and strong base.

$$H^+ + OH^- \rightarrow H_2O \qquad \Delta_N H = -13.7 \text{ kcal /eq.}$$

(IV) Heat of hydrogenation ($\Delta H_{Hydrogenation}$) :

The heat evolved during the complete hydrogenation of one mole unsaturated organic compound. It is exothermic process.

(V) Heat of atomization (ΔH_{atom}) :

The amount of heat required to convert 1 mol gaseous molecule (stable substance) into constituent gaseous atoms. It is endothermic reaction.

(VI) (A) Heat of fusion (ΔH_{fusion}) :

The required amount of heat to convert 1 mol solid into liquid.

(B) Heat of vapourization (ΔH_{vapour}) :

The required amount of heat to convert 1 mol liquid into gas.

(C) Heat of sublimation ($\Delta H_{Sub.}$) :

The required amount of heat to convert 1 mol solid into gas.

(VII) (A) Heat of hydration ($\Delta H_{hydration}$) :

Amount of heat evolved when one mol of anhydrous salt converted into its hydrated form. It is exothermic.

(B) Heat of solution ($\Delta H_{solution}$) :

Amount of heat absorbed or evolved when one mole of substance is dissolved in excess of solvent. It may be endothermic or exothermic.

(VIII) Bond Enery (B.E.)

(Bond dissocation energy) :

(i) The required amount of heat to dissociate one mole gaseous bond into separate gaseous atoms is called bond dissociation energy.

$$\Delta H = \sum (\text{B.E.})_R - \sum (\text{B.E.})_P$$

(ii) The average amount of energy required to break one mole gaseous bond into separate gaseous atoms is called bond energy.

For polyatomic molecules.

$$\text{average bond energy} = \frac{\text{energy required to break all bonds}}{\text{total number of bonds}}$$

1. Laws of thermochemistry :

(I) Lavosior and laplace law :

Enthalpy of formation of compound is numerically equal to the enthalpy of decomposition of that compounds with opposite sign.

2. Resonance Energy :

R.E. = (Observed ΔH) – (Calculated ΔH)

10 Chemical Equilibrium

1. Equilibrium is a dynamic process : Equilibrium is estabilised in a system when reactants combine to form products at the same rate at which products combine to form reactants.

$$\left(\frac{dx}{dt}\right)_f = \left(\frac{dx}{dt}\right)_b \text{ or } R_f = R_b$$

Chemical equilibrium can be approached from either side. A catalyst can fasten the approach of equilibrium but does not alter the state equilibrium.
System can be homogeneous or heterogeneous.
For a reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{in terms of active mass}$$

$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} \quad \text{in terms of partial pressure}$$

$$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b} \quad \text{in terms of mole fraction}$$

Partial pressure of solid is taken as unity and in calculation of partial pressure of solids their number of moles are not considered.
$K_P = K_C (RT)^{\Delta ng}$
(i) When $\Delta n_g = 0$ then $K_P = K_C$
(ii) When $\Delta n_g > 0$ then $K_P > K_C$
(iii) When $\Delta n_g < 0$ then $K_P < K_C$
$\Delta n_g = (c + d) - (a + b)$
M. Imp : While determining Δn_g, take only gaseous species.

Properties of equilibrium constant :

For $A + B \rightleftharpoons C + D \quad K_C = K$

then (i) $C + D \rightleftharpoons A + B \quad K_C = \frac{1}{K}$

(ii) $2A + 2B \rightleftharpoons 2C + 2D, \quad K_C = K^2$

(iii) $\frac{A}{2}+\frac{B}{2} \rightleftharpoons \frac{C}{2}+\frac{D}{2}, K_C = \sqrt{K}$

(iv) $A \rightleftharpoons B \quad K_C = K_1$

$B \rightleftharpoons C \quad K_C = K_2$

$C \rightleftharpoons D \quad K_C = K_3$

then $A \rightleftharpoons D \quad K_C = K_1.K_2.K_3$

(v) $A \rightleftharpoons B \quad K_C = K_1$

$B \rightleftharpoons C \quad K_C = K_2$

then $A \rightleftharpoons C \quad K_C = \frac{K_1}{K_2}$

Reaction quotient Q for the reversible reaction

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C]\ [D]}{[A]\ [B]}$$

Q is taken at any condition of system.

$\Rightarrow$ If $Q = K_{eq.}$ then system is in equilibrium

$\Rightarrow$ If $Q > K_{eq.}$ system proceeds in backward side to attain equilibrium

$\Rightarrow$ If $Q < K_{eq.}$ system proceeds in forward side to attain equilibrium

For the equilibrium $A \rightleftharpoons nB$

Degree of dissociation $\alpha = \frac{D-d}{D(n-1)}$

where n is the number of moles of products from one mole of reactant, D is the theoretical vapour density (if no dissociation takes place) and d is the observed vapour density (due to dissociation or association) vapour density × 2 = molecular weight.

Vapour density × 2 = molecular weight.

$$\text{Degree of dissocaition } (\alpha) = \frac{\text{Number of dissociation moles (x)}}{\text{Initial number of moles (a)}}$$

Equilibrium constant (K) depends upon temperature and way of writting the reaction.

Le-Chatelier's principle : If the system at equilibrium is subjected to change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to nullify the effect of that change.

The following conclusion have been derived from this principle.
(i) Increases in concentration of any substance favours the reaction in which it is used up.

(ii) High pressure is favourable for the reaction in which there is decreases in volume or number of moles.

(iii) A rise in temperature favours the endothermic reaction.

Application of Le-Chatelier's principle :

(i) Ice water system (melting of ice) :

$$\text{Ice} + \text{Heat} \rightleftharpoons \text{Water}$$

It is an endothermic process and there is decrease in volume.
Thus, the favourable conditions for melting of ice are ; (a) High temperature and (b) High pressure.

(ii) Solubility of gases in liquids :

When a gas dissolves in a liquid, there is decreases in volume. Thus, increase in pressure will favour the dissolution of gas in liquid.

11 Ionic Equilibrium

Acid and Base

- **Arrhenius Concept :** Acid ionises in water to give H_3O^+, ion while base ionises to give OH^- ion. Ex. HCl, NaOH
- **Bronsted-Lowry's Protonic Concept :** Acid is H^+ ion donor and base is H^+ ion acceptor.
  HCl and Cl^- is a conjugate acid-base pair. If acid is weak, its conjugate base is strong and vice-versa.
  A substance that can accept H^+ ion as well as can donate H^+ ion is called amphiprotic or amphoteric.

$$H_3O^+ \xrightarrow{H^+} \underset{\text{amphiprotic}}{H_2O} \rightarrow H^+ + OH^-$$

  A Bronsted Lowery acid - base reaction is always favoured in the direction from the stronger to the weaker acid/base combinations.
- **Lewis Concept :**
  Lewis acid is an electron - pair acceptor.
  Lewis base in an electron pair donor.
  All lewis bases are bronsted Lowry bases but all the lewis acid are not bronsted acids.
  $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ at 298 K
  K_w is called ionic product of water or autoionisation or autoprotolysis constant.
  In a mixture of strong acid or bases.

$$\left[H^+\right] = \left[H_3O^+\right] = \frac{\sum NV}{\sum V}, \left[OH^-\right] = \frac{\sum NV}{\sum V}$$

  In a mixture of acid and base, resultant is

(a) acidic mixture if N_1V_1 (acid) $> N_2V_2$ (base)

$$\left[H_3O^+\right] = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

(b) basic mixture if N_2V_2 (base) $> N_1V_1$ (acid)

$$\left[OH^-\right] = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

(c) neutral mixture if N_1V_1 (acid) $= N_2V_2$ (base)

For conjugation acid-base pairs

$K_a K_b = K_w = 1 \times 10^{-14}$ at 25ºC

$K_a K_b = K_w = 10^{-12}$ at 90ºC

Where K_a is the ionisation constant of acid and K_b is the ionisation constant of its conjugate base.

$HA + H_2O \rightleftharpoons H_3O^+ + A^-, K_a$

$A^- + H_2O \rightleftharpoons HA + OH^-, K_b$

$pK_a + pK_b = 14 = pKw$

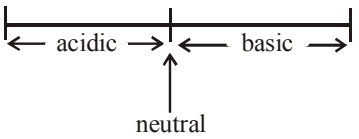
$pH = -\log [H_3O^+]$

$pOH = -\log [OH^-]$

$pX = -\log X$

$pH + pOH = pK_w = 14$

$0 \leq pH < 7 \quad 7 \quad 7 < pH \leq 14$



According to ostwald dilution low $\alpha \propto \sqrt{\text{dilution}}$

At infinite dilution , $\propto = 100\%$

For a weak acid by Ostwald dilution law

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad [H^+] = C\alpha$$

$$\left[H^+\right] = \sqrt{K_a C}, pH = \frac{1}{2}\left[pK_a - \log C\right]$$

and for weak base

$$K_b = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad [OH^-] = C\alpha$$

$$\left[OH^-\right] = \sqrt{K_b C} \qquad pOH = \frac{1}{2}\left[pK_b - \log C\right]$$

Ostwald dilution law is only applicable for weak electrolytes

Buffer solutions are which have resistive nature for pH change

(i) On dilution pH of buffer solution remains unchanged.

(ii) When small amount of SA or SB is mixed in buffer solution then pH of buffer solution remains almost unchanged.

Types of buffer solution :

(i) Simple buffer solution (Aq. solution of WAWB salts)

(ii) Mixed buffer solution :

(a) Acidic buffer solution (WA + WASB salts)

(b) Basic buffer solution (WB + WBSA salt)

Henderson - Hasselbalch equation for buffer

Acidic : $pH = pK_a + \log \frac{[\text{conjugate base}]\text{or}[\text{salt}]}{[\text{weak acid}]}$

Basic : $pOH = pK_b + \log \frac{[\text{conjugate acid}]\text{or}[\text{salt}]}{[\text{weak base}]}$

Ionisation of weak electrolyte is decreased in the presence of common ion is called common ion effect.

Solubility product of the sparingly soluble salt A_xB_y with solution (s) mol/litre in saturated solution.

$$A_xB_y \rightleftharpoons xA + yB \qquad K_{sp} = x^x\, y^y\, (s)^{x+y}$$

Salt analysis of inorganic mixture depends on common ion effect and values of solubility products.

In the presence of common ion solubility of electrolyte always decreases.

Solute AB is precipitate if $[A^+][B^-] > K_{sp}$

Salt and Salt Hydrolysis :

$$\text{Salt} + \text{Water} \underset{\text{Neutralisation } (\Delta H = -ve)}{\overset{\text{Hydrolysis } (\Delta H + ve)}{\rightleftharpoons}} \text{Acid} + \text{base}$$

Types of salt :

(i) General (ii) acidic (iii) basic (iv) Mixed (v) Double (vi) Complex.

Types of general salts :

(a) SASB (b) SAWB (c) WASB (d) WAWB

Types of salt	*Name of hydrolysis*	*Nature of aqueous solution and pH*
SASB	—	*Neutral, pH = 7*
SAWB	*Cationic*	*Acidic, pH < 7*
WASB	*Anionic*	*Basic, pH > 7*

For WA – SB type of salt :

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
Hydrolysis	*Cationic – anionic*	*Anionic – Cationic*	*Neutral hydrolysis*
Nature	*Acidic*	*Basic*	*Neutral*
pH	$pH < 7$	$pH > 7$	$pH = 7$

Summary :

Type of salt	$K_b = \frac{K_w}{Ionisation\ cons\ tant\ of\ weak}$	$h = \sqrt{\frac{K_b}{C}}$	$\left[H^+\right]$	*pH*
SASB	–	–	–	7
WASB	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a \times C}}$	$\sqrt{\frac{K_w \times K_a}{C}}$	$7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$
SAWB	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \times C}}$	$\sqrt{\frac{K_w \times C}{K_b}}$	$7 - \frac{1}{2}pK_a - \frac{1}{2}\log C$
WAWB	$K_h = \frac{K_w}{K_a \times K_b}$	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$\sqrt{\frac{K_w \times K_a}{K_b}}$	$7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

Group precipitation

(i) K_{sp} > [ ] [ ] > Ionic product $\Rightarrow$ unsaturated

(ii) K_{sp} = [ ] [ ] = Ionic product $\Rightarrow$ saturated

(iii) $K_{sp} <$ [ ] [ ] < Ionic product $\Rightarrow$ super saturated
$\Rightarrow$ precipitation occurs

= For precipitation of common salt (NaCl),
HCl gas is passed & for soap ($C_{17}H_{35}$ COONa), NaCl is mixed.
For amphiprotic anion (as HCO_3^-)

$$pH = \frac{pK_1 + pK_2}{2}$$

For acidic indicator (Hln), For basic indicator (lnOH)

$Hln \rightleftharpoons H^+ + ln^-$, $lnOH \rightleftharpoons ln^+ + OH^-$

$pH = pK_{ln} + \log \frac{[ln^-]}{[H ln]}$, $pOH = pK_{ln} + \log \frac{[ln^+]}{[ln OH]}$

Colour change of the indicator is explained by:

(i) Ostwald's Theory

Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
Methyl red	Red	Yellow	4.2 to 6.2
Phenol red	Yellow red	Red	6.2 to 8.2
Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

Acid-Base Titration

Type of Titration	pH range of Titration	Suitable indicators
SA/SB.	3 - 11	All indicators (MeOH, HPh etc.)
SA/WB	3 - 7	Methy orange (MeOH) and methyl red
WA/SB	7 - 11	Phenolphthalein (Hph)
WA/WB	6.5 – 7.5	Phenol red

12 Solid State

Seven Crystal System :-

Name of System	Axes	Angle	Forms of Lattices
1. Cubic	a = b = c	$\alpha = \beta = \gamma = 90^o$	Primitive, Face-Centred, Body Centred] 3
2. Tetragonal	a = b ≠ C	$\alpha = \beta = \gamma = 90^o$	Primitive, Body Centred] 2
3. Rhobohedral or Trigonal	a = b = c	$\alpha = \beta = \gamma \neq 90^o$	Primitive] 1
4. Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90$	Primitive, Face-centred, Body centred, End centred] 4
5. Monobclinic	a ≠ b ≠ c	$\alpha = \gamma = 90°$ $\beta \neq 90°, \neq 120^o, \neq 60^o$	Primitive, End centred] 2
6. Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90°$	Primitive] 1
7. Hexagonal	a = b ≠ c	$\alpha = \beta = 90°$ $\gamma = 120°$	Primitive] 1 Total = 14

Geometry of a cube

Number of corners = 8

Number of faces = 6

Number of edges = 12

Number of cube centre = 1

Number of cube diagonals = 4

Number of face diagonals = 12

Contribution of atom at different sites of cube

At corner = 1/8

at face = 1/2

at edge = 1/4

At body centre = 1

Types of unit cell (Bravail Lattice)

	Simple Cubic Cell (SCC)	Body centred Cubic Cell (BCC) (SCC + Body centred = BCC)	Face centred Cubic Cell (FCC) (SCC + Face Centred = FCC)
Geometry	a = 2r	$4r = \sqrt{3}a$	$4r = \sqrt{2}a$
Number of atoms per unit cell (n)	$= 8 \times 1/8 = 1$ Corners	$= (8 \times 1/8) + (1 \times 1) = 2$ corners body centre	$= (8 \times 1/8) + (6 \times 1/2) = 4$ corner face centre
Co - Ordination No.	6	8	12
Relation between a and r	a = 2r	$4r = \sqrt{3}a$	$4r = \sqrt{2}a$
Packing efficiency $\text{P.E.} = \frac{n \times 4/3\pi r^3}{V = a^3}$	$\frac{\pi}{6}$ or 52.4%	$\frac{\sqrt{3}\pi}{8}$ or 68%	$\frac{\pi}{3\sqrt{2}}$ or 74%

Density of the unit cell = $\frac{n \times M}{V \times N_A}$ g cm^{-3}

Where M = Molecular weight or atomic weight

Three dimensional close packing

Contents	BCC	CCP/FCC	HCP
Type of packing	ABAB..... Packing but not close packing	ABCABC..... Close Packing	ABAB..... Close Packng
No. of Atoms	2	4	6
Co- Ordination No.	8	12	12
Packing efficiency	68%	74%	74%
Examples	IA, BA V & Cr group Fe	Ca, Sr, Al Co Group, Ni group, Copper group All inert gases Except helium	Remaining d-Block Elements Be & Mg

Note : Only Mn crystallizes in S.C.C.

Voids in close packing structure :

per atom $\begin{cases} 2 \text{ Tetrahedral void} \\ 1 \text{ Octahedral void} \end{cases}$

Limiting Radius Ratio = r/R	Coordination Number of Cation	Structural Arrangement (Geometry of Voids)	Example
0.155 – 0.225	3	Plane Trigonal	Boron Oxides (B_2O_3)
0.225 – 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 – 0.732	6	Octahedral	NaCl, MgO_2
0.732 – 1.000	8	Cubic	CsCl

NaCl Type :

For NaCl : Distance between two nearest ions $(r^+ + r^-)$:-

$$2r^+ + 2r^- = a$$

i.e. $$r^+ + r^- = \frac{a}{2}$$

CsCl type :

For CsCl : Distance between two nearest ions $(r^+ + r^-)$:-

$$2r^+ + 2r^- = \sqrt{3a}$$

i.e. $$r^+ + r^- = \frac{\sqrt{3a}}{2}$$

Defects or imperfections in solids :

Schottky defect	Frenkel defect	F-Centre
Equal number of cations and anions are missing from their respective position leaving behind a Pair of holes	This type of defect is created when an ion levels its appropriate site in the lattice and occupies an interstitial site	A compound may have excess metal in ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron
Density decreased C. No. is high L.R.R. is high Electrically neutral Ex. NaCl. CsCl, KCl, KBr	Density unchanged C. No. is low L.R.R. is low Electrically neutral Ex. ZnS, AgBr, AgCl etc.	Ex. NaCl – Yellow KCl – Voilet

B. TYPES OF IONIC CRYSTAL

Type of Ionic Crystal	Geomertry	Co-ordination Number	No. of formula's per U.C.C.	Examples
NaCl (1 : 1) (Rock Salt Type)	C.C.P. — Cl^- - every element of C.C.P. Na^+ - at every OHV	6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of II - A (Some exception) AgF, AgCl, AgBr, NH_4X
CsCl Type (1 : 1)	B.C.C. — Cl^- - at every corner Cs^+ - at body centre or at cubic void	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS
ZnS Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P. — S^{-2} - every element of C.C.P. Zn^+ - at 50% of T.H.V. or at alternate tetrahedral void	4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
CaF_2 Type (1 : 2) (Fluorite Type)	C.C.P. — Ca^{+2} - every element of C.C.P. F^- - at every T.H.V.	$4Ca^{+2}$, 8F 4 : 8	$4Ca^{+2} + 8F$ $4CaF_4$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2 $CaCl_2$, CaF_2
Na_2O Type (2 : 1) (Antifluorite)	C.C.P. — Na^+ - at every T.H.V. O^{-2} - every element of C.C.P.	$4Na^+$, $4O^{-2}$ 8 : 4	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S Na_2O, Na_2S K_2O, K_2S
ZnS Type (1 : 1) (Wurtzite another geometry of ZnS	C.C.P. — S^{-2} - every element of H.C.P. Zn^{+2} - 50% of T.H.V. or (at alternate T.H.V.)	4 : 4	$6Zn^{+2} + 6S^{-2}$ 6ZnS (6)	Same as sphalerite

13 Surface Chemistry

Classification based on interaction of phases:-

Lyophilic and Lyophobic sols

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols. (solvent -liking).
For example - Dispersion of gelatin, Starch, gum and proteins in water.
Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called lyophobic collidal (Solvent hating) Solutions.

Comparision of Lyophobic and Lyophilic sols

Property	Lyophilic Sol. [Liq. Loving Solution] (Emulsoid)	Lyophobic sol [Solvent hating colloid] (Suspensoid)
1. Preparation	Can be easily prepared by Shaking or warming the substance with solvent	Can not be prepared Easily special methods are required
2. Stability	are more stable	are less stable
3. Reversibility	are reversible	are irreversible
4. Viscocity	viscosity is much higher than that of solvent	viscosity is nearly same as that of the solvent
5. Surface tension	Surface tension is usually low	Surface tension is almost same as that of solvent
6. Hydration or Solvation	These are highly solvated as the particles have great affinity for solvent	These are less solvated as the particles have less affinity for the solvent
7. Charge	The particles have little Charge or no charge at all	The particles carry a characteristic charge either positive or negative
8. Visibility	Particles can not be seen under microscope	Particles can be seen Under microscope
9. Coagulation or Precipitation	Precipitated by high concentration of electrolytes	precipitated by low concentration of electrolytes
10. Tyndall Effect	Less scattering	More scattering
11. Migration in electric field	may or may not migrate as they may or may not carry charge.	migrate towards anode or cathode as these particles carry charge.
12. General example	Mostly of organic nature Ex. Gelatin, Starch, Gum, Albumin & Cellulose solution	Mostly of Inorganic nature Ex. Transiton metal Salt in water. Gold, As etc.

PEPTIZATION :

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptization. The electrolyte used is called **Peptizing agent.**

Hardy Schulze Rule : This rule state that the precipitating effect of an ion on dispersed phase of oposite charge increasing with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its precipitating power of As_2S_3 sol (–ve) the precipitating power of Al^{3+}, Ba^{2+} and Na^{+} ion is in the order

$$Al^{3+} > Ba^{2+} > Na^{+}.$$

Similarly for precipitating $Fe(OH)_3$ sol (positive) the precipitating power of $[Fe(CN)_6]^{-3}$, So_4^{2-} and Cl^{-} ions is in the order.

$$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^{-}$$

The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

$$\text{Flocculation value } \alpha \ \frac{1}{\text{Flocculation Power}}$$

GOLD NUMBER

The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 100% NaCl solution is know as Gold Number of that protector (Lyophillic colloid).

The precipitation of the gold solution is indicated by a colour change from red to blue when the particle size just increases.

The smaller the gold number of a protective Lyophilic colloid, Greater is its protection power.

$$\text{Protection capacity } \alpha \ \frac{1}{\text{Protection Number}}$$

(Gold Number)

$$\text{GN.} = \frac{\text{Wt. of lyophilic sol. in mg}}{\text{Vol. of gold solution in mL}} \times 10$$

Note : Gelatin is best protecting colloid because it has least gold number.

Types of colloids according to their size		
Multi Molecular	**Marco Molecular**	**Associated colloids**
Formation by Aggregation a large number of atoms or smaller molecules of substance. Ex. – **Gold Sol (Au), Sulphur sol. (S_8)**	Formation by Aggregation of big size molecules. These are polymers with high molecular mass. Ex. – **Starch,** Cellulose, Protein etc.	These are the substances of which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal. These Associated particles are Also called micelles. Ex. Sodium stearate.

Comparison of physisorption and chemisorption	
Physical adsorption	**Chemical Adsorption (Activated ad.)**
1. It is caused by intermolecular. Vander waal's forces.	It is caused by chemical bond Formation.
2. It is not specific.	It is highly specific.
3. It is reversible.	It is irreversible.
4. Heat of adsorption is low. –20 to –40 KJ/mol	Heat of adsorption is high. –200 to –400 KJ/mol
5. No appreciable activation energy is involved.	High activation energy is involved.
6. It forms multimolecular layers On adsorbent surface. under high pressure	It forms unimolecular layer.

General characteristics of catalysts :

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.

(ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.

(iii) A catalyst does not initiate a reaction.

(iv) Solid catalyst is more efficient when used in finaly divided state.

(v) Generally catalyst does not change the nature of products.

(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.

(vii) The catalyst is generally specific in nature.

(viii) Change rate constant of reaction.

(ix) Does not change free enrgy of reaction.

(x) Participate in mechanism of reaction.

14 Some Important increasing order

1. Acidic Property

(i) SiO_2, CO_2, N_2O_5, SO_3

(ii) MgO, Al_2O_3, SiO_2, P_4O_{10}

(iii) HClO, $HClO_2$, $HClO_3$, $HClO_4$

(iv) CH_4, NH_3, H_2O, HF

(v) SiH_4, PH_3, H_2S, HCl

(vi) H_2O, H_2S, H_2Se, H_2Te

(vii) HF, HCl, HBr, HI

(viii) $lnCl_3$, $GaCl_3$, $AlCl_3$

(ix) BF_3, BCl_3, BBr_3, BI_3

2. Bond Angle

(i) CH_4, C_2H_4, C_2H_2 (Hint : % S लक्षण)

(ii) H_2O, NH_3, CH_4, CO_2

(iii) H_2O, NH_3, CH_4, BH_3

(iv) NO_2-, NO_2, NO_2+

(vi) AsH_3, PH_3, NH_3

(vii) PF_3, PCI_3, PBr_3, PI_3

(viii) NF_3, NCI_3

(ix) NF_3, NH_3, NCI_3,

(x) OF_2, OH_2, CI_2O

3. Basic character

(i) LiOH, NaOH, KOH, RbOH, CsOH

(ii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$

(iii) BeO, MgO, CaO, SrO

(iv) NiO, MgO, SrO, K_2O, Cs_2O

(v) CO_2, B_2O_3, BeO, Li_2O

(vi) SiO_2, Al_2O_3, MgO, Na_2O

(vii) SbH_3, AsH_3, PH_3, NH_3

(viii) F^-, OH^-, NH_2^-, CH_3^-

4. Thermal Stability

(i) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3
(ii) $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$
(iii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
(iv) LiOH, NaOH, KOH, RbOH, CsOH
(v) $BeSO_4$, $MgSO_4$, $CaSO_4$
(vi) CsH, RbH, KH, NaH, LiH
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) H_2Te, H_2Se, H_2S, H_2O
(ix) HI, HBr, HCI, HF

] Polarisation

5. Solubility

(i) $BaCO_3$, $CaCO_3$, $MgCO_3$, $BeCO_3$
(ii) Be(OH)2, $Mg(OH)_2$, $Ca(OH)_2$
(iii) $BaSO_4$, $SrSO_4$, $CaSO_4$, $MgSO_4$, $BeSO_4$
(iv) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3
(v) LiOH, NaOH, KOH, RbOH, CsOH
(vi) LiF, LiCl, Libr, LiI
(vii) LiF, NaF, KF, RbF, CsF
(viii) BaF_2, SrF_2, MgF_2, CaF_2, BeF_2
(ix) CaF_2, $CaCl_2$, $CaBr_2$, CaI_2
(x) AgI, AgBr, AgCl, AgF
(xi) PbO_2, CdI_2, RbI

] $\text{Solubility} \propto \frac{1}{\text{Covelent char.}}$

6. Ionic Character

(i) LiBr, NaBr, KBr, RbBr, CsBr
(ii) LiF, NaF, KF, RbF, CsF
(iii) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$
(iv) BCl_3, $AlCl_3$, $GaCl_3$
(v) VCl_4, VCl_3, VCl_2
(vi) AlF_3, MgF_2, NaF
(vii) AlN, Al_2O, AlF
(viii) HI, HBr, HCl, HF
(ix) CuCN, AgCN
(x) AgCl, KCl

7. Atomic /Ionic Size

(i) Mg^{2+}, Na^+, F^-, O^{2-}, N^{3-} (Hint : Isoelectronic series)
(ii) Ca^{2+}, Ar, Cl^-, S^{2-}
(iii) O, C, S, Se
(iv) B, Be, Li, Na
(v) F, O, F^-, O^{2-}

8. Atomic /Ionic Size

(i) $Cr_2O_7^{2-}$, MnO_4^-
(ii) MnO_4^{2-}, MnO_4^-
(iii) WO_3, MoO_3, CrO_3
(iv) $GeCl_4$, $SnCl_4$, $PbCl_4$
(v) I_2, Br_2, Cl_2, F_2
(vi) Zn^{+2}, Fe^{+2}, Pb^{2+}, Cu^{2+}, Ag^+

9. Ionization Energy

(i) Na, Al, Mg, Si
(ii) Li, B, Be, C, O, N, F, Ne, He (I^{st} I. P.)
(iii) Be, C, B, N, O, Ne, Li, He (II^{nd} I.P.)

10. Melting Point

(i) Cs, Rb, K, Na, Li
(ii) Mg, Ba, Sr, Ca, Be
(iii) CaI_2, $CaBr_2$, $CaCl_2$, CaF_2
(iv) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$
(v) NaI, NaBr, NaCl, NaF
(vi) CsCl, RbCl, KCl, NaCl
(vii) $AlCl_3$, $MgCl_2$, NaCl

11. Density

(i) Na, Al, Fe, Pb, Au
(ii) Li, K, Na, Rb, Cs
(iii) Ca, Mg, Be, Sr, Ba
(iv) Highest Density = Os/Ir
(v) Lowest density = H
(vi) Metal of lowest Density = Li

12. Boiling Point

(i) PH_3, AsH_3, NH_3, SbH_3
(ii) H_2S, H_2Se, H_2O
(iii) HCl, HBr, HI, HF
(iv) NH_3, HF, H_2O
(v) He, Ne, Ar, Kr
(vi) H_2O, D_2O
(vii) H_2, Cl_2, Br_2

13. Electrical Conductivity :

(i) Cr, Pt, Fe, Al, Au, Cu, Ag

14. Reactivity with water

(i) Li, Na, K, Rb, Cs

(ii) Be, Mg, Ca, Sr, Ba

15. Extent of Hydrolysis

(i) CCl_4, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5

(ii) $BiCl_3$, $SbCl_3$, $AsCl_3$, PCl_3, NCl_3

16. Bond Strength

(i) HI, HBr, HCl, HF

(ii) $-\overset{\diagdown}{\underset{\diagup}{C}} - I$, $-\overset{\diagdown}{\underset{\diagup}{C}} - Br$, $-\overset{\diagdown}{\underset{\diagup}{C}} - Cl$, $\overset{\diagdown}{\underset{\diagup}{C}} - F$

(iii) $N - N$, $N = N$, $N \equiv H$

(iv) As – H, Sb – H, P – H, N– H

(v) N_2^{2-}, N_2^{-}, N_2^{+}, N_2

(vi) O_2^{-2}, O_2^{-}, O_2, O_2^{+}, O_2^{2+}

LiI, LiBr, LiCl, LiF

NaI, NaBr, NaCl, NaF

CsCl, RbCl, KCl, NaCl

BaO, SrO, CaO, MgO

(vii) F_2, H_2, O_2, N_2

(viii) NO^{-}, NO, NO^{+}

(ix) I_2, F_2, Br_2, Cl_2

(x) O–O, S–S

(xi) F–F, O–O, N–N, C–C, H–H

17. Reduction Power

(i) $PbCl_2$, $SnCl_2$, $GeCl_2$

(ii) HF, HCl, HBr, HI

(iii) Ag, Cu, Pb, Fe, Zn

(vi) HNO_3, H_2SO_3, H_2S

(v) H_3PO_4, H_3PO_3, H_2PO_2

18. Chovalent character
(i) LiCl, $BeCl_2$, BCl_3, CCl_4
(ii) $SrCl_2$, $CaCl_2$, $MgCl_2$
(iii) $TiCl_2$, $TiCl_3$, $MgCl_4$
(iv) LiCl, LiBr, LiI
(v) Na_2O, Na_2S
(vi) AlF_3, Al_2O_3, AlN
(vii) HF, HCl, HBr, HI

19. Strength of Hydrogen Bonding (X....H–X)
(i) S, Cl, N, O, F
(ii) NH_3, H_2O, HF

20. Ionic Radii in water
(i) Cs^+, Rb^+, K^+, Na^+, Li^+
(ii) Li^+, Be^{+2}
(iii) Al^{+3}, Mg^{+2}, Na^+

21. Molar conductivity in water
(i) Li^+, Na^+, K^+, Rb^+, Cs^+

22. Reactivity with Hydrogen
(i) Cs, Rb, K, Na, Li
(ii) Ba, Sr, Ca, Mg, Be

23. Reactivity Towards Air
(i) Be, Mg, Cs, Sr, Ba

24. Hydration of Ions/Hydration Energy
(i) Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}, Be^{+2}
(ii) Cs^+, Rb^+, K^+, Na^+, Li^+
(iii) Na^+, Mg^{+2}, Al^{+3}

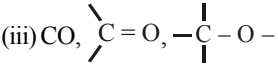
25. Electron Affinity
(i) I, Br, F, Cl
(ii) Cu, Ag, Au (EA, of Au is very high = 222 kJ mol^{-1})
(iii) O, S, F, Cl
(iv) N, P, O, S

26. Electronegativity
(i) As, P, S, Cl
(ii) I, Br, Cl, F
(iii) C, N, O, F

27. Bond Length

(i) N_2, O_2, F_2 Cl_2

(ii) $N \equiv N$, $C \equiv N$, $C \equiv C$

(iii) CO, 

(iv) NO^+, NO, NO^-

(v) O_2, O_3, H_2O_2 (O-O bond length)

(vi) CO, CO_2, CO_3^{-2}

(vii) N_2, N_2^-, N_2^{-2}

(viii) O_2^{+2}, O_2, O_2^-, O_2^{-2}

(ix) HF, HCl, HBr, HI

28. Dipole Moments

(i) CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl

(ii) NF_3, NH_3, H_2O, HF

(iii) Cis-Chloropropene, Trans-Chloropropene

(iv) p, m, o-dichlorobenzene

(v) CH_3I, CH_3Br, CH_3F, CH_3Cl

(vi) NH_3, SO_2, H_2O, HF

(vii) H_2S, H_2O

(viii) HI, HBr, HCl, HF

(ix) PH_3, ASH_3, SbH_3, NH_3

(x) H_2O, H_2O_2

29. Abundance of Elements

(i) Elements on earth crust -	Fe, Al, Si, O
(ii) Metals on earth crust -	Ca, Fe, Al
(iii) Non-metals -	Si, O
In atmosphere -	Si, O
In Universe -	He, Si, H

GENERAL TREND OF DIFFERENT PROPERTIES IN THE PERIOD AND GROUPS

Property	PERIODS ⟶	GROUPS ⟶
Atomic Radius	Decreases	Increases
Ionisation potential	Increases	Decreases
Electronegativity	Increases	Decreases
Electron Affinity	Increases	Decreases
Covalent Character of halides	Increases	Decreases
Metallic Character	Decreases	Increases
Oxidising nature	Increases	Decreases
Reducing nature	Decreases	Increases
Screening effect	Increases	Increases
Effective nuclear charge ($Z_{eff.}$)	Increases	Constant
Valency w.r.t. oxygen	Increases	Constant
Basic character of hydrides	Decreases	(Metals) Increases
Basic character of oxides	Decreases	(Non metal) Decrease (Metals) Increases
Basic character of oxy acids	Decreases	Increases
Strength of oxy acids	Increases	Decreases
Thermal stability of sulphate	Decreases	Increases
Thermal stability of carbonates	Decreases	Increases
Thermal stability of nitrates	Decreases	Increases
Thermal stability of hydroxide	Decreases	Increases
Density	First Increase Then Decreases	Increases
Electro positivity	Decreases	Increases

15 Periodic Table

Arrangement of known element in horizontal rows and in vertical column in such a way that elements of similar properties are grouped together in one vertical column.

Development of periodic table :

(i) Prout Concept :-

All element made up of H-atom

At. wt of an element : n × [At wt of H]

Drawback: Could not explain fractional atomic mass.

(ii) Dobereiner low of triads:

Triads: The atomic mass of middle element is the avg. of 1st & 3rd element.

Li^7 $\qquad \frac{7+39}{2} = \frac{46}{2} = 23$

Na^{23}

K^{39}

Triads: (Li, Na, K) (Be, Mg, Ca) (Ca, Sr, Ba) (K, Rb, Cs)
(P, As, Sb) (S, Se, Te) (Cl, Br, I)

Drawback: Not applicable for all element.

(iii) Newland law of octave:

Base : Increasing order of atomic mass

Low : Properties of 1st and 8th elements are almost similar.

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

Drawback:

(i) Applicable only upto Ca.

(ii) discover of inert gas give death blow.

(iv) Lother meyer :

Curve between atomic mass and atomic volume.

Advantage: Elements of similar properties finds similar position e.g. alkali metals finds top position on curve, alkaline earth metals on descending position, halogen are on ascending position.

(v) Mendeleef Periodic Low : Physical & chemical properties of elements are the periodic function of atomic mass.

Characteristics :

(i) 8 group (I to VIII)

(ii) I to VII group divides into A & B

(iii) A sub group - Normal element

(iv) B sub group & VIII - Transition element

Advantage:

(i) Study of element become easy.

(ii) Prediction of elements : four elements named EKA.

EKA Boron $\longrightarrow$ Scandium

EKA Al $\longrightarrow$ Gallium

EKA Si $\longrightarrow$ Germanium

EKA Mn $\longrightarrow$ Technitium

(iii) Correction of doubtful masses: Atomic mass of three elements (U, Be, In, Au, Pt) were corrected.

Drawback :

(i) Position of hydrogen : Not fixed can be placed in IA & VIIA.

(ii) Position of Isotopes.

(iii) **Anomalous Pair:** Where increasing order of atomic mass not considered.

$$\left[\underset{39.9}{Ar},\ \underset{39.1}{K}\right]\left[\underset{58.9}{Co},\ \underset{58.6}{Ni}\right]\left[\underset{127.5}{Te},\ \underset{127}{I}\right]\left[\underset{232}{Th},\ \underset{231}{Pa}\right]$$

(iv) Similar property elements find position in different group.

(v) Different property elements find position in same group.

(vi) Could not explain why the property of element repeated after a regular interval.

(vi) Mosely Base: Charged from atomic mass to atomic number.

Characteristics: (group zero) of inert gas included in the periodic table.

Advantage:

(i) Position of isotopes resolved

(ii) Short coming of anomalous pair resolved.

Drawbacks:

(i) Position of hydrogen.

(ii) Problem of periodic function. could not be solved.

Long form of periodic table

(Given by Bohr-Bury & Rang-Werner)

Based on electronic configuration of outermost shell.

Achievement : Electronic configuration of outermost shell of elements repeats at regular interval i.e. why property repeats.

Characteristics : Having 18 group & 7 periods.

Period	n	Sub shell	No. of Elements	Element	Name of Period
1.	1	1s	2	$_{1}H$, $_{2}He$	Shortest
2.	2	2s, 2p	8	$_{3}Li - _{10}Ne$	Short
3.	3	3s, 3p	8	$_{11}N - _{18}Ar$	Short
4.	4	4s, 3d, 4p	18	$_{19}K - _{36}Kr$	Long
5.	5	5s, 4d, 5p	18	$_{37}Rb - _{54}Xe$	Long
6.	6	6s, 4f, 5d, 6p	32	$_{55}Cs - _{86}Rn$	Longest
7.	7	7s, 5f, 6d	26	$_{87}Fr - _{112}Uub$	Incomplete

IUPAC Nomenclature

(a) IUPAC gave names to elements above atomic No. 100 as follows :-

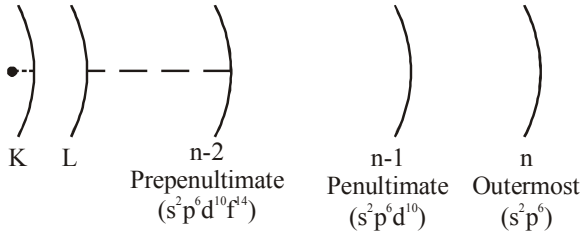
0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

(b) In all the elements suffix is - ium.

STUDY OF LONG FORM OF PERIODIC TABLE

Classification of elements :

(A) Bohr Classification : Based on electronic configuration.



Classify element into four type

(I) Noble gas :

(a) Element in which outermost/ultimate shell is completely filled.

(b) General configuration - ns^2np^6

(c) Present in '0' group & from 1st to 6th period.

(d) Total element 6 (He, Ne, Ar, Kr, Xe, Rn)

(II) Normal or representative element

(a) Element in which outermost/ultimate shell is incomplete.

(b) 'B' General configuration $ns^{1-2}np^{0-5}$

(c) Element of 'A' subgroup of mendeleef & from 1st, 2nd and 13th to 17th group in the long form of periodic table.

(III) Transition elements:

(a) Element in which ultimate as well as penultimate shell are incomplete either in ground state as well as in ionic state.

(b) 'B' subgroups & VIII group of Mendeleev & from 3rd to 12th group of long form of periodic table belongs to transitional element.

(c) According to this concept Zn, Cd, Hg, Uub are not transitional element.

(d) General electronic configuration = $ns^2np^6(n-1)d^{1-10}$

(IV) Inner transition elements

(a) Element in which ultimate (n), penultimate (n–1) & prepenultimate (n–2) all the three shells are incomplete.

(b) Elements of IIIB(except La, Ac) are known as Inner transition elements.

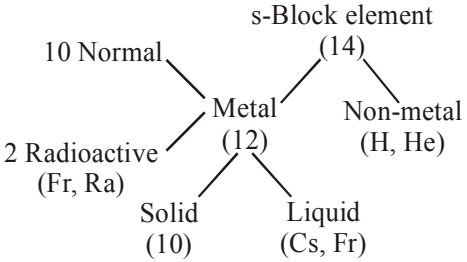
(c) Total elements (28)

(B) Classification based on last electron entry :

(I) s-Block elements : Last electron enters in s-subshell.

Lies in two group 1st/IA and 2nd/IIA & period from 1st to 7th.

General formula ns^{1-2}.



(II) p-block elements : in which last electron enters in p-subshell.

Electronic configuration - $ns^2\ np^{1-6}$

IIIA to 'O' group or 13^{th} to 18^{th} group & from period 2nd to 6th.

Total element - 30

In this block metal, non metal & metalloid are present.

(III) d-block elements : in which last electron enters in d-subshell.

Lies in between 3rd to 12th group.

Period 4th to 7th.

General configuration $(n-1)\ d^{1-10}\ ns^2$

(IV) f-block elements : f -block last electron enters in f-subshell.

Lies IIIB/3rd group & period 6th to 7th period.

General configuration - $(n-2)f^{1-14}\ (n-1)d^{1-10},\ ns^2$

Total element 28

14 Lanthanoids - found rarely on earth.

14 Actinoides - All are radioactive.

Determination of Period, block and group of an element

Period Number : Maximum principal quantum number in the electronic configuration of an element denotes period number.

Block number : Can be decided by last e^- entrance.

Last e^- enters in

s-subshell - s-block

p - subshell - p-block

d-subshell - d-block

f - subshell - f-block

Group number :

(A) s-block element:

Group number = Number of electron in ns subshell.

(B) p-block element:

Group number = Number of electron in np subshell + 10.

(C) d-block element :

Group No. = Number of electron in (n-1) d sub shell +2.

(D) f-block element : Group No. - IIIB/3rd

Que. Predict the period block & group number of element having atomic number 17.

$$17 = \underbrace{1s^2}_{n-2}\ \underbrace{2s^2\,2p^6\,3s^2}_{n-1}\ \underbrace{3p^5}_{n}$$

Period = 3rd; block = p ; group number = 7 + 10 = 17th.

Periodicity :

Regular gardation in properties from top to bottom in a group and from left to right in a period.

Cause of periodicity : Due to repeatition of same outermost shell configuration coming at regular internal.

Periodic Properties :

There are two type of periodic properties.

(I) Atomic properties : Properties shown by individual atom i.e. valency, I.P., E.A., E.N. and atomic radius.

(II) Molecular property : Properties shown by molecule i.e. density, M.P. & B.P.

(I) Atomic Properties :

Valency : Combining capacity of an atom.

Two concept :

(a) Old concept (i) w.r.t. 'H' & 'Cl'

(ii) w.r.t. 'O'

w.r.t. H & Cl valency of an element in a period initially increases from 1 to 4 & then decrease to 1.

w.r.t. 'O' along the period increases from 1 to 7.

(B) New concept (electronic concept) :- The number of electron required to gain or donate to achieve the nearest inert gas configuration.

For Example: Na = $1s^2$, $2s^2$, $2p^6$, $3s^1$ $\rightarrow$ one electron required to donate i.e. valency = 1

Cl = $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^5$ $\rightarrow$ One electron required to gain i.e. valency = 1

Valency in a group remains same.

(II) Screening effect/shielding effect (σ) : –

Repulsive force created by inner electron on a last electron is known as screening effect. In single electron system σ is absent.

Slater : Rule of calculation of σ.

(a) ns, np e^-	=	0.35
(b) (n–1) s, p	=	0.85, (n-1) d & f$\rightarrow$1
(c) (n–2) s, p, d, f	=	1.0
(d) (n–3) & all innershell	=	1.0

Calculation of σ

[(Number of electron in n^{th} shell - 1) × 0.35 + number of electron in (n–1) shell × 0.85 + number of electron in (n–2) shell & all inner shell × 1]

Variation σ, along the period & down the group increases.

Order of σ, $s > p > d > f$

(III) Effective nuclear charge (Zeff)

Net nuclear attraction force exert by nuclei on a valence electron is known as Zeff.

$$\boxed{Zeff = Z - \sigma}$$

For single e^- species = $\boxed{\sigma = 0}$

$$\boxed{Z_{eff} = Z}$$

Variation :

(a) Along the period

(i) Normal elements:

Z increases by 1

σ increases by 0.35

Zeff increases by 0.65

(ii) d-block :

Z increases by 1
s increases by 0.85
Zeff increases by 0.15

(b) Down the group : Remains constant.

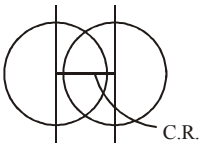
(IV) Atomic radii : Average distance between nucleus & valence electron cloud accurate value of atomic radii cannot be measured due to

(i) Isolation of atom is quite difficult.
(ii) Not measure.

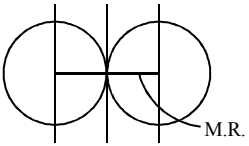
Type of Radii

(a) Covalent radii(C.R.)
(b) Metallic radii (M.R.)
(c) Vanderwall radii (VWR)
(d) Ionic radii (I.R.) $\left\{\begin{matrix}\text{Cationic radius}\\ \text{Anionic radius}\end{matrix}\right\}$

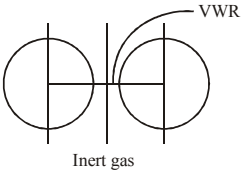
(a) Covalent radii : Half of the internuclear distance.
when two homo atom bonded together with single bond.



(b) Metallic radii : Also called as crystal radii. Half of the inter nuclear distance when two adjacent atom (metal) bonded together with metallic bond.



(c) Vanderwall radii : Half of the internuclear distance between two non-bonded atom of a inert gas Vanderwall radii is almost double of a covalent radii



$$VWR = 2 \times C.R.$$

(d) Ionic radii:

(a) Cationic radii : Cation is always smaller than its parent atom due to.

(i) Either outermost shell is remove.

(ii) Increased Zeff to remaining electron.

$$Mn^{+7} < Mn^{+4} < Mn^{+2} < Mn$$

(b) Anionic radii : Anion is always more then its parent atom due to increases in σ & decrement in Zeff.

Isoelectronic sepecies:

Anion > neutral > Cation

$O^{-2} > F^{-}, Ne > Na^{+} > Mg^{+2}$

Variation

(a) Along the period : Radius decreases.

(b) Down the group : Radius Increases.

Imp. In each period max. measured Atomic radii- Inert gas

In each period Max. Masured covalent radii - Alkali metal

In d-block along the period, Initially atomic size decreases at constant & then increases due to increment in σ.

Except: $B < Al \simeq Ga < In \geq Tl$

Due to transition Contraction

Due to lanthanide Contraction

Size of 4d = Size of 5d due to lanthanide contraction.

Factor Affecting atomic size

(i) $\text{Number of shells} \propto \dfrac{1}{\text{atomic size}}$

(ii) $\text{Zeff} \propto \dfrac{1}{\text{atomic size}}$

(iii) $\text{Bond order} \propto \dfrac{1}{\text{atomic radii}}$

(iv) Magnitude of +ve charge $\propto \frac{1}{\text{atomic size}}$

(v) Magnitude of –ve charge $\propto$ atomic size.

IONISATION POTENTIAL

Sufficient amount of energy required to remove most loosely bonded outermost shell electron from an isolated gaseous atom.

$M_{(g)} + E \longrightarrow M^+ + e^-$

Property of metal.

Tendency to form cation.

Always an endothermic process.

Successive I.P.

$IP_3 > IP_2 > IP_1$, Due to increment in Zeff.

Factors affecting I.P.

(i) I.P. $\propto$ Zeff.

(ii) I.P. $\propto \frac{1}{\text{atomic size}}$

(iii) I.P. $\propto$ Magnitude of +ive charge

(iv) I.P. $\propto \frac{1}{\text{Magnitude of –ive charge}}$

(v) Stability of Half filled & fully filled orbital $\rightarrow$ half filled to p^3, d^5, f^7 or fully filled s^2, p^6, d^{10}, f^{14} are more stable i.e. why more amount of energy is required to remove electron so I.P. is more.

For ex. I.P. of 'N' > I.P. of 'O'

Inert gas has maximum I.P. in respective period.

(vi) Pentration power : s > p > d > f

IP of Mg > IP of Al

IP of Be > IP of B

Periodicity :-

(i) Along the period I.P. generally increases.

Except : IIA > IIIA, VA > VIA

(ii) Along the group I.P. Generally decreases.

Except : last two element due to Lanthanoid contraction.

Application of I.P. :

(i) Metallic character $\propto \frac{1}{\text{I.P.}}$

(ii) Reactivity of metal $\propto \frac{1}{\text{I.P.}}$

(iii) Basic character $\propto \frac{1}{\text{I.P.}}$

(iv) Number of valence electron : Number of valence electron can be predicted by counting lower value of successive I.P.

Number of valence electron = Number of lower I.P. value.

(v) Stability of oxidation state:

(a) If $\Delta IP \leq 11eV$ then higher oxidation state is stable.

(b) If $\Delta IP \geq 16$ eV then lower oxidation state is stable.

Electron Affinity/(Electron gain enthalpy) (Δ eg. H)

Amount of energy released or absorb when an electron is added to neutral gaseous atom.

$$X_{(g)} + e^- \longrightarrow X_{(g)}^-$$

EA_1 = exothermic generally (+Ve E.A,)

EA_2 = endothermic

$$\boxed{\begin{array}{l}+\text{ve E.A.} = -\Delta \text{egH} \\ -\text{ve E.A.} = +\Delta \text{egH}\end{array}}$$

Inert gas has +ve value of Δeg H. Due to stable configuration.

Formation of polynegative ion is always an endothermic.

Factors :

(i) Size $\propto \frac{1}{\text{E.A.}}$

(ii) Zeff $\propto$ E.A.

(iii) Stable configuration : Be, N & inert gas have a very low value of EA

due to stable configuration.

Max. $\xleftarrow{IP}$ stable configuration $\xrightarrow{EA}$ min

$\downarrow$ EN

Unaffected

Variation :-

(a) –Along the period size $\downarrow$ EA $\uparrow$

– Along the period $\Delta_{eg}H$ becomes more –ve.

– In each period halogen has a maximum E.A. due to more Zeff.

(b) Down the group size $\uparrow$EA$\downarrow$

Exception :

EA of 2nd period < EA of 3rd period.

Imp. : Max. E.A. $\rightarrow$ Cl

$$X_{(g)} + e^- \underset{IP}{\overset{EA}{\rightleftharpoons}} X^-_{(g)} + E$$

$$\boxed{EA \text{ of } X = IP \text{ of } X^-}$$

ELECTRONEGATIVITY

Tendency of a bonded atom to attract shared pair of electron towards itself.

Unit less property.

No energy released or absorbed.

Factor :

(i) EN $\propto$ Zeff (ii) EN $\propto \dfrac{1}{\text{Atomic size}}$

(iii) % s-character $\propto$ EN

$sp > sp^2 > sp^3$

Periodicity :

Along the period Zeff $\uparrow$ EN $\uparrow$

Down the group atomic size $\uparrow$ EN $\downarrow$

Max. EN –F

Min. EN –Cs

Inert gas has zero value of EN

Exception : EN scale Zn < Cd < Hg

According to Mulliken scale:-

$$\boxed{X_m = \frac{IP + EA}{2}} \qquad \boxed{2X_m = -IP - EA = 0}$$

Relation between X_m & X_p :-

$$\boxed{X_p = \frac{X_m}{2.8}}$$

Application of Electronegativity

(i) Nature of element

$EN \propto$ Non metallic element $\qquad EN \propto \frac{1}{\text{Metallic element}}$

(ii) Bond length $\propto \frac{1}{\Delta EN}$

$$\boxed{d_{A-B} = r_A + r_B - 0.09(\Delta EN)}$$

Schoemaker & Stevenson law

(iii) Bond strength $\propto \Delta EN$

(iv) Bond energy $\propto \Delta EN$

(v) Acidic character of Hydride $\propto \frac{1}{\Delta EN}$

Basic character of hydride $\propto \Delta EN$

(vi) Nature of Oxide

Basic nature $\propto \Delta EN$

Acidic Nature $\propto \frac{1}{\Delta EN}$

(vii) % ionic character $\propto \Delta EN$

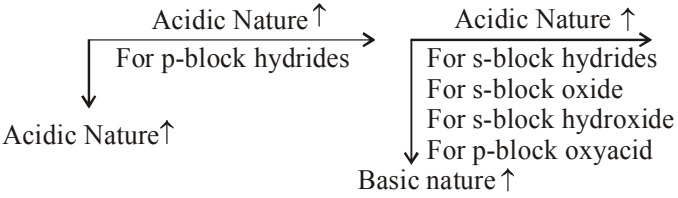
% I.C. $= 16(\Delta EN) + 3.5(\Delta EN)^2$

(viii) Acidic strength of oxy acid $\propto$ EN of central atom.

(ix) Lewis base strength $\propto \frac{1}{EN}$

(x) Bond polarity $\propto \Delta EN$

In short :



16 Chemical Bonding

Introduction :

Force of attraction exist between various atom to hold them in a molecule.

Reason for chemical bonding : To attain the maximum stability (inert gas configuration)

Condition for chemical bonding :

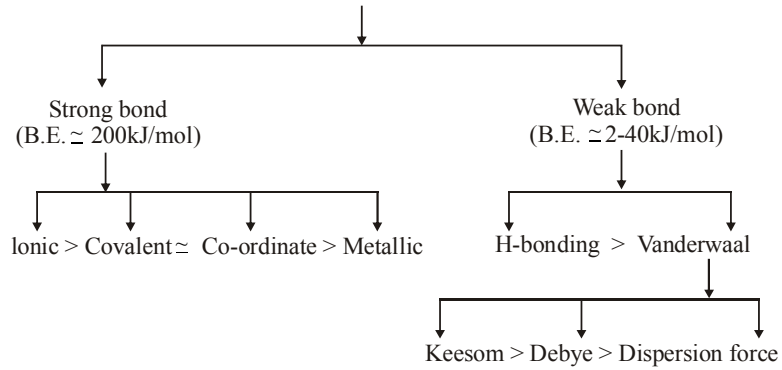
(a) Force attraction > force of repulsion

(b) Potential energy should be minimum

Lewis octet rule : Every atom try to attain $8e^-$ or nearest inert gas configuration by donating, by gaining or by sharing the electron.

Exception of lewis law :

1. **Electron deficient molecule : Compound in which central atom has less then $8e^-$ in its valence shall.**
   For example BeI_2, BH_3, $AlCl_3$, BF_3, BCl_3, BBr_3, BeF_2, $BeCl_2$, etc.
2. **Electron rich compound :** compound in which central atom has more then $8e^-$ in the outermost shall.
   For example IF_7, SF_6, PCI_5, XeF_6 etc.
3. **Odd electron molecule:** The compound in which central atom has odd number of electron in their valence shall. e.g. NO, ClO_2, NO_2.
4. **H, Li, never obeyed octet law.**



Ionic bond :

(a) Bond between cation & anion.

(b) Bond between metal & non-metal.

Except : LiCl, $MgCl_2$, $AICI_3$, BeO etc.

(c) Δ EN > 1.7

Condition for ionic bond formation :

(a) Size of metal should be large

I.P. should be low.

(b) Size of non-metal should be small.

E.A. should be more.

(c) Lattice energy should be high.

Energy involved in ionic bond formation (Born haber cycle)

ΔH = (S.E.+I.E. + D/2) – (EA +U)

= (Total energy absorbed) – (Total energy released)

For bond formation ΔH =– ive (exothermic process)

Properties of ionic compound:

1. **Physical state**: Due to strong electrostatic force of attraction between cation & anion these compounds are hard, crystalline & brittle.
2. **Isomorphism:** Two compounds are said to isomorphs if they have similar number of electron i.e. similar configuration of cation & anion.

e.g. [NaF, MgO] [$Cacl_2$, K_2S]

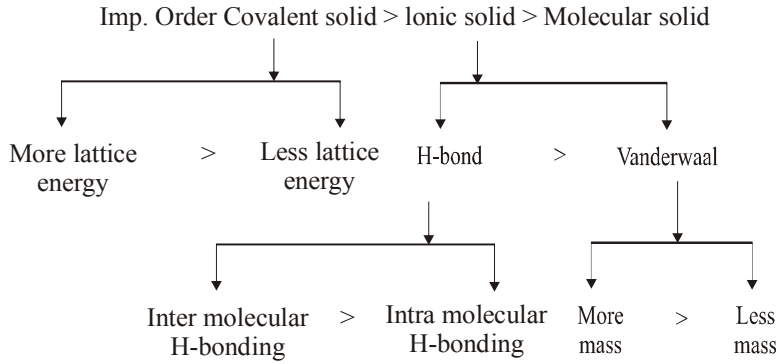
Melting point & boiling point: High M.P. & B.P. due to presence of strong electrostatic force between ions.

Covalent solid like SiO_2, B_4C, have more m.p. due to 3-D giant network.

lonic solid like NaCl, Al_2O_3, have more m. p. due to high lattice energy.

Molecular solid like CO_2 have least m.p.t. due to presence of weak vanderwaal force.

M.P. & B. P.



If molecular mass of two covalent compound are same then ΔEN will be consider.

Imp. order $LiH > NaH > KH > CsH$

$MgO > CaO > BaO$

$LiCl < NaCl > KCl > RbCl > CsCl$

$LiF > NaF > KF > RBF > CsF$

$Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$

Among metal halide, fluoride has maximum m.p.

$LiF > LiCl > LiBr > LiI$

$NaF > NaCl > NaI$

Solubility : Ionic compounds are souble in polar solvent like water.

Factor affecting solubility:

(i) Dielectric constant α solubility

(ii) Lattice energy $\alpha \frac{1}{\text{solubility}}$

(iii) Hydration energy α solubility

For any compound to be soluble in water

$$\boxed{\text{Hydration energy} > \text{Lattice energy}}$$

Imp. order:

No compound is 100% ionic. Every compound contain some covalent charactor due to polarization

Due to strong electrostatic force of attraction between cation & anion electron density of anion becomes more in between two ions & covalent character is developed.

$$\boxed{\text{Covalent character} \propto \text{Polarization} \propto \text{Zeff of cation}}$$

Polarization power (lonic potential) : capacity of cation to polarize anion represented by (ϕ)

$$\boxed{\phi = \frac{\text{Charge on cation}}{\text{Size of cation}}}$$

Polarisability : Tendency of an anion to get polarized by cation.

Factor affecting polarization (fajan's rule)

(i) Charge on cation/anion α polarization α covalent character

(ii) Size of cation $\propto \frac{1}{\text{Polarization}} \propto \frac{1}{\text{Covalent Character}}$

(iii) Size of anion α polarization α covalent character

(iv) Pseudo inert gas configuration : Cation having pseudo inert gas configuration

(i.e. 18 electron in outermost shall have more polarization power due to high Zeff.

CuCl > NaCl (Covalent Character)

[due to poor shielding effect of d e^- in Cu^{+1}]

Some important facts :

(i) Sulphides are less soluble in water than oxides of metal.

(ii) Li salt are soluble in organic solvents.

Polarization increases Covalent character increases

M.P. decreases $\rightarrow$

NaF > NaCl > NaBr > NaI

$NaCl > MgCl_2 > AlCl_3$

$BaCl_2 > SrCl_2\ CaCl_2\ MgCl_2 > BeCl_2$

Covalent bond : Bond between two highly electronegative element

Mutual sharing of electron takes place.

Orbital concept of covalent bond :

An orbital can accomodate at the most 2 electrone with opposite spin.

Only those orbital will participate in bond formation which have unpaired electron.

Empty orbital accepts two electrons to complete the orbital.

Pairing of electron elements due to presence of vacant d-orbital can expand their octet in the presence of highly eletronegative element like F, Cl, O, N etc.

PCl_5, SF_6, IF_7, is possible but NCl_5, OF_6, are not possible.

PF_5, PCl_5, are possible but PH_5, is not.

An element which have even valency will always show even valency in excited state.

PCl_4, SF_3, SF_5 are not possible but PCl_3, PCl_5, SF_2, SF_4 & SF_6 are possible.

$\Rightarrow$ Short coming : Couldnot provide in formation regarding shape of molecule & strength of bonds.

Wave Mechanical model

Two Model :

(i) Valence bond theory (VBT)

(ii) Molecular orbital theory (MOT)

(1) Valence bond theory:

Given by Heitler & London Extended by pauling & Slater.

Strength of bond α Extent of overlapping.

Extent of overlapping depends on two factor.

(i) Nature of orbital:

(a) directional orbital : p, d & f (more extent of overlapping)

(b) non- directional orbital : s (less extent of overlapping)

order of overlapping $\boxed{p - p > s - p > s - s}$

Exception $\boxed{1s - 1s > 2p - 2p}$

Nature of overlapping :

(a) Co-axial overlapping (Along the internuclear axis)

(b) Perpendicular to internuclear axis

Extent of overlapping is maximum, σ–bond is formed.

π-bond is formed after σ–bond.

For maximum bond strength :-

(i) Lower value of principal quantum number.

(ii) σ is stronger than π (when value of n is same)

(iii) Directional nature (when type of overlapping is same)

Limitation :

(i) Does not difine the shape of the molecule.

Hybridisation (Pauling & Slater)

Imaginary concept

Mixing of different shape and approximate equal energy atomic orbital to give new orbital of same shape.

Hybrid orbital always forms σ–bond. (Except - Benzyne)

In hybridization all type of orbitals participated.

(Vacant, Half-filled or Fully filled)

Number of hybrid orbital forms will be equal to the number of atomic orbitals taking part in hybridization.

Valence shell electron pair repulsion theory (VSEPRT):

Given by Gillespie & Nyholm

Defines the shape of molecule

Case-I Molecules in which central atom does not have any lone pair are called symmetric structure & their shape will be according to their hybridization.

Case-II Molecules in which central atom has lone pair are known as asymmetric structure, In this case lone pair should be kept at that position where lone pair exerts minimum repulsive force.

Order of requlsion : L.P. – L.P . > L.P. – B.P. > BP. – B.P.

TYPES OF HYBRIDIZATION & POSSIBLE STRUCTURE

Type of Hybridization	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridization	2	-	Linear	BeF_2, CO_2 CS_2, $BeCl_2$
2. (a) sp^2-hybridization	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridization	2	1	V-shape Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridization	4	0	Tetrahedral	CH_3, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-2} SO_4^{-2} $AlCl_4^-$
(b) sp^3-hybridization	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3^+O, PCl_3, XeO_3, $N(CH_3)_3$, CH_3^-
(c) sp^3-hybridization	2	2	V-shape, Angular	H_2O, H_2S, NH_2^-, OF_2, Cl_2O, SF_2, I_3^+
4. (a) sp^3d-hybridization	5	-	Trigonal bipyramidal	PCl_5, SOF_4, AsF_4^-,
(b) sp^3d-hybridization	4	1	See Saw,	SbF_4^-, XeO_2F_2
			folded square distorted tetrahedral	SbF_4^- , XeO_2F_2
(c) sp^3d-hybridization	3	2	almost T-shape	ClF_3, ICl_3
(c) sp^3d-hybridization	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, ClF_2^- , XeF_2
5. (a) sp^3d^2-hybridization	6	-	Square bipyramidal/ octahedral	PCl_6^- , SF_6
(b) sp^3d^2-hybridization	5	1	Square pyramidal/ distorted octahedral	$XeOF_4$, ClF_5, SF_5^- XeF_5^+
(c) sp^3d^2-hybridization	4	2	Square planar	XeF_4
6. (a) sp^3d^3-hybridization	7	-	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridization	6	1	Pentagonal pyramidal/ distorted octahedral	XeF_6
(c) sp^3d^3-hybridization	5	2	Pentagonal planar	XeF_5

Co-ordinate bond

This type of bond is formed by one side sharing of pair of electron between atoms. Electron pair of one atom is shared between two atom.

Atom which provide lone pair for sharing is called donor.

Atom which accepts electron pair is called acceptor.

Shown by '$\rightarrow$' & direction is from donor to acceptor.

Necessary condition :

Acceptor should have vacant orbital.

Donor should have complete octet.

Example :

(i) Protonation : $H_2O \rightarrow H_3O^+$, $NH_3 \rightarrow NH_4^+$, $N_2H_4 \rightarrow N_2H_5^+$

(ii) Polymerization : $AlCl_3 \rightarrow Al_2Cl_6$, $BeCl_2 \rightarrow (BeCl_2)_n$

During the formation of coordinate bond, structure & shape of the molecule changed.

Dipole moment (μ)

Measure the polarity in molecule (μ) = q × d

Unit debye = esu - cm

1 Debye = 10^{-10} esu-cm.

Homonuclear diatomic H_2, N_2, O_2, F_2, ($\mu = 0$) $\rightarrow$ non- polar

Heteronuclear diatomic ($\mu \alpha \Delta EN$) HF > HCl > HBr > HI

Polyatomic molecule resultant dipole moment is a vector addition of dipole moment of various bond.

$$\overleftarrow{O} = C = \overrightarrow{O} \quad \mu = 0 \quad \text{non} - \text{polar}$$

Imp. order

(a) $NH_3 > Nl_3 > NBr_3 > NCl_3 > NF_3$ **(b)** $NH_3 > SbH_3 > AsH_3 > PH_3$,

(c) $HF > HCl > HBr > Hl$ **(d)** $H_2O > H_2S$,

(e) $CH_3Cl > CH_3F > CH_3Br > CH_3l$ **(f)** $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4 = CH_4$

Application :

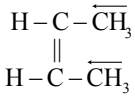
(i) Predict shape & polarity of molecule

If central atom contain lone pair than $\mu \neq 0$, moelcule will be polar & unsymmetrical shape.

If central atom surrounded with all identical atom then $\mu \neq 0$, molecule non-polar.

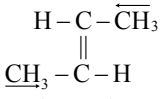
(ii) Distinguish between cis & trans form

$\mu_{cis} > \mu_{trans}$



Additive

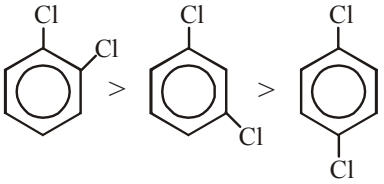
$\mu \neq 0$



Substractive

$\mu = 0$

(iii) To find out dipole moment of a substituent of benzene ring.



$$\mu \propto \frac{1}{\text{bond angle}}$$

H-bonding

Given by Latimer & Rodebush.
Electrostatic force of attraction between H & highly electronegative atom.
This is intermolecular force. i.e. why exist only in covalent molecule.
Also known as dipole-dipole attraction.

Necessary conditions :

(i) Hydrogen should be covalently bonded with highly electronegative element.
(ii) Highly electronegative element should have EN ≥ 3.
(iii) Hydrogen bonding is possible only in those moelcule in which H is directly attached with F, O, N,

Strength of H – bond $\propto$ EN of highly electronegative element

Type of hydrogen bonding

- Intermolecular → When H-bonding takes place in between molecule
- Intramolecular → When H-bonding takes place with in a molecule

Strength of intermolecular H-bond > Intramolecular H-bond.

Imp. Intramolecular H-bonding taking place only in ortho-derivative of aromatic compound.

Application :

(i) **Physical state :** H_2O is liquid H_2S gas.
HF is liquid HCl gas.

(ii) **M.P. & B.P.** : Due to presence of H-bonding M.P. & B.P. increases M.P. of alcohol > M.P. of thiol

(iii) Volatility : M.P. & B.P. $\uparrow$ volatility $\downarrow$

(iv) Viscosity & Surface tention :

$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} > \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} > CH_3-OH$$

(v) **Solubility in H_2O :** Any organic compound which get dissolve in H_2O is due to H-bonding.
Extent of solubility $\propto$ H-bonding

(vi) **Association of molecule :**

KHF_2 is possible but not $KHCl_2$. $[K^+ + [F^- \ldots\ldots\ldots\ldots H-F]$
(H.Bond)

MOLECULAR ORBITAL THEORY

Imaginary concept
Given to explain

(i) Paramagnetic nature of O_2 molecule.

(ii) Existence of species like $H_2^+ . H_2^-$ & species having fractional bond order.

Main point of M.O.T.

(a) Atomic orbital represented by ψ (wave function) participate to form moelcular orbital.

(b) Z-axis is considered as main axis so p_z combination form σ moelcular orbital.

(c) The number of orbital participating in combination must have almost same energy & same symmetry. Will produce same number of orbital.

(d) Two type of molecular orbital formed.
(i) Bonding molecular (ii) Anti-bonding molecular

(e) Number of atomic orbital participating

$$= \frac{1}{2} \text{ number of B.M.O.} + \frac{1}{2} \text{ number of ABMO.}$$

(f) BMO is formed by addition of two wave function ($\psi_A + \psi_B$) when they are in same phase, represented by σ, π

(g) ABMO is formed by subtraction of two wave function ($\psi_A - \psi_B$) when they are in opposite phase, represented by σ^*, π^*.

Energy of ABMO > Energy of A.O. > energy of BMO

Imp. sequence order

for B_2, C_2, N_2 (Number of e^-'s ≤ 14) = σ_{1s}, σ^*_{1s}, σ_{2s}, σ^*_{2s}

B.O. of $C_2 = \dfrac{8-4}{2} = 2$ $\quad (\pi_{2px} = \pi_{2py})$, σ_{2pz}

(It contains two π bonds with out d bond $\quad (\pi^*_{2px} = \pi^*_{2py})$, σ^*_{2pz}

$\because$ last four e^- enters in π B.M.O.)

for O_2, F_2, Ne_2 (Number of e^-'s > 14) = σ_{1s}, σ^*_{1s}, σ_{2s}, σ^*_{2s}, σ_{2pz} $(\pi_{2px} = \pi_{2py})$ $\left(\pi^*_{2px} = \pi^*_{2py}\right)$, σ^*_{2pz}

Significance of M.O.T. :

(a) Concept of bond order :

$$\text{Bond order} = \frac{1}{2}\,[N_b - N_a]$$

N_a = number of antibonding e^-'s

N_b = number of bonding e^-'s

If $N_b > N_a$ B.O. = +ve molecule exist

$N_b < N_a$ B.O. = –ve moelcule does not exist

$N_b = N_a$ Does not exist

(b) Stability $\propto$ B.O. α bond dissociation energy

(c) $\text{B.O.} \propto \dfrac{1}{\text{Bond length}}$

Iso electronic species have same bond order & have same magnetic property.

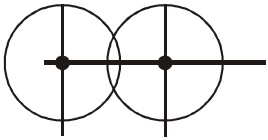
If species have fractional bond order it will always be paramagnetic.

If in two species bond order is same the stability, will be decided by counting number of antibonding e^-'s. If number of antibonding is more, than number of bonding e^-'s then molecule will be unstable.

Bonding parameters

Imp. points :

1. **Bond length :** Internuclear distance between two atom when they are bonded together.



Factor affecting bond length

(i) ΔEN value

$$d_{A-B} = r_A + r_B - 0.09\,(\Delta EN)$$

$\Delta EN \uparrow$ B.L. $\downarrow$

H–F < H–Cl < H–Br < H–I

(ii) Atomic size

$$\boxed{\text{B.L.} \propto \text{Atomic size}}$$

(iii) Bond order : $\text{B.O.} \propto \dfrac{1}{\text{B.L.}}$

$$\boxed{C-C > C=C > C\equiv C}$$

(iv) Hybridisation : B.L.

$$sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$$

25% 33.33% 50%

$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ $-\overset{|}{C}=\overset{|}{C}-$ $-C\equiv C-$

2. **Bond angle :** The angle between any two adjacent bond is known as bond angle.

Factor affecting bond angle

(a) Hybridization : On increasing % s-character bond angle also increases.

$-\overset{|}{\underset{|}{C}}-C$	$>C=C<$	$-C\equiv C-$
sp^3	sp^2	sp
25%	33.33%	50%
Bond angle 109.5°	120°	180°

Case-I When hybridization is same, bonded atom are same but central atom & lone pair are different.

$$\text{B.A.} \propto \frac{1}{\text{Number of L.P.}}$$

Example :

CH_4	$\ddot{N}H_3$	$H_2\ddot{O}:$
↓	↓	↓
sp^3	sp^3	sp^3
|	|	|
109.5º	107º	104.5º
No L.P.	1 L.P.	2 L.P.

Case-II When hybridization is same, number of lone pair is same central atom is different & side atom are same then

$$\boxed{\text{Bond angle} \propto \text{EN of central atom}}$$

$\ddot{N}H_3 > \ddot{P}H_3 > \ddot{A}sH_3 > \ddot{S}bH_3$

Examle : Bond angle 107º 93º 91º

$\xrightarrow[\text{Bond angle decrease}]{\text{EN of central atom decrease}}$

$H_2\ddot{O}: > H_2\ddot{S}: > H_2\ddot{S}e: > H_2\ddot{T}e:$ (Bond angle decreases)

Case - III When hybridization is same , number of lone pair are same and central atom are same, but side atoms are different.

$$\boxed{\text{B.A} \propto \frac{1}{\text{EN of side atom}}}$$

$OF_2 < OCl_2 < OBr_2 < OI_2$ $\quad NF_3 < NCl_3 < NBr_3 < NI_3$

Note : Symmetrical mol. having no. l.p. and same hyb. B.A. are same.

e.g (i) $BF_3 = BCl_3 = BBr_3 = BI_3$

(ii) $SO_4^{2-} = PO_4^{3-} = ClO_4^-$

Imp. point :

In ethers oxygen has sp3 hybridization having two L.P. but still bond angle is 110º because of large size of alkyl group.

$$R—\ddot{O}—R$$

17 S - Block Elements

1. Order of metallic or Ionic radii:

   Cs > Rb > K > Ba > Sr > Ca > Na > Mg > Li > Be

2. Order of density:

   Ist A Cs > Rb > [Na > K] > Li

   IInd A Ba > Sr > [Be] > [Mg > Ca]

3. Order of MP & BP:

   Ist A Li > Na > K > Rb > Cs

   IInd A Be > Ca > Sr > Ba > Mg

4. Order of hydration in cation:

   IA $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

   IIA $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$

5. Order of Conductivity of cations in polar solvent

   IA $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

   IIA $Be^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2} > Ba^{+2}$

6. Order of conductivity in non-polar solvent

   IA $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

   IIA $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$

7. Colour of s-block metal in flame test

   Li (Crimson red) Na (Golden yellow) K (Pale violet) Rb (Reddish Violet) Cs (Sky Blue)

   Be Mg
   [X X]
   Due to high IP

   Ca (Brick red) Sr (Crimson red) *Ba* (Apple green)

Chemical property of alkali of metal & Alkaline earth metal :

1. Reaction with air (N_2 & O_2)

   All Forms their normal oxide & nitrides.

   Exception : Nitride of Na, K, Rb, Cs is not possible.

2. Reaction with O_2 & Excess of air

Li - Normal oxide	Be - Normal oxide
Na - peroxide	Mg - Normal oxide
K - Super oxide	Ca - peroxide
Rb - Super oxide	Sr - Peroxide
Cs - Super oxide	Ba - peroxide

3. Reaction with H_2O : All form their hydroxide & H_2 gas

Order of Basic strength

$Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O$

$BaO > SrO > CaO > MgO > BeO$

$CsOH > RbOH > KOH > NaOH > LiOH$

$Ba(OH)_2 > Sr(OH_2) > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$

Exception :

Be does not react with H_2O:

Order of reactivity with H_2O in IA and IIA group

$Cs > Rb > K > Na > Li$

$Ba > Sr > Ca > Mg > Be$

4. CO_3^{-2} & S_4^{-2} salt of Na, K, Rb and Cs only are not decomposed on heating due to large size and weak polarising power.

5. In Butyrate salts

$$2Na/K/Rb/CsNO_3 \xrightarrow[800^oC>]{\Delta} Na/K/Rb/CsNO_2 + \frac{1}{2} O_2$$

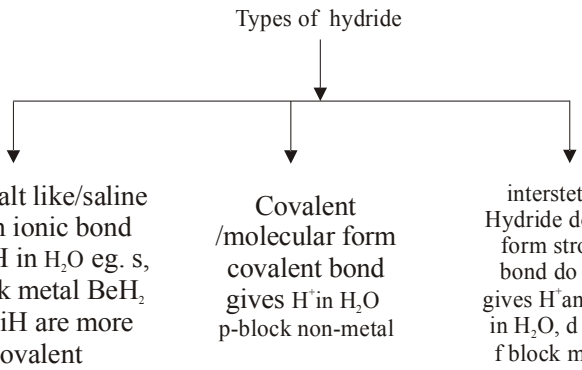
$$2Na/K/Rb/CsNO3 \xrightarrow[800^o \text{ or } 800^o C>]{\Delta} Na/K/Rb/Cs_2O + N_2 + \frac{5}{2} O_2$$

In other

$$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2} O_2$$

and IlA nitrate $Ba(N0_3)_2 \longrightarrow BaO + 2NO_2 + O_2$

6. Types of hydride



7. The higher oxides, peroxides and superoxides are strong oxidising agents. They react with water and dilute acids forming H_20_2 and O_2.
8. Sodium is obtained on large scale by Down's process.
9. The alkali Metals dissolve in liquid ammonia without evolution of hydrogen.
10. The colour of dilute solutions is blue. On heating colour charges to bronze. The colour is due to ammoniated electron.

$$M + (x+y)\,NH_3 \longrightarrow [M(NH_3)_x]^{2-} + 2[2(NH_3)^4]$$

11. These solutions are good conductors of electricity and have strong reducing properties. The solutions are paramagnetic in nature.
When dry ammonia is passed over hot metal, amides are formed.
12. Alkali metals have a very little tendency to form complexes. Lithium being small in size form certain complexes but this tendency decreases as the size increases.
13. Lithium shown abnormal properties due to its small size (atom and ion). Lithium ion on account of its small size exerts polarising effect on negative ions. consequently, covalent character is developed in Li-salts. Li has highest ionisation energy and electronegativity as compared to other alkali metals.

(i) LiCl is more covalent than NaCI. LiCl is soluble in alcohol, pyridine, etc. Its Melting points is lower than that of NaCl.

(ii) LiOH, Li_2CO_3, $LiNO_3$ behave differently than other alkali corresponding salts towards heating.

$2LiOH \longrightarrow Li_2O + H_2O$; $Li_2CO_3 \longrightarrow Li_2O + CO_2$;

$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$

Hydroxides and carbonates of other alkali metals are stable. The nitrates of

other metals decompose giving only oxygen.

(iii) Lithium directly combines with nitrogen.

$$6Li + N_2 \longrightarrow 2Li_3N$$

(iv) $LiHCO_3$ is known only in solution but not is solid state.

(v) Li_2SO_4 does not form double salt.

(vi) LiF, Li_3PO_4, $Li_2C_2O_4$, Li_2CO_3 are sparingly soluble in water.

(vii) LiOH is weaker base in comparison to NaOH or KOH.

(viii) Although Li has the Highest ionisation potential, yet it is strongest reducing agent because of its heat of hydration.

11. Table salt becomes wet in rainy season due to presence of impurities of $MgCl_2$ and $Cacl_2$.

12. Sodium carbonate (washing soda) Na_2CO_3. $10H_2O$. is generally prepared by a process called ammonia-soda process or Slavay process.

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

Solvay process cannot be employed for the manufacture of K_2CO_3 because $KHCO_3$ is fairly soluble in water.

13. Sodium hydroxide (caustic soda) is manufactured on a very large scale by the following processes:

Electrolytic Process: The electrolysis of sodium chloride is carried out in an electrolytic cell. The following electrolytic cells are used:

(a) **Nelson Cell :**

(b) **Castner- Kellner Cell:**

14. Sodium peroxide (oxone) Na_2O_2, is formed by heating sodium at about 350^o C in excess of air free from moisture. It is a pale yellow powder. It is used as an oxidising agent, for purification of air, for production of oxygen and for the preparation of H_2O_2 and benzoyl peroxide.

15. Except Be, alkaline earth metals are easily tarnished in air as a layer of oxide is formed on their surface. The effect increases and barium in powdered form bursts into flame on exposure to air.

16. Like alkali metals, alkaline earth metals react with acids and displace hydrogen. However, Be dissolves in caustic/Alkalies with liberation of H_2.

17. $Be(OH)_2$ is amphoteric but rest are basic so is not alkaline earth metal.

18. Alkaline earth metals directly combine with halogens, when heated with them. Be-Halides are covalent. This is due to small size and high charge of Be^{2+} ion i.e., it has high polarising power. Halides of Be are known to have chains of ------X_2BeX_2Be--------.
The halides of rest of the members are ionic.
The halides are hygroscopic and readily from hydrates.

19. Alkaline earth metals burn in nitrogen and form nitrides of the type, M_3N_2. Be_3N_2 is volatile while rest are non-volatile being ionic crystalline solids. these are hydrolysed with water liberating NH_3.

20. With the exception of Be, other combine with carbon in an electric furnace to form carbides of the type, MC_2.
These are called acetylides as on hydrolysis evolve, C_2H_2. Mg also forms Mg_2C_3 by heating, Mg_2C_3 on hydrolysis froms propyne.
Beryllium oxide when heated with carbon forms Be_2C. This on hydrolysis gives methane.

21. Like alkali metals, alkaline earth metals also dissolve in liquid ammonia to form coloured solutions, dilute solutions are bright blue due to solvated ions.

22. Quick lime (CaO) is obtained when limestone is heated at about 1000°C. On adding water, quick lime gives a hissing sound and forms calcium hydroxide, known as slaked lime. The paste of lime in water is called milk of lime while the filtered and clear solution is known as lime water, Chemically both are $Ca(OH)_2$.

23. Quick lime is used for making caustic soda, bleaching powder, calcium carbide, mortar, cement, glass, dye stuffs and purification of sugar.
Mortar: It is building material. It consists slaked lime and silica in the ratio of 1: 3. The mixture made a paste with water. It is called mortar.

24. Gypsum ($CaSO_4$. $2H_2O$) found in nature, when heated, it first changes from monoclinic form to other rhombic form without loss of water. At 120°C, it loses three- fourth of its water of crystallisation and froms hemihydrate ($CaSO_4$. $\frac{1}{2}H_2O$) Known as plaster of Paris. It becomes anhydrous at 200°C is known as dead burnt plaster and on strong heating it decomposes to give either calcium oxide and SO_3 or mixture of SO_2 and O_2.

25. Plaster of Paris has the property of setting to a hard mass $CaSO_4.2H_2O$, slight expansion occurs during setting addition of alum to plaster of Paris makes the setting very hard. The mixture is known as Keene's cement.
Plaster of Paris is used for setting broken or disslocated bones, castes for statues. toys and in dentistry.
When plaster of Paris is heated as 200°C, it forms anhydrous calcium sulphate which is known as dead plaster. it has no setting property.

26. (a) Hydroxyapatite, $Ca_5(PO_4)_3$ OH is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resident enamel-fluorapatite.
$Ca_5(PO_4)_3$. F.
(b) Mg^{2+} and Ca^{2+} ions present in water are responsible for hardness of water.
(b) CaC_2 is obtained by heating a mixture of CaO and carbon. It reacts with nitrogen forming nitrolium, used as a fertilizer.

$$CaC_2 + N_2 \longrightarrow \underbrace{CaCN_2 + C}_{nitrolium}$$

27. Cement is an important building material. The average composition of portland cement is : CaO 61.5%, SiO_2 22.5%, Al_2O_3 7.5%.Cement is a dirty greyish heavy powder containing calcium silicates and aluminates. Cement consists of:
Tricalcium silicate $3CaO.SiO_2$
Dicalcium silicate $2CaO.SiO_2$
Tricalcium aluminate $3CaO.Al_2O_3$
Tetracalcium alumino - ferrite $4CaO.Al_2O_3.Fe_2O_3$
For manufacture, Limestone and clay are fused at 1400 - 1600°C in a rotary kiln. The product obtained is called clinker. It is mixed with 2–3% gypsum and powdered.
When cement is mixed with water, it sets to a hard mass, this is called setting. Setting is an exothermic process. During setting dehydration occurs.

28. Solutions of beryllium salts are acidic and dissolve appreciable quantities of $Be(OH)_2$.In alkali solution $[Be(OH)_4]^{2-}$ is formed.

$$[Be(H_2O)_4]^{2+} \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H^+$$
$$[Be(H_2O)_3(OH)]^+ \rightleftharpoons [Be(H_2O)_2(OH)_2] + H^+$$
$$[Be(H_2O)_2(OH)_2] \rightleftharpoons [Be(H_2O)(OH)_3]^- + H^+$$
$$[Be(H_2O)(OH)_3]^- \rightleftharpoons [Be(OH_4)^{2-}] + H^+$$

29. $BaSo_4$ is used in medicine as a contrast medium for stomach and intestinal X-rays.

18 p-Block Elements

GROUP 13 ELEMENTS

PHYSICAL PROPERTY

- Boron to indium show +3 oxidation state in their compounds while thallium also show +1 oxidation state (due to inert pair effect) in their compounds. Relative stability of M^+ and M^{3+} ions may be given as:

$$B^+ < Al^+ < Ga^+ < In^+ < Tl^+$$
$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$$

CHEMICAL PROPERTIES

- **Action of air:**

$$4M + 3O_2 \longrightarrow 2M_2O_3$$

Reaction occurs at high temperature. With Al, a protective oxide layer is formed which makes it passive. Tl also forms Tl_2O, Ga_2O_3, In_2O_3 also form.

- **Action of Water:**

$$2M + 3H_2O \longrightarrow M_2O_3 + 3H_2$$

Boron is not affected by water. It reacts with steam at red hot. Al decomposes cold water if it is not passive by oxide layer formation. Ga and In are not attacked by cold or hot water unless oxygen is present. Tl reacts with moist air to form TlOH.

- **Action of nitrogen :** $2M + N_2 \longrightarrow 2MN$
- **Action of halogen :** $2M + 3X_2 \longrightarrow 2MN_3$

All the group 13 elements form trihalide except Tl. Tl from TlX. TlI reacts with I_2 and form TlI_3 ($Tl^+I_3^-$)

- **Action of acids :** $2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2$

Boron is not affected by non-oxidizing acids like HCl and dilute H_2SO_4 while other elements dissolve to form trivalent salts.

$$3Mg + 2B \longrightarrow Mg_3B_2$$

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$

The rest of the elements do not combine with metals. This shows that boron is a non-metal and rest of the lements are metal.

Important compounds of group 13 elements

Boron is known to exist in two form (a) amorphous and (b) crystalline.

Amorphous boron is obtained by reduction of B_2O_3 with Na or K and Mg at high temperature in a covered crucible.

Crystalline form is obtained by the reduction of B_2O_3 with Al-powder.

Crystalline boron is black and chemically inert in nature. It is very hard. Amorphous boron is brown and chemically active. Boron is used as a deoxidiser in the casting of copper and for making boron steel which are used as control rods in nuclear reactors.

- **Hydrides**

Boron forms a number of stable covalent hydrides called diboranes with general formula B_nH_{n+4} (Called nido boranes) and B_nH_{n+6} (Called) arachno boranes, less stable).

Aluminium forms a polymeric hydride called alane /alumane with general formula $(AlH_3)_n$. Ga forms Ga_2H_6 and In forms $(InH_3)_n$. Tl does not form hydrides.

- **Oxides and hydroxides**

The members of boron family form oxides and hydroxides of the general formula M_2O_3 and $M(OH)_3$ respectively.

Oxides :	B_2O_3	> Al_2O_3	> Ga_2O_3	> In_2O_3	> Tl_2O_3
Hydroxides:	$B(OH)_3$	> $Al(OH)_3$	> $Ga(OH)_3$	> $In(OH)_3$	> $Tl(OH)_3$
Nature :	Acidic	Amphoteric	Amphoteric	Basic	Strongly Basic

- **Halides :**

BX_3 is electron deficient so behaves as a Lewis acid.

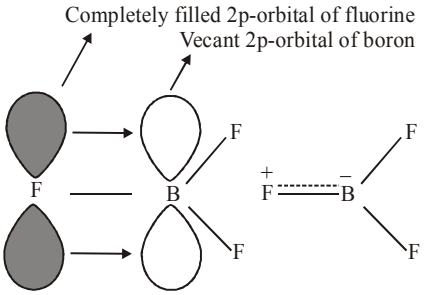
$$BX_3 \quad + \quad :NH_3 \longrightarrow [H_3N \longrightarrow BX_3]$$

Lewis acid Lewis base Adduct

Relative Lewis acid strength of boron halides are as follows:

$Bl_3 > BBr_3 > BCl_3 > BF_3$ (due to $p\pi - p\pi$ back bonding)

In BF_3, each F has completely filled unutillised 2p orbitals while B has a vacant 2p-orbital. Now since both of these orbitals belong to same energy level (2p) they can overlap offectively as a result of which electrons of B resulting in the formation of an additional $p\pi-p\pi$ bond. This type of bond formation of back as dative or back bonding. Formation of back bonding between B and F in BF_3 molecule as given below figure.



As a result of back donation of electrons from F to B, the electron dificiency of B is reduced and Lewis acid character is decreased. the tendency for the back bonding is maximum in BF_3 and decreases from BF_3 to Bl_3. Thus Bl_3, BBr_3 and BCl_3 are stronger Lewis acids then BF_3.

Anomalous behaviour of boron :

Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of d-orbitals.

IMPORTANT COMPOUNDS OF BORON

Boric acid (H_3BO_3)

- **Preparation :**

(a) From borax ($Na_2B_4O_4.10H_2O$):

Boric acid can be prepared by adding a hot concentrated solution of borax to a calculated quantity of conc. H_2SO_4. The solution on cooling gives crystals of boric acid, which can be separated by filtration.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3\downarrow$$

(boric acid)

(b) From colemanite ($Ca_2B_6O_{11}.5H_2O$):

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3\downarrow$$

- **Properties :**

(a) Action of heat:

$$\underset{\text{boric acid}}{H_3BO_3} \xrightarrow[-H_20]{100^oC} \underset{\text{meta boric acid}}{HBO_2} \xrightarrow[-H_2O]{160^oC} \underset{\text{tetra boric acid}}{H_2B_4O_7} \xrightarrow[-H_2O]{\text{redhot}} \underset{\text{boron trioxide}}{B_2O_3}$$

(b) Reaction with alcohol (test of boric acid):

$$H_3BO_3 + 3(C_2H_5OH) \rightarrow \underset{\text{Triethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

Borax $(Na_2B_4O_7.10H_2O)$ or $Na_2[B_4O_5(OH)_4].8H_2O$

- **Properties :**

(i) Its solution is basic in nature due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \rightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{weak acid}}{4H_3BO_3}$$

(ii) $$Na_2B_4O_7.10H_2O \xrightarrow[-10H_20]{\Delta} \underset{\substack{\text{anhydrous}\\\text{(Swell up)}}}{Na_2B_4O_7} \xrightarrow{740^oC} \underbrace{2NaBO_2 + B_2O_3}_{\text{(transparent beadglassy)}}$$

(iii) Borax bead test : Borax on strong heating forms B_2O_3 which forms coloured glassy bead with coloured compounds of certain metals. It is called borax bead test.

Colour of beads $\underset{\text{Green}}{Cr}$ $\underset{\text{Pink}}{Mn}$ $\underset{\text{Green}}{Fe}$ $\underset{\text{Blue}}{Co}$ $\underset{\text{Brown}}{Ni}$ $\underset{\text{Blue}}{Cu}$

eg. $\underset{\text{Blue bead}}{Cu(BO_2)_2}$

Dibrorane (B_2H_6)

- **Preparation :**

(i) $$3Mg + 2B \xrightarrow{\Delta} Mg_3B_2 \xrightarrow{H_3PO_4} \text{Mixture of boranes} \xrightarrow{\Delta} \underset{\text{diborane}}{B_2H_6}$$

(ii) $$B_2O_3 + 3H_2 + 2Al \xrightarrow[\text{pressure}]{150^oC} B_2H_6 + Al_2O_3$$

(iii) $$2BF_3 + 6NaH \xrightarrow{180^oC} B_2H_6 + 6NaF$$

- **Properties :**

(i) Reaction with ammonia:

$$B_2H_6.2NH_3 \xleftarrow[temperature]{low} \underset{(excess)}{B_2H_6 + NH_3} \xrightarrow[temperature]{high} \underset{\substack{Inorganic\ graphite\\or\ Borazone}}{(BN)_n}$$

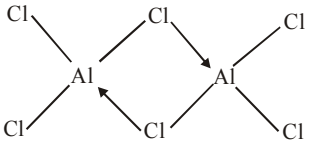
$$[BH_2(NH_3)_2]^+[BH_4]^- \text{ or } \underset{\text{Ratio 1:2}}{B_2H_6 + NH_3} \xrightarrow{high\ Temperarure} \underset{\text{(borazine)}}{B_3N_3H_6}$$

(ii) Reaction with amine :

$$\underset{\text{(Lewisacid)}}{B_2H_6} + 2\underset{\text{(Lewis base)}}{(Me_3N)} \rightarrow \underset{\text{adduct}}{[N(Me_3)_3} \rightarrow 2BH_3]$$

– Borazine is known as inorganic benzene.

Anhydrous $AlCl_3$ is prepared by passing dry HCl or Cl_2 gas over heated aluminium turnings in absence of air. It is also obtained by passing Cl_2 gas over heated mixture of Al_2O_3 and coke. It is used as a catalyst in Friedel - Craft's reaction. The molecule is an autocomplex and is represented at:



Anhydrous $AlCl_3$ is a Lewis acid. Anhydrous form is covalent while hydrated $AlCl_3.6H_2O$ is ionic.

ALUMS

Alums are the double sulphates of the type $M_2SO_4.M_2(SO_4)_3.24H_2O$ where M is a univalent cation like Na^+, K^+ and NH_4^+ and M' is a trivalent cation like Al^{3+}, Fe^{3+} and Cr^{3+}.

Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Sodium	$Na_2SO_4.Al_2(SO_4)_3.24H_2O$
Ferric alum	$(Na_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$
Ammonium alum	$(NH_4)Al(SO_4)_2.12H_2O$
Chrome alum	$K_2SO_4.Cr_2(SO_4)_3.24H_2O$

Ultramarine is an artifical Lapis-Lazuli, a rare mineral ($Na_3Al_3Si_3S_3O_{12}$) which has fine blue colour. It is used in making blue paint.

Precious stones such as sapphire, ruby, topaz etc., are Al_2O_3 containing oxides of transition metals.

(GROUP 14 ELEMENTS)

PHYSICAL PROPERTIES

Stability order

$$C^{+4} > Si^{+4} > Ge^{+4} > Sn^{+4} > Pb^{+4}$$

$$C^{+2} < Si^{2+} < Ge^{+2} < Sn^{2+} < Pb^{2+}$$

(due to inert pair effect)

I.P. order

$$C > Si > Ge > Sn < Pb$$

(due to lanthanoid contraction)

Catenation $C >> Si > Ge = Sn = Pb$

Except lead, all other elements of this group show allotropy.

Diamond, fullerene and graphite are allotropes of carbon.

CHEMICAL PROPERTIES

Action of air:

(i) **Monoxides :** $2M + O_2 \longrightarrow 2MO$

eg. $\xrightarrow[\text{unstable}]{\text{COSiOGeO SnO PbO}}$

(ii) **Dioxides :** $M + O_2 \longrightarrow MO_2$

Acidic Nature $\underbrace{CO_2 > SiO_2}_{\text{Acidic}} > \underbrace{GeO_2 \quad > \quad SnO_2}_{\text{Amphoteric}} > \underbrace{PbO_2}_{\text{Basic}}$

- **Action of water :**
  S, Ge and Pb are unaffected by H_2O.
  $Sn + 2H_2O$ (steam) $\longrightarrow SnO_2 + 2H_2O$

- **Action of acids :** Non-oxidising acids do not attack C and Si, Ge is not attacked by dilute HCl. When Ge is heated in a steam of HCl gas, germanium chloroform is formed.
  Sn dissolves slowely in dilute HCl but readily in concentrated HCl.
  Pb dissolves in conc. HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of $PbCl_2$.

- **Action of alkali :** C is unaffected by cold alkali, Si reacts slowly with cold aqueous NaOH and readily with hot NaOH forming silicate.
  Sn and Pb form stannate and plumbate respectively on reaction with hot alkali.

Important compounds of group 14 elements :

- **HYDRIDES :** MH_4 (General formula)

  CH_4 Methane — On moving top to bottom

  SiH_4 Silane $\rightarrow$ B.L. $\uparrow$

  GeH_4 Germane $\rightarrow$ T. Stability $\downarrow$

  SnH_4 stanane $\rightarrow$ Acidic nature $\uparrow$

  Pbh_4 Plambane $\rightarrow$ reducing Nature $\uparrow$

- **Halides :**
  All the element forms covalent halides, MX_4 (except $PbBr_4$ and PbI_4) the thermal stability of halide decreases as:
  $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$.

$MF_4 > MCl_4 > MBr_4 > MI_4$

The halides are readily hydrolysed by water (except CX_4, due to absence of d-orbital). the order of ease of hydrolysis is

$SiCl_4 > GeCl_4\ SnCl_4 > PbCl_4$.

Degree of hydrolysis α covalent chr.

- **Carbides :**

The binary compounds of carbon with elements other than hydrogen are called carbides.

Ionic carbides are formed by the most electropostive metals such as alkali and alkaline earth metals and Al.

both Be_2C and Al_4C_3 are called methamides because they react with H_2O yielding methane.

Covalent carbides are formed by metalloids like Si and B.

SiC (carborundum) has a diamond like structure, hence it is called artificial diamond. B_4C (Norbide) is hardest known artificial substance.

Interstitial carbides are formed by transition elements in which C-atoms occupy tetrahedral holes in the close-packed metal atoms. W, Zr, Ti and Mo can form ideal intersitial carbides.

- **Silicones :**

Silicones are polymeric organo-silicon compounds contaning Si-O-Si linkages. The name silicon has been given from similarity of their empirical formula (R_2SiO) with ketones (R_2O)

Silicones are formed by the hydrolysis of alkyl or aryl substituted chlorsilanes and their subsequent polymerisation.

$$2RCl + Si \xrightarrow[570K]{\text{Cu powder}} \underset{\text{dialkyldichloro silane}}{R_2SiCl_2}$$

$$R_2SiCl_2 \xrightarrow[-HCl]{+H_2O} [R_2SiO] \xrightarrow{H_2O} \underset{\text{Silicone}}{\left[\begin{array}{cccc} & R & R & \\ & | & | & \\ -O- & Si & -O- & Si-O- \\ & | & | & \\ & R & R & \end{array}\right]_n}$$

Silicones have good thermal, oxidative stability. These are excellent water repellants and chemically inert substances. Liquid silicones are used as excellent lubricants.

Silicates: Silicates are metal derivatives of silicic acid [H_4SiO_4 or $Si(OH)_4$]. Silicates are made up of SiO_4^{4-}tetrahedral units in which Si is sp^3 hybridised and

is surrounded by four oxygen atoms.
All these elements combine with halogens forming corresponding halides.
Note: Boron and aluminium combine with nitrogen and carbon on heating to form nitride, carbide respectively.

(Group 15 elements)

Physical Properties

Melting and boiling points

$$\overbrace{N_2 < P_4 < As}^{\text{due to molecular wt.}} > \underbrace{Sb > Bi}_{\text{due to metallic bond}}$$

Oxidation state : These elements can show negative as well as positive oxidation states.
As we go down the group the stalility of +3 oxiddation state increases while that of +5 ozidation state decreases due to inert effect.
Non-metallic and metallic character : Down the group, metallic character increases.
Allotropy : All the elements except bismuth show allotropy. Phosphorus exists in three Allotropic forms such as white or yellow, red or violet and black phosphorus.

Property	White Phosphorus	Red Phosphorus	Black Phosphorus
Colour	White turns yellow on exposure	Dark red	Black
State	Waxy solid, can be cut with knife	Brittle Colour	Crystalline with greasy touch
smell	Garlic smell	Odourless	—
Ignition Temperature	307 K	543 K	673 K

CHEMICAL PROPERTIES

- **Hydrides :**

General formula for hydrides is MH_3.
eg. NH_3, PH_3, AsH_3, SbH_3, BiH_3
All these hydrides are covalent in nature and have pyramidal structure (sp^3 hybridised).

e.g.

As we go down the group, the bond angle decreases. This is due to the increase in size and decrease in electron negativity of central metal ion.

$$\underset{\substack{\text{Basic strength}\downarrow\\ \text{Thermal stability}\downarrow\\ \text{Reducing nature.}\uparrow}}{NH_3\,PH_3\,AsH_3\,SbH_3\,BiH_3} \longrightarrow$$

- **Halides :**

Elements of group 15 form two types of halides viz. (i) trihalides and (ii) pentahalides. The trihalides are predominantly basic. (Lewis base in nature) and have lone pair of electrons (central atom is sp^3 hybridised). The pentahalides are thermally less stable than the trihalides.

Property	Gradation	Reason
Stability of trihalides of nitrogen	$NF_3 > NCl_3 > NBr_3$	Large size difference between N and the halogens
Lewis base strength	$NF_3 < NCl_3 < NBr_3 < NI_3$	Decreasing electron Density
Bond angle among the halides of phosphorus	$PF_3 < PCl_3 < PBr_3 < PI_3$	Due to increases in size of X, steric repulsing increases, due to which bond angle increases

- **Formation of oxides :**

All the elements of this group form two types of oxides, i.e. M_2O_3 and M_2O_5 and are called trioxides and pentoxides.

Property	Gradation	Reason
Acidic Strength of trioxides	$N_2O_3 > P_2O_3 > As_2O_3$	Electro negativity of central atom decreases
Acidic strength of pentaoxide	$N_2O_5 > P_2O_5 > As_2O_5$ Bi_2O_5	Electronega tivity of central atom decreases
Acidic strength of oxide of nitrogen	$N_2O < NO < N_2O_3$ $< N_2O_4 < N_2O_5$	Oxidation state of central atom increases
The stability of pentaoxide	$P_2O_5 > As_2O_5 > Sb_2O_5$ $> N_2O_5 > Bi_2O_5$	Stability of oxides of a higer oxidation state i.e. M_2O_5 decreases with increasing atomic number

Uses :

- **Nitrogen (N_2)**

  Manufacture of HNO_3, NH_3, $CaCN_2$, etc.

  Provides inert atmosphere in many metallurgical processes.

- **Phosphorus (P_4)**

  Uses in manufacture of matches, in rat posion, in the manufacture of traces bullets, etc.

Important compounds of group 15 elements

1. Ammonia (NH_3)

(i) $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$

(ii) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

- **Manufacture NH_3 (haber's process) :**

$$N_2 + 3H_2 \underset{}{\overset{Fe+Mo,750K,200\text{-}300atm}{\rightleftharpoons}} 2NH_3$$

- **Physical properties :**

Colourless, pungent smell, basic in nature.

Liquefies on cooling under pressure.

- **Chemical properties :**

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 4O_2 \xrightarrow{Pt,\ 1100K} 4NO + 6H_2O$$

$$\underset{excess}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

$$NH_3 + \underset{excess}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

- **Uses :**
  It is used as refrigerant.
  In the manufacture of fertilizers and HNO_3.
  It is uses for removing grease.
  Used as a solvent.

2. **HNO_3, nitric acid was earlier called as aqua fortis** (meaning strong water).
It usually acquires yellow colour. Due to its decomposition by sunlight into NO_2.
It acts as a strong oxidising agent. Non-metals converted into hightest oxyacids by hot and cons. HNO_3, NO_2 gas is evolved.
(S to H_2SO_4; P to H_3PO_4; C to H_2CO_3; I_2 to HIO_3; As to H_3AsO_4; Sb to H_3SbO_4 and Sn to H_2SnO_3).
Most of the metals except noble metals are attacked by HNO_3. It plays double role in action on metals, i.e., it acts as an acids as well as an oxidising agent.

Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2 + metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Zn, Fe, Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	$NO_2 + H_2SnO_3$ (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

3. **Phosphine (PH_3)**
Preparation:

(i) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

(ii) $P_4 + 3H_2O + 3NaOH \longrightarrow 3NaH_2PO_2 + PH_3$

Laboratory preparation:

$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

Physical Properties:
Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

Chemical properties:

(i) $2PH_3 + 3O_2 \longrightarrow P_2O_3 + 3H_2O$

(ii) $4PH_3 \xrightarrow{713K} P_4 + 6H_2$

(iii) $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

Uses:

As Holme's signals in deep seas and oceans.

For the Production of smoke screens.

4. Phosphorus halides:

Phosphorus form two types of halides, phosphorus trihalides PX_3 and phosphorus pentahalides $PX_5 (X = F, Cl, Br)$

(i) PCl_3:

Preparation:

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

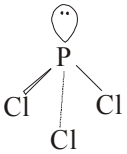
Properties:

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

Structure :



(ii) PCl_5:

Preparation :

$$P_4 + 10Cl_{2(g)} \longrightarrow 4\,PCl_{5(s)}$$

$$PCl_3 + Cl_{2(g)} \longrightarrow PCl_{5(s)}$$

$$P_4 + 10SO_2Cl_2 \longrightarrow 4\,PCl_3 + 10SO_2$$

Properties:

Pale yellow crystalline solid.

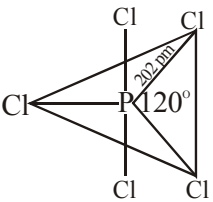
In solid state it exists as $[PCl_4]^+[PCl_6]$.

It sublimes on heating.

$$PCl_5 \underset{}{\overset{\text{heat}}{\rightleftharpoons}} PCl_3 + Cl_2$$

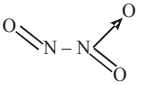
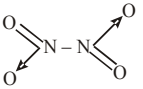
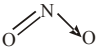
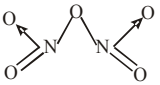
$$PCl_5 + H_2O \overset{\text{Partial hydrolysis}}{\rightleftharpoons} POCl_3 + 3H_2O \xrightarrow{H_2O} H_3PO_4 + 3HCl$$

structure :



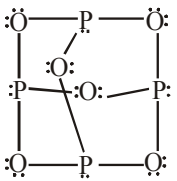
Structure of oxides of nitrogen of nitrogen and phosphorus

Nitrogen

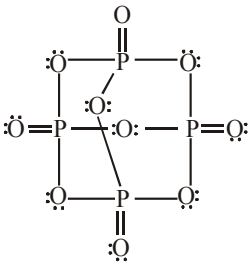
Oxide of N	Oxid. State	Physical appearance	Structure
N_2O nitrous oxide	+1 } Neutral	Colourless gas	N = N – O
NO Nitric oxide	+2 } Neutral	Colourless gas	N = O
N_2O_3 Dinitrogen trioxide	+3	Blue colour solid	
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	
NO_2 Nitrogen dioxide	+4 } Acidic	Brown gas	
N_2O_5 Dinitrogen penta oxide	+5 } Acidic	Colourless solid	

- **Phosphorus**

Structure of phosphorus trioxide (P_4O_6):



Structure of phosphorus pentaoxide (P_4O_{10}):



(GROUP 16 ELEMENTS)

PHYSICAL PROPERTIES

Melting and boiling points:

$$O_2 < S_8 < Se_8 < Te_8 < Po_{metal}$$

Metallic and non-metallic character :

$$O < S < Se < Te < Po$$

IP. ↓ metallic character ↑

Elemental state : Oxygen exists as diatomic gaseous molecule. Sulphur and selenium exist as octa-atomic molecules. Both have puckered ring structure.

Allotropy : All the elements of this group show allotropy. Oxygen exists in two non-metallic forms i.e., O_2 and O_3. Sulphur provides a very good example of an element that exhibits allotrophy.

Allotropic forms of sulphur :

Rhombic sulphur or octahedral or α-sulphur : This is the common and stable form of sulphur. It is a pale yellow crystalline solid consisting of S_8 structural units and packed in octahedral shape.

Monoclinic or prismatic or β-sulphur: This form is stable above 95.6ºC. It exists as amber yellow, needle shaped crystals soluble in carbon disulphide.

Plastic sulphur: It is an amber brown, soft rubber like mass which hardens on standing.

Chemical Properties :

Hydrides : All these element form stable hydrides of the type H_2M

$$H_2 + O_2 \longrightarrow 2H_2O$$

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

$$Na_2Se + H_2SO_4 \longrightarrow H_2Se + Na_2SO_4$$

H_2O is a liquid due to hydrogen bonding. Other are colourless gases with unpleasant smell.

Compound :	H_2O >	H_2S	> H_2Se	> H_2Te
Bond angle	105.5º	92.5º	91º	90º

(All sp^3 hybridised)

The weakening of M–H bond with the increase in the size of M (not the electronegativity) explain the increasing acid character of hydrides down the group.

Halides :

All these elements form a number of halides. The halides of oxygen are not very stable. Selenium does not form dihalides.

e.g. OF_2, Cl_2O_6, I_2O_5, etc.

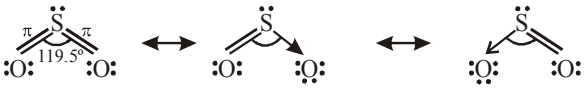
Oxides :

Oxides of other elements are as follows :-

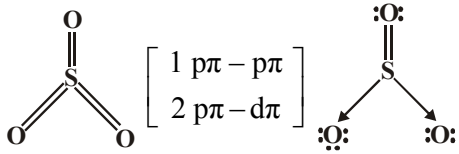
Element	Monoxide	Dioxide	Trioxide
S	SO	SO_2	SO_3
Se	–	SeO_2	SeO_3
Te	TeO	TeO_2	TeO_3
Po	PoO	PoO_2	

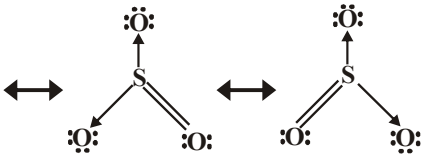
SO_2 is a gas having sp^2 hybridisation and V-shape.

$$\begin{bmatrix} 1p\pi - p\pi \\ 1p\pi - d\pi \end{bmatrix}$$

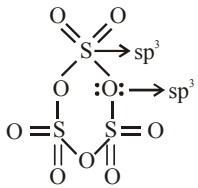


SO_3 is a gas, sp^2 hybridised and planar in nature.





In solid state it exists as a cyclic trimer $(SO_3)_3$, α–form or as linear cross-linked sheets, β-form:



S = 0 bond $\Rightarrow$ 6

S – O – S bond $\Rightarrow$ 3

IMPORTANT COMPOUNDS OF GROUP 16 ELEMENTS

1. Oxygen (O_2):

- **Preparation :** By action of heat on oxygen rich compounds:

  From oxides:

  $$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

  From peroxides:

  $$2Na_2O_2 + 2H_2O \xrightarrow{\Delta} O_2 + 4NaOH$$

  $$2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$$

  From decomposition of certain compounds:

  $$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

  $$2KNO_2 \longrightarrow 2KNO_2 + 3O_2$$

- **Properties :** It is colourless, odourless, tasteless, slightly heavier than air, sparingly soluble in water but soluble in pyrogallol.
- **Chemical properties :** On heating it combines directly with metals and non metals.

  $$C + O_2 \longrightarrow CO_2$$

  $$S + O_2 \longrightarrow SO_2$$

  $$Pb + O_2 \longrightarrow PbO_2$$

  $$2CH_3OH + O_2 \longrightarrow 2HCHO + 2H_2O$$

- **Uese :**

  When mixed with He or CO_2 it is used for Artificial respiration.
  In welding and cutting.

  As a fuel in rockets.

2. Ozone (O_3):

- **Preparation :**
- **Lab method :**

  $$3O_2 \underset{}{\overset{\text{Electric discharge}}{\rightleftharpoons}} 2O_3 \ (\Delta H = +ve)$$

- **Properties :** pale blue gas with characteristic strong smell, Slightly soluble in water but more soluble in terpentine oil or glacial acetic acid.

- **Decomposition :**

$$2O_3 \xrightarrow{573K} 3O_2 + 68kcal$$

- **Oxidising action :**

$$O_3 \longrightarrow O_2 + O$$
$$PbS + 4O \longrightarrow PbSO_4$$

- **Reducing action :**

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$
$$BaO_2 + O_3 \longrightarrow BaO + 2O_2$$

- **Structure :**

(B.O. = 1.5)

Oxidation state of O is +1 and –1.

- **Uses :**

Bleaching ivory, flower, delicate fabrics, etc.
As germicide and disinfectant for sterilising water.
Manufacture of $KMnO_4$ and artificial silk.

3. Sulphur dioxide (SO_2) :

- **Preparation :**

By heating sulphur in air.

$$S + O_2 \xrightarrow{\Delta} SO_2$$

Lab method:
By Heating Cu with conc. H_2SO_4

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

- **Properties :**

As reducing agent :

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$
$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

As oxidising agent :

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S\downarrow$$

Bleaching action :
Its bleaching action is due to reduction.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

Coloured matter + H $\longrightarrow$ Colourless matter.
(Nascent hydrogen)

- **Uses :**

In the manufacture of sulphuric acid, sulphites and hydrogen sulphide.
As a disinfectant and fumigate.
For bleaching delicate articles like silk.

4. Sulphuric acid (H_2SO_4) :

It is also known as oil of vitriol and king of chemicals.

- **Manufacture of sulphuric acid (Lead chamber process):**

The various steps involved are :

(a) Production of SO_2 : By burning S or iron pyrites.

$$S + O_2 \xrightarrow{\Delta} SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(b) Production of catalyst : Oxides of nitrogen.

$$2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_3$$

$$2HNO_3 \longrightarrow H_2O + NO + NO_2 + O_2$$

(c) Reaction in lead chamber

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$2NO + O_2 \longrightarrow 2NO_2 \text{ (used again)}$$

- **Contact process :**

The steps involved are :

(a) **Production of SO_2 :** It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.

(b) **Conversion of SO_2 to SO_3 :** It is done in container or catalyst chamber after being pre-heated to 450ºC.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x \text{ cal}$$

Catalyst : Formerly, platinised asbestos was uses which is costly and easily poisoned. These days V_2O_5 is used.

(c) SO_3 is absorbed by conc. H_2SO_4 and then water is added to produce the acid of desired concentration.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

- **Properties :** Its specific gravity is 1.8 and it is 98% by weight.

It is strong dibasic acid.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

It acts as an oxidising agent.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

Non metals are oxidised to their oxides and metals to the corresponding sulphates.

$$C + 2O \longrightarrow CO_2$$

Dehydrating agent : It is strongly dehydrating in nature.

$$\text{(Dehydration of sugar) } C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

- **Uses :**

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

(GROUP 17 ELEMENTS)

PHYSICAL PROPERTIES

Oxidation state : All the halogen show an oxidation state of –1. Except fluorine, all halogens show positive oxidation states also.

Metallic character :

$$F < Cl < Br < I < At$$

Bond dissociation energy : Bond dissociation energy of fluorine is lower than those of chlorine (Cl – Cl) and bromine (Br – Br) because inter-electronic repulsions present in the small atom of fluorine. Hence bond energy decreases in the order.

$$Cl_2 > Br_2 > F_2 > I_2.$$

Bond length :

$$F_2 < Cl_2 < Br_2 < I_2$$

Melting point and boiling point :

$$F_2 < Cl_2 < Br_2 < I_2$$

CHEMICAL PROPERTIES

Reactivity : All halogens are chemically very reactive elements. This is due to their low dissociation energy and high EN. Fluroine is the most reactive and iodine is the least reactive halogen.

Oxidising power : F is the most oxidising element due to high hydration enthalpy.

$F_2 > Cl_2 > Br_2 > I_2$.

Hydrogen halides :

Bond strength, bond length and thermal stability :

Since size of halogen atom increases from F to I down the group, bond length of H – X bond increases down the group.

$\therefore$ reactivity and acidic character $\uparrow$.

$HF < HCl < HBr < HI$.

Bond strength is inversely, proportional to bond length i.e., larger the bond length, lower the bond strength is

$HF > HCl > HBr > HI$.

Higher the bond dissociation energy greater will be thermal stability. Thus, thermal stability follows the order.

$HF > HCl > HBr > HI$.

Reducing character : The reducing character of hydrogen halides increases down the group as

$HF < HCl < HBr < HI$.

$2HX \longrightarrow H_2 + X_2$

A less thermally stable compound has more tendency to release hydrogen easily and shown greater reducing property.

- **Acidic strength :** The acidic strength of these acids increases down the group and hence follows the order.

$HF < HCl < HBr < HI$.

Since H-I bond is weakest, it can be easily dissociated into H^+ and I^- ions while HF with greater bond dissociation energy can be dissociated with maximum difficulty.

CHLORINE (Cl_2)

- **Preparation :** By oxidation of conc. HCl.

$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

- **Manufacture :**
  Weldon's process : By heating pyrolusite with conc. HCl.
  $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

- **Properties :** It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate.
  Bleaching action and oxidising property
  (i) $Cl_2 + H_2O \longrightarrow HOCl + HCl$
  $HOCl \longrightarrow HCl + [O]$
  Coloured matter + nascent [O] $\longrightarrow$ Colouless matter
  The bleaching action of chlorine is permanent and is due to its oxidising nature.
  (ii) $SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$
  Action of hydrogen :

$$H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{U.V. light}} 2HCl$$

  Displacement reactions :
  $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$
  $2KI + Cl_2 \longrightarrow 2KCl + I_2$
  Action of NaOH :

$$\underset{\text{(cold)}}{2NaOH} + \underset{\text{dry}}{Cl_2^0} \longrightarrow NaCl^{-1} + \underset{\text{sodium hypo chlorite}}{NaOCl^{+1}} + H_2O$$

$$\underset{\text{(hot and conc.)}}{6NaOH} + \underset{\text{(dry)}}{3Cl_2^0} \longrightarrow 5NaCl^{-1} + \underset{\text{sodium chlorate}}{NaCl^{+5}O_3} + 3H_2O$$

  Addition reactions :
  $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$
  $CO + Cl_2 \longrightarrow COCl_2$

- **Uses :**
  It is used as a
  (i) bleaching agent
  (ii) disinfectant
  (iii) in the manufacture of $CHCl_3$, CCl_4, DDT, bleaching powder, poisonous gas phosgene ($COCl_2$), tear gas ($C_{10}H_5ClN_2$) and mustard gas ($ClC_2H_4SC_2H_4Cl$).

HYDROCHLORIC ACID, (HCl)

- **Preparation :** By dissolving hydrogen chloride gas in water.

Hydrogen chloride gas required in turn HCl can be prepared by the following methods :

By the direct combination of hydrogen and chlorine.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl_{(g)}$$

Hydrogen chloride gas can also be obtained by buming hydrogen in chlorine.

- **Properties :** Hydrogen chloride is a covalent compound but when dissolved in water it ionizes to form hydrogen ions and chloride ions.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Thus anhydrous HCl does not show acidic properties. Only aqueous HCl or in presence of moisture, HCl behaves as an acid.

Metal + Hydrochloric acid $\longrightarrow$ Metal chloride + Hydrogen

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2\uparrow$$

It react with bases and basic oxides or hydroxides to form their respective chlorides and water.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites etc, to form their respective chlorides.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

It reacts with silver nitrate and lead nitrate solution to form thier white precipitates.

$$AgNO_3 + HCl \longrightarrow HNO_3 + AgCl\downarrow$$

Reducing property : HCl is a strong reducing agent.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

- **Uses :**

In the production of dyes, paints, photographic chemicals, etc.

Used in the preparation of chlorides, chlorine, aqua-regia, etc.

Used as a laboratory reagent.

INTERHALOGEN COMPOUNDS :

These compounds are regarded as halides of more electropositive (i.e. less electronegative) halogens.

Types of interhalogen compound :

AB type : ClF, BrF, BrCl, ICl, IBr

AB_3 type : ClF_3, BrF_3, ICl_3

AB_5 type : BrF_5, IF_5

AB_7 type : IF_7

Variation of the general properties of oxyacids of halogens

Halogen	Hypohalous acids (X = + 1)	Halous acids (X = + 3)	Halic acids (X = + 5)	Phalic acid (X = + 7)
Cl	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Br	HBrO	–	$HBrO_3$	–
I	HIO	–	HIO_3	HIO_4

Oxidation number of the central atom increases

(X = + 1, + 3, + 5, +7) →

Thermal stability increases →

Covalent character of X – O bond increases →

Oxidising power decreases →

Basicity decreases →

← Electronegativity of the central atom decreases –

← Thermal stability decreases –

← Oxidising power decreases –

← Acidic strenght decreases –

19 Coordination Chemistry

Complex formation : Due to high polarising power and partially filled 'd' subshell, transition elements form complex.

Terminology :

Ligand : The species which donate the e^- pair is called as ligand. On the basis of the number of e^- pairs avaible for donation ; ligands are classified as :

(a) Monodentate (One pair of e^-)

(b) Bidentate (Two pair of e^-)

Ambidentate ligand : It is the monodentate ligand having more than one e^- pair to donate, but always acts as unidentate due to inactivation of the second e^- pair of donation.

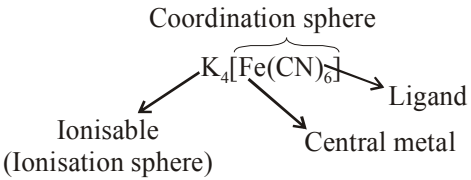
For example, $-CN^-$ and $-NC^-$, $-SCN^-$ and $-NCS^-$, NO_2^- and ONO^-, $-OCN^-$ and NCO^-.

These ligands are responsible for linkage isomerism.

Flexidentate ligands : Exhibit variable denticity eg. SO_4^{2-}, CO_3^{2-}, EDTA.

Chelating ligand : These are the polydentate ligands which bind to the central metal to form a puckered ring structure. Chelation always, leads to extra stability for example - EDTA (ethylene diamine tetra acetate).

Coordinate complex :



Ionisation sphere constitutes of the ions which may satisfying the primary valency. **Coordination sphere** constitute the metal coordinates with ligands, which cannot be ionised after dissolution and exist as stable identities – either neutral or charged.

Coordination number : It is the number of metal is surround in coordination sphere or it is the number of coordinate bonds arround central metal ion in a complex entity.

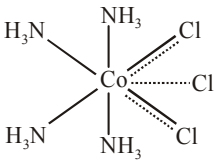
Charged ligands can satisfy primary valency beside being the part of coordination sphere hence, satisfy both primary and secondary valencies but still remain unionisable.

Werner's theory :

Metal in a complex shows two type of valences – Primary & secondary.

Primary valency	Secondary Valency
It is oxidation no. of metal.	It is coordination no.
It is variable	It is non variable.
Satisfied by anions (present in coordination or ionisable sphere).	Satisfied by ligands (present in coordination sphere)
Ionisable	Nonionisable
Ionic ∴ nondirectional	Directional ∴ Decide geometry of complex ion.
Represented by dotted line in Werner structure.	Represented by solid lines in Werner structure.

eg. $COCl_3.4NH_3$ (Molecular formula) $[Co(NH_3)_4Cl_2]Cl$ (Complex formula)



{ 3 dotted line shows – Primary Valence
6 solid line shows – Secondary Valence

Werner structure

Primary valency – Loss of electrons.
Secondary valency – gain of electrons.

EAN rule : (According to sidzwick and Lowrry)

∴ Total number of electron associated with metal ion in a complex entity is called EAN.

central metal ion have tendency to achieve atomic number to nearest inert gas element during formation of complex called EAN rule.

EAN = Atomic number of Central metal ion – Oxidation state + (2 × Coordination number)

$K_4[Fe(CN)_6]$ EAN of Fe $= 26 - 2 + (2 \times 6)$

Stable according to EAN rule $= 24 + 12$

$= 36$

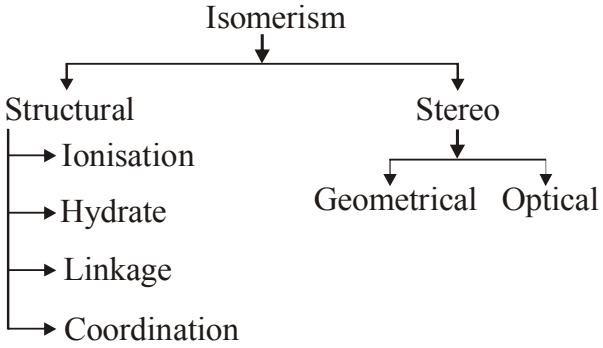
(equals to atomic number of Kr_{36})

$K_3[Fe(CN)_6]$ EAN $= 26 - 3 + 12$

(Less stable) $= 35$

∴ act as oxidising agent.

Isomerism :



Structural :

(a) **Ionisation isomerism :** Same molecular formula, but gives different ionisable species. (Only anionic)

eg. $PtCl_2Br_2.4NH_3$ → (a) $[Pt(NH_4)_4Cl_2]Br_2$

$PtCl_2Br_2.4NH_3$ → (b) $[Pt(NH_3)_4Br_2]Cl_2$

(b) **Hydrate isomerism :** Same molecular formula but different number of water moelcules associated with central metal.

eg. $CrCl_3.6H_2O$ → (a) $[Cr(HO)_6]Cl_3$

$CrCl_3.6H_2O$ → (b) $[Cr(H_2O)_5Cl]Cl_2.H_2O$

$CrCl_3.6H_2O$ → (b) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

(c) **Linkage isomerism :** Linkage isomerism shown by ambidentable ligands

(NO_2^-, CSN^-, CN^-, CNO^-)

$[Fe(NH_3)_5(SNC)]^{2+}$

$[Fe(NH_3)_5(NCS)]^{2+}$

(d) **Coordination isomerism :** Isomers having both anion and cation as complex entity. Can inter change position of ligands as well as metal.

$[Cr(NH_3)_6]\,[Co(CN)_6]$

$[Co(NH_3)_6][Cr(CN)_6]$

10. Stereoisomerism :

(a) Geometrical Isomerism (GI)

- CN = 4
  - Tetrahedral (No G.I.)
  - Square planar
    - Ma_4 – NO GI
    - Ma_3 – NO GI
    - Ma_2b_2 – 2 GI (cis & trans)
    - Ma_2bc – 2 GI (cis & trans)
    - Mabcd – 3 GI
- CN = 6 (Octahedral)
  - Mabcdef – 15 GI
  - Ma_2bcde – 9 GI
  - Ma_2b_2cd – 6 GI
  - $Ma_2b_2c_2$ – 5 GI
  - Ma_3bcd – 4 GI
  - Ma_3b_2c – 3 G
  - Ma_3b_3 – 2(Fac - Mer)
  - Ma_4bc – 2(cis-trans)
  - Ma_4b_2 – 2(cis-trans)
  - Ma_5b – NO GI
  - Ma_6 – NO GI

Sq. planar complex with symmetrical bidentate ligand – No. GI

Sq. planar complex can exhibit GI only in two types $\begin{bmatrix} M(AB)_2 \\ M(AB)ab \end{bmatrix}$

On increasing number of one type of ligand total number of geometrical isomers decreases.

Octahedral $[M(AA)a_4]$ and $[M(AA)_3]$ type of complex can not exhibit G.I.

$[M(AA)_2a_2]$ type of complex have two GI (cis & trans)

(b) Optical Isomerism (OI)

- CN = 4
  - Sq. planar (NO optical isomerism)
  - Tetrahedral complex can exhibit OI in following types
    - (1) Mabcd – 2 O.I.
    - (2) $M(AB)_2$ – 2 O.I.
- CN = 6 (Octahedral are optically active in following conditions)
  - (1) Mabcdef
  - (2) $[M(AA)a_4]$
  - (3) $[M(AA)_2a_2]$ – cis-optically active
  - (4) $[M(AA)_3]$ – trans-optically inactive

* $[M(AA)_2a_2]$ type of complex gives three stereoisomer :
(1) cis (2) trans (3) mirror image of cis

Crystal field theory (CFT) :

If the complex is formed by the use of inner d-orbitals for hybridisation (d^2sp^3), it is called inner orbital complex.

If the complex is formed by the use of outer d-orbitals for hybrdisation (sp^3d^2), it is called an outer orbital complex. Such a complex is also called as high spin complex.

Crystal field splitting.

The splitting of five degenerate d-orbitals of the metal into different sets of orbitals having different energies in the presence of electrostatic field of ligands is called crystal field splitting.

eg set – $dx^2–y^2$, dz^2

t_2g set – dxy, dyz, dxz

Crystal field splitting energy, (Δ_o for octahedral structure and Δ_t for tetrahedral structure) is the difference between the various sets of energy levels formed by crystal field splitting.

Weak field ligands are those ligands which cause a small degree of crystal field splitting

e.g. $I^–$, $Br^–$, $Cl^–$, $NO_3^–$, $F^–$, $OH^–$, $C_2O_4^{2–}$, H_2O, etc.

Spectrochemical series

$I^– < Br^– < Cl^– < NO_3^– < F^– < OH^– < ox^{2–} < H_2O < py \sim en < dipy < o\text{-}phen < NO_2^– < CN^– < CO$.

(C and N donar act as a SEF except $N_3^–$)

12. Organometallic compounds :

Compounds in which the central metal atoms are bonded directly to carbon atoms of hydrocarbon molecules are called organometallic compounds.

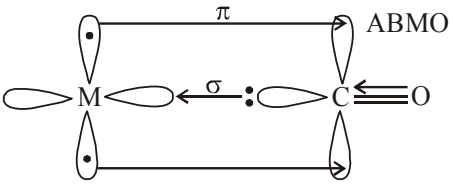
d-bonded compounds formed by nontransition elements.

R–Mg–X, $(CH_3–CH_2)_2Zn$, Ziegler natta catalyst, etc.

p-bonded organometallic compounds are generally formed by transition elements e.g. Zeise's salt, ferrocene, dibenzen chromium, etc.

s-and p-bonded organometallic compounds : Metal carbonyls, compounds formed between metal and carbon mono-oxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$ etc.

Synergic bonding :



IUPAC nomenclature of complex compounds :

(A) For anionic complex (like $K_4[Fe(CN)_6]$)
Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + O.S (in roman number).
e.g. : Potassium hexacyanoferrate (II)

(B) For cationic complex (like $[Cu(NH_3)_4]SO_4$)
Name of ligands (with numeral prefix) + Common name of CMI + O.S (In roman number) + Name of anion (without numeral prefix)
e.g. : Tetraammine copper (II) sulphate.

(C) For neutral complex (like $[Fe(CO)_5]$)
Name of ligands (with numeral prefix) + Common name of CMI + O.S (In roman number)
e.g. : pentacarbonyl iron (O)
$[Pt(NH_3)_2Cl_2]$
Diamminedichloroplatinum (II)

Some important rules :

Ligands are to be written in alphabetical order
Repetition of organic ligands and ligands having numeral prefix in their name is to be done by using prefix – bis, tris, tetrakis etc.

20 d-Block Element

Definition :

Incomplete n and n–1 shell in atomic or in ionic state. Zn, Cd & Hg – are d-block nontransition elements.

General electronic configuration : $ns^{0-2}\ (n-1)d^{1-10}$

$$\text{Exceptions} \begin{cases} Cr\ 4s^1\ 3d^5 \\ Cu\ 4s^1\ 3d^{10} \end{cases}$$

Transition series :

1st	3d series $Sc_{21} - Zn_{30}$	$9+1=10$
2nd	4d series $Y_{39} - Cd_{48}$	$9+1=10$
3rd	5d series La_{57}, $Hf_{72} - Hg_{80}$	$9+1=10$
4th	6d series Ac_{89}, Unq – Unb	$9+1=10$

Atomic radius :

3d series $Sc > Ti > V > Cr > Mn \geq Fe \simeq CO \simeq Ni \leq Cu < Zn$

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f e^- (Lanthanide contraction)

$$\boxed{3d < 4d \simeq 5d}$$

e.g. : $Ti < Zr \simeq Hf$ | Smallest radius – Ni; Largest radius – La

Melting point : s-block metals < d-block metals

In a series on increasing number of unpaired e^- mp increases upto Cr then decreases.

$Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn$

↓ Half filled d^5 ∴ weak metallic bond

↓ Fully filled d^{10} ∴ weak metallic bond

E.N. Exception $Zn < Cd < Hg$

Density :

s-block metals < d-block metals

3d series Sc < Ti < V < Cr < Mn < Fe < Co ≤ Ni < Cu > Zn

Density in a Group 3d < 4d << 5d

Matallic character : They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is liquid.

Elect. cond. $\underbrace{Ag > Cu > Au}_{d-block} > \underset{p-block}{Al}$

Oxidation state : Transition elements exhibit variable oxidation state due to small energy difference of ns and (n – 1)d electrons.
Sc(+ 3) and Z(+2) exhibit only one oxidation state.
Common oxidation state is +2
3d series highest oxidation state is +7 (Mn)
In d-block series highest oxidation state is +8 (Os)
In carbonyl compound oxidation state of metals is zero due to synergic effects.
Their higher oxidation states are more stable in fluoride and oxides.
Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.
eg. stable fluoride in higher ox. st. of Mn is MnF_4 while oxide is Mn_2O_7

Some more stable oxidation states of d-block elements :

Cu +2	Mn +2	Pt +4
Ag +1	Cr +3	Sc +3
Au +3	Ni +2	

Common oxidation states :

Ti(+4)	V(+5)	Cr(+3, +6), Mn(+2, +4, +7),
Fe(+2, +3)	Co(+2, +3),	Ni (+2), Pt(+2 +4)

In p-block lower oxidation states of heavier elements are more stable while in d-block heavier element, higher oxidation state are more stable.
e.g. In VIB gp Mo(+6) & W(+6) are more stable than Cr(+6)

Magnetic property :

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula $\mu = \sqrt{n(n+2)}$ Bohr magneton.

(n is number of unpaired e^-).

If n is 1 $\mu = 1.73$ BM
n is 2 $\mu = 2.84$ BM
n is 3 $\mu = 3.87$ BM
n is 4 $\mu = 4.90$ BM
n is 5 $\mu = 5.92$ BM

Subtances that are not attracted by applied magnetic field are diamagnetic. They have all the electrones paired. d-block element and ions having d^o and d^{10} configuration are diamagnetic.

Colour :

Colour in transition metal ions is associated with d–d transition of unpaired electron form t_{2g} to e_g set of energies.

This is achieved by absorption of light in the visible spectrum, rest of the light is no longer white.

Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc

Coloured – Fe^{3+} yellow, Fe^{2+} green, Cu^{2+} blue, Co^{3+} blue etc.

Interstitial compounds : When less reactive nonmetals of small atomic size eg. H, B, N, C, trapped in the interstitial space of transition metals, interstial compounds are formed, like :-

TiC, Mn_4N, Fe_3H etc.
They are nonstoichiometry compounds.
They have high melting point than metals.
They are chemically inert.

Alloys :

Solid mixture of metals in a defenite ratio (15% difference in metallic radius)
They are hard and having high melting point.

eg. Brass (Cu + Zn)
Bronze (Cu + Sn) etc.

Hg when mix with other metals form semisolid amalgam except Fe, Co, Ni, Li.

Catalyst :

Transition metals & their compounds act as catalyst due to –
Variable oxidation state
Tendency to form complex

eg. V_2O_5 – Contact process
Fe – Haber process
Ni – Catalytic hydrogenation

Important reactions of d-block elements :

(a) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_{2(s)} + I_2$

(b) $CuSO_4 + \underset{\text{Excess}}{KCN} \longrightarrow K_2SO_4 + \underset{\text{Excess}}{Cu(CN)_2}$

$2Cu(CN)_2 \longrightarrow 2CuCN + \underset{\text{Cyanogen}}{(CN)_2}$

$CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$

(c) $Cu \xrightarrow[\text{moist air}]{H_2O + CO_2} \underset{\text{green}}{CuCO_3.Cu(OH)_2}$

$Au \xrightarrow[(3HCl + HNO_3)]{\text{Aqua regia}} H[AuCl_4] + NOCl + H_2O$

(d) $AgNO_3 \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$AgCO_3 \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$

(e) $CuSO_4.5H_2O \xrightarrow{100°C} \underset{\text{light greenish blue}}{CuSO_4.H_2O} \xrightarrow{100°C} \underset{\text{Colourless}}{CuSO_4}$

$\xrightarrow{720°C} CuO + SO_2 + \frac{1}{2}O_2$

(f) $Hg_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Black}}{Hg\begin{matrix}NH_2\\ \diagup\\ \diagdown\\ Cl\end{matrix}} + Hg + NH_4Cl + 2H_2O$

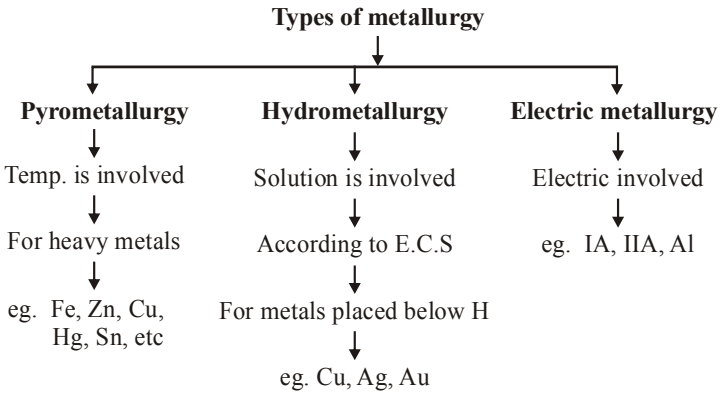
(g) $NO_3^- / NO_2^- \xrightarrow{FeSO_4 + H_2SO_4} \underset{\text{Brown ring complex}}{[Fe(H_2O)_5NO^+]SO_4}$

(h) $AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Photographic complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$

21 Metallurgy

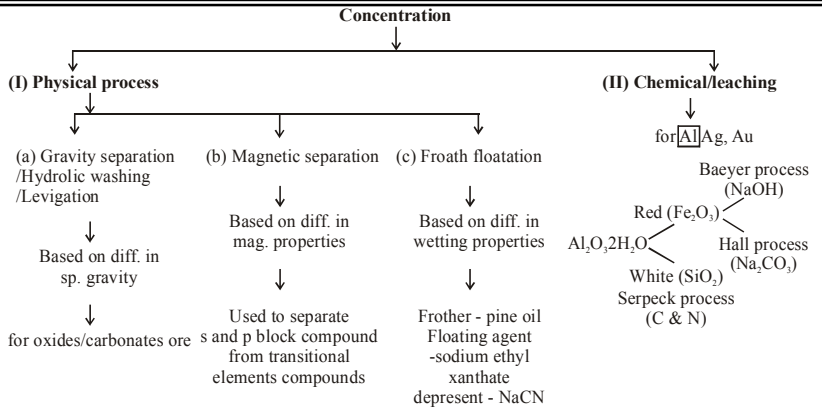
Branch of process to extract metal from their respective ore

Ore : Minerals from which metal can be extracted economically & easily.

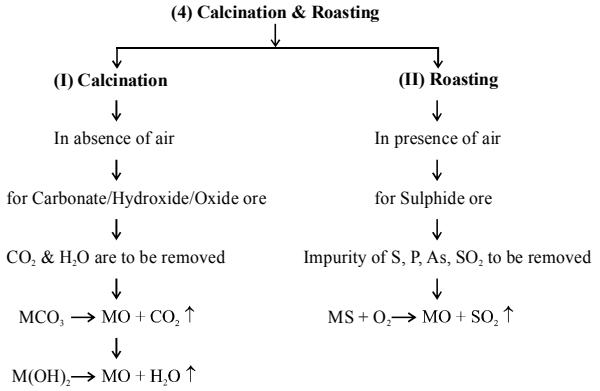


Metallurgical process :

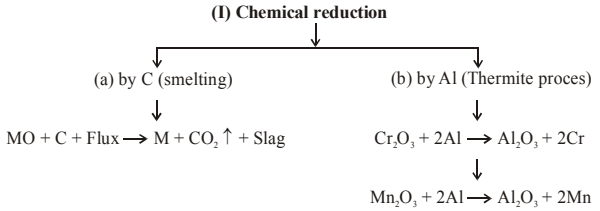
1. **Mining :** Ore obtain in big lumps (less reactive)
2. **Crushing/grinding/pulversization :** big lumps convert into powder (more reactive)
3. **Concentration :** To remove matrix/gangue (major impurities) from ore to increases the concentration of ore particle in ore sample.



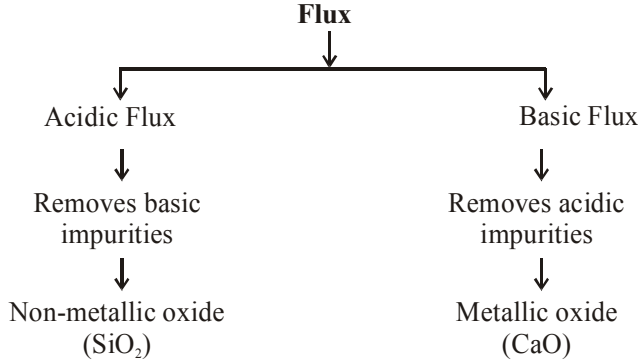
Ag, Au, are concentrated by cyanide process.



5. Reduction : To obtains metal (95 to 98%) from metal oxide.



Flux - substance to convert non-fusible impurities to fusible one.



Imp. point - At high temp. C is reducing agent.
- At low temp. CO is reducing agent.

(II) Self reduction

↓

For Cu, Pb, Hg

↓

For sulphide ore only

(III) Metal displacement reduction

↓

Metal placed below H. in E.C.S

↓

Ag, Au, Cu

↓

(i) Cyano complex or Mac-Arther process

$$Ag_2S + 4NaCN \xrightarrow{2O_2} 2Na[Ag(CN)_2] + Na_2SO_4$$

$$2Au + 4KCN + H_2O \xrightarrow{O_2} 2K[Au(CN)_2] + 2KOH$$

(ii) Reduction to free metal

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

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au \downarrow$$

(IV) Electrolytic reduction

↓

For IA, IIA, Al

↓

Electrolysis of molten sol.

↓

(i) Extraction of Al (Hall-Herault Process)
- Al can be extracted from Al_2O_3
- To decrease fusion temp. of Al_2O_3, Na_3AlF_6 & CaF_2 is to added
- Na_3AlF_6 and CaF_2 (Neutral flux) increase the conductivity and reduce the fusion temp.

(ii) Extraction of Na (Down cell process)
- Na can be extracted from NaCl
- Neutral flux ($CaCl_2$) to be added to decrease the fusion temp. of NaCl
- Neutral flux - substance used to increase the conductivity of NaCl
- Decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal.

Refining : To obtain metal (99.98%) pure

↓

(I) Physical Process

↓

(a) Liquation → Low M.P. metal Sn, Pb, As, Sb

(b) Distillation → Low M.P. metal → Volatile metal (Zn, Cd, Hg)

(c) Zone refining/ Fractional crystallization → Ultrapure metal → Volatile metal Ge, Ga, Si

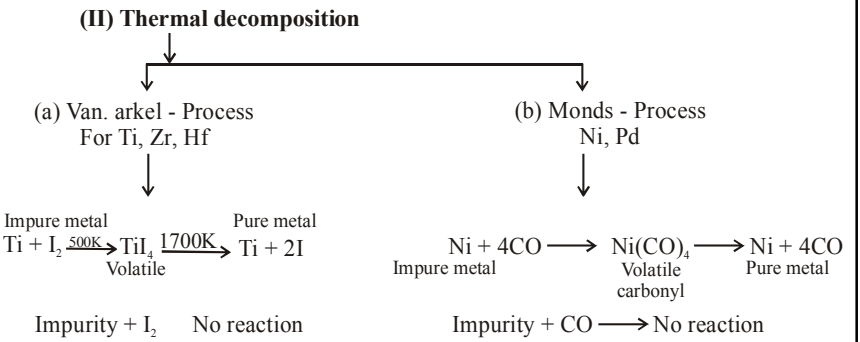
(II) Chemical Process

↓

(a) Cupellation → For Ag having the impurity of Pb → Impure metal + O_2 → pure metal + $O_2 \longrightarrow$ X

(b) Polling → Cu, Pb having the impurity of their own oxide → $CuO + C \rightarrow Cu + CO$; $CuO + H_2 \rightarrow Cu + H_2O$

(c) Bessemerization → For Cu, Pb → impure + $O_2 \longrightarrow$ Volatile oxide



(IV) Electrolytic refining

Anode - made up of impure metal (Impurity deposited below anode as anode mud)
Cathode - made up of pure metal (pure metal deposited)

Thermodynamics principle of metallurgy

The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering be choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram such diagram help us in predicting the feasibility of thermal reduction of an ore.
The criteria of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.
In blast furnace reduction takes place at low temperature i.e.Organic Chemistry.

22 Salt Analysis

Group	Radicals	Condition for Precipitation (Group Reagent)	Forms of Precipitation
Zero	NH_4^+, K^+, Na^+	1-2 drops of CH_3COOH	NH_3
First	Ag^+, Hg^{+1} (Hg_2^{+2}), Pb^{+2}	By mixing of dilute HCl	Chloride $AgCl$, Hg_2Cl_2, $PbCl_2$
Second	Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Sn^{+2}, Sn^{+4}, As^{+3}, Sb^{+3}, Bi^{+3}	H_2S gas passed in the presence of Acidic medium dil. HCl	Sulphide PbS, HgS, CuS, CdS, SnS, SnS_2, As_2S_3, Sb_2S_3, Bi_2S_3
Third	Al^{+3}, Fe^{+3}, Cr^{+3}	NH_4OH mixed in the presence of NH_4Cl	Hydroxide $Al(OH)_3$, $Fe(OH)_3$ $Cr(OH)_3$
Fourth	Mn^{+2}, Co^{+2}, Ni^{+2}, Zn^{+2}	H_2S gas passed in presence of Basic medium	Sulphide MnS, CoS, NiS, ZnS
Fifth	Ba^{+2}, Sr^{+2}, Ca^{+2} ($K_{sp}\uparrow$)	$(NH_4)_2CO_3$ mixed in the presence of NH_4OH	Carbonate $BaCO_3$, $SrCO_3$, $CaCO_3$
Sixth	Mg^{+2}	By mixing of Na_2HPO_4	Hydrogen Phosphate ($MgHPO_4$)

Purification Methods of organic Compounds :

(A) Simple distillation	(i) When liquid sample has non volatile impurities (ii) When boiling point difference is 30K or more	(i) Mixture of chloroform (BP=334K) and Aniline (BP=457K) (ii) Mixture of Ether (BP=308K) and Toluene (BP=384K) and Toluene (384K) (iii) Hexane (342K) and Toluene (384K)
(B) Fractional distillation	When BP difference is 10K	(i) Crude oil in petroleum industry (ii) Acetone (329K) and Methyl alcohol (338K)
(C) Distillation under reduced pressure (Vacuum distillation)	When liquid boils at higher temperature and it may decompose before BP is attained	(i) Concentration of sugar juice (ii) Recovery of glycerol from spent lye. (iii) Glycerol
(D) Steam distillaion	When the substance is immiscible with water and steam volatile. $P = P_1 + P_2$ Vapour pressure; P_1 Vapour pressure of Organic liquid; P_2 Vapour pressure of water	(i) Aniline is separated of water (ii) Turpentine oil (iii) Nitro Benzene (iv) Bromo Benzene (v) Naphthalene (vi) o-Nitrophenol

Qualitative Analysis of organic compound :-

Element	Sodium extract	Confirmed test
Nitrogen	$Na + C + N \longrightarrow NaCN$	$(NaCN+FeSO_4+NaOH)$ Boil and Cool $+FeCl_3$ + conc. $HCl \longrightarrow Fe_4[Fe(CN)_6]_3$ Prussian blue colour
Sulphur	$2Na + S \longrightarrow Na_2S$	(i) $Na_2S+Na_2[Fe(CN)_5NO] \longrightarrow$ Sodium nitrosopruside $Na_4[Fe(CN)_5NOS]$ a deep violet colour (ii) $Na_2S + CH_3COOH + (CH_3COO)_2Pb \longrightarrow$ a black ppt. (PbS)
Halogen	$Na + X \longrightarrow NaX$	$NaX + HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl (ii) Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 or NH_4OH confirms I.
Nitrogen and Sulphur together	$Na+C+N+S \longrightarrow NaCNS$ Sodium thiocyanate (Blood red colour)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirm presence of N and S both $FeCl_3 + 3NaCNS \rightarrow Fe(CNS)_3 + 3NaCl$

23 Nomenclature

Functional group	Structure	Prefix	Suffix
Carboxylic acid	$-\overset{\overset{O}{\|\|}}{C}-OH$	Carboxy	-oic acid
Sulphonic acid	$-SO_3H$	Sulpho	Sulphonic acid
Ester	$-\overset{\overset{O}{\|\|}}{C}-OR$	Alkoxy Carbonyl	alkyl....oate
Acid chloride	$-\overset{\overset{O}{\|\|}}{C}-Cl$	Chloroformyl or Chlorocarbonyl	- oyl chloride
Acid amide	$-\overset{\overset{O}{\|\|}}{C}-NH_2$	Carbamoyl or Amido	- amide
Carbonitrile/Cyanide	–C N	Cyano	nitrile
Aldehyde	$-\overset{\overset{O}{\|\|}}{C}-H$	Formyl or Oxo	- al
Ketone	$-\overset{\overset{O}{\|\|}}{C}-$	Keto or Oxo	- one
Alcohol	–OH	Hydroxy	- ol
Thio alcohol	–SH	Mercapto	thiol
Amine	$-NH_2$	Amino	amine
Ether	R–O–R	Alkoxy	–
Oxirane	$-C-\underset{\diagdown\ \diagup}{\overset{}{C}}-$ (O)	Epoxy	–
Nitro derivative	$-NO_2$	Nitro	–
Nitroso derivative	–NO	Nitroso	–
Halide	–X	Halo	–
Double bond	C = C	–	ene
Triple bond	C ≡ C	–	yne

24 Isomerism

Isomerism

1. **Stereochemistry** involves the study of the relative spacial arrangement of atoms within molecules.

. **Structural isomerism** is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

. **Various types of structural isomerism :**

(i) Chain isomerism : This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

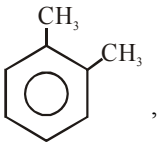
e.g. C_5H_{12} : $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$,
n-pentane

$H_3C - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$, $H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$

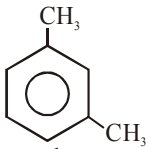
iso-pentane neo-pentane

(ii) Position isomerism : It occurs when functional groups or multiple bonds or substituents are in different position on the same carbon chain.

e.g. $C_6H_4(CH_3)_2$:


o-xylene

,


m-xylene

,


p-xylene

(iii) Functional isomerism : It occurs when substances have the same molecular formula but different functional groups.

e.g. C_3H_9N : $CH_3 - CH_2 - CH_2 - NH_2$,
propanamine

$CH_3 - CH_2 - NH - CH_3$,

N-methylethanamine

$CH_3 - \underset{\displaystyle CH_3}{\overset{|}{N}} - CH_3$,

N, N-dimethylmethanamine

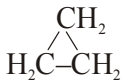
(iv) Metamerism : This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

e.g. $C_4H_{10}O$: $CH_3 - O - CH_2 - CH_2 - CH_3$
n-methylether

$CH_3 - CH_2 - O - CH_2 - CH_3$
diethyl ether

(V) Ring-chain isomerism : In this type of isomerism, one isomer is open chain but another is cyclic.

e.g. C_3H_6 : $CH_3 - CH = CH_2$
propene


cyclopropane

(Vi) Tautomerism : This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

Conditions :

(i) Presence of a $-\overset{\displaystyle O}{\overset{\|}{C}}-$ or $-\overset{\displaystyle O}{\overset{\|}{C}} \rightarrow O$

(ii) Presence of at least one α-H atom which is attached to a saturated C-atom.
e.g. Acetoacetic ester

$$\underset{\text{keto form}}{CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - CH_2COOC_2H_5} \rightleftharpoons \underset{\text{enol form}}{CH_3 - \overset{\displaystyle OH}{\overset{|}{C}} = CHCOOC_2H_5}$$

- For chain, position and metamerism, functional group must be same.
- Metamerism may also show chain and position isomerism but priority is given to metamerism.

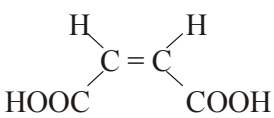
2. **Stereoisomerism :** Compounds with the same molecular formula and structural formula but having difference in the spacial arrangement of atoms or group are called stereoisomers and the phenomenon is called stereoisomerism.

- **Various types of stereoisomerism**

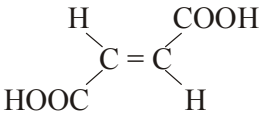
(i) Geometrical isomerism : Compounds with double bonds, or alicyclic rings can exhibit isomerism, due to the attached groups in plane of double bond or below and above the plane of the ring.

- **cis-trans isomerism :** The cis compound is one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



cis
maleic acid



trans
fumaric acid

- General physical property of geometrical isomer

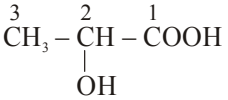
(i)	Stability	trans > cis
(ii)	Dipole moment	cis > trans
(iii)	Boiling point	cis > trans
(iv)	Melting point	trans > cis

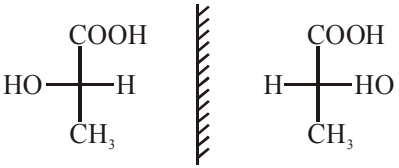
(ii) Optical isomerism : Compounds having similar physical and chemical properties but differing only in the behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomersim.

- The carbon atom linked to four different groups is called **chiral carbon.**
- Non-superimposable mirror images are called **enantiomers** which rotate the plane polarised light up to same extent but in opposite direction.

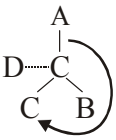
- **Fischer projection :** An optically active compound can be represented by Fischer projection which is planar representation of three dimensional structure.

Fischer projection representation of lactic acid
(2-hydroxypropanoic acid)

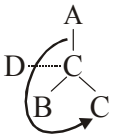




- **Absolute configuration :** It is a three dimensional representation of optically active compound. It is also said to be R, S-system. (R-Rectus, S-Sinister).



R-Configuratoin



S-Configuratoin

- **Determination of R, S configuration :** It involves the following steps:

(i) Assignment of priority sequences of the group, Let the priority sequence among the given groups A, B, C and D are A > B > C > D.

(ii) Rotation of eye from higher to lower priority sequence by keeping eye towards opposite side of lowest priority group i.e. rotating eye from 1 to 3 (A to C) via 2(B), while doing so if eye is rotating in clockwise then it is R-configuration and if in anticlockwise, then it is S-configuration.

- **CIP Sequence rule :** The following rules are followed for deciding the precedence order of the atoms or groups.

(i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.

(ii) If the first atom of a group attached to asymmetric carbon atom is same then

we consider the atomic number of 2nd atom or subsequent atoms in group.

(iii) If there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.

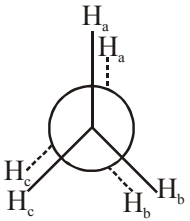
- **Diastereomers** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.
- **Meso compounds** are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.
- An equimolar mixture of the enantiomers (d & ℓ) is called racemic mixture.

  The process of converting d-and ℓ-form of an optically active compound into recemic form is called racemisation.
- The process by which dℓ mixture is separated into d and ℓ forms with the help of chiral reagents or chiral catalyst is known as resolution.
- Compound containing chiral carbon may or may not be optically active but show optical isomerism.
- For optical isomer chiral carbon is not the necessory condition.

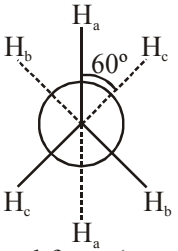
The compound if contains	Optically active forms	Optically inactive forms (meso)
n different chiral carbon atoms and the molecule cannot be divided into two equal halves	2^n	Zero
an even number of n chiral carbons, but the molecule can be divided into two equal and similar halves	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
an odd number of n chiral carbons and the molecule can be divided into two equal and similar halves via the central carbon	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

- **Conformational isomerism :** The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360º are called conformers or conformational isomers or rotational isomers and this phenomenon is called conformational isomerism.

- **Newmann projection :** Here two carbon atoms forming the σ bond are represented one by circle and other by centre circle. Circle represents back side C and its centre represents front side carbon. The C-H bonds of front carbon are depicted from the centre of the circle while C-H bond of the back carbon are drawn from the circumference of the circle.



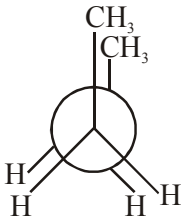
Eclipsed form (least stable)



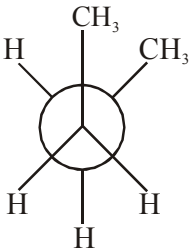
Staggered form (most stable)

- **Conformations of butane:**

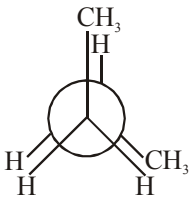
$\overset{4}{CH_3} - \overset{3}{CH_2} - \overset{2}{CH_2} - \overset{1}{CH_3}$



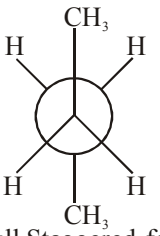
Fully eclipsed (less stable)



Gauche (more stable)



Eclipsed form



Full Staggered-form
(most stable) (Anti form)

- The order of stability of conformations of n-butane
  Anti > Gauche > Eclipsed > Fully eclipsed

- Relative stability of varous conformance of cyclohexane is
  Chain > twist boat > boat > half chair

25 Alkyl Halides

Comparison of S_N1 and S_N2

		S_N1	S_N2
A	Kinetics	1st Order	2nd Order
B	Rate	k[RX]	k[RX][Nu:$^-$]
C	Stereochemistry	Racemic Mixture	Inversion
D	Substrate	3º > 2º > 1º	MeX > 1º > 2º > 3º
E	Nucleophile	Rate independent to Nu^-	Needs Strong Nu
F	Solvent	Good ionizing	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Comparison of E_1 and E_2

		E_1	E_2
A	Kinetics	1st Order	2nd Order
B	Rate	k[RX]	k[RX] [B:$^-$]
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	3º > 2º >>> 1º	3º > 2º > 1º
E	Nucleophile	Rate independent of base strength Nu^-	Needs Strong bases
F	Solvent	Good ionizing	Polarity not important
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Summary of S_N1 , S_N2 , E_1 , and E_2 reactions

RX	Mechanism	Nu:$^-$ /B:$^-$	Solvent	Temp.
1º	S_N2	Better Nu:$^-$ $HO:^-$, $C_2H_5O:^-$	Polar aprotic	Low
	E_2	Strong & bulky base $(CH_3)_3CO:^-$		High
2º	S_N2	$OH:^-$, $C_2H_5O:^-$	Polar aprotic	Low
	E_2	$(CH_3)_3CO:^-$		High
	S_N1	Solvent	Polar	Low
	E_1	Solvent	Protic	High
3º	S_N1	Solvent	Protic	Low
	E_1	Solvent	Protic	High

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	$S_{N}2 >> E_2$	$S_{N}2 + E_2$ (if weak base, $S_{N}2$ favoured)	100% E_2
Weak nucleophile weak base	Mostly $S_{N}2$	Mostly $S_{N}2$ / $S_{N}1$ (Aq. increases $S_{N}1$)	Mostly $S_{N}1$ at low T mostly E_1 at high T
Weak nucleophile strong base	Mostly E_2	Mostly E_2	100% E_2

Alkyl halide

- Order of reactivity of alkyl halide towards

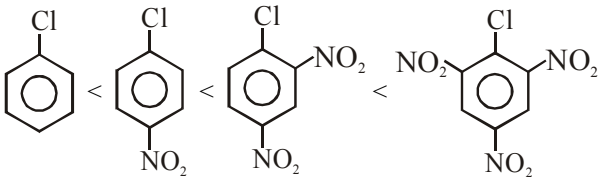
  $S_{N}1$ $3° > 2° > 1°$

  $S_{N}2$ $1° > 2° > 3°$

- Reactivity order towards $S_{N}1$ or $S_{N}2$ and E_1 or E_2

  R–I > R–Br > R–Cl > R–F

- With increase in number of strong electron withrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitutiion increases.



26 General Organic Chemistry

Basic strength of amine :

$R \Rightarrow -CH_3$ $\quad 3^o > 2^o > 1^o > NH_3$

$R \Rightarrow -CH_2CH_3$ $\quad 2^o > 3^o > 1^o > NH_3$

$\Rightarrow$ decreasing order of reactivity towards nucleophile (NAR)

(1) $HCHO > CH_3CHO > (CH_3)_2CO$

(2) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$

(3) Reactivity order towards acyl nucleophilic substitution
Acid chloride > anhydride > carboxylic acid > ester > amide

Order of electronic effect

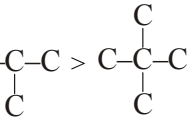
Mesomeric > Hyperconjugation > Inductive effect

Stability of alkene :

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CH-R > R-CH=CH_2 > CH_2=CH_2$

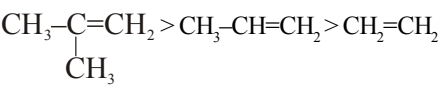
Alkane

- Reactivity of alkane towards free radical halogenation is α stability of free radical.
  $C_6H_5-CH_3 > CH_2=CH-CH_3 > (CH_3)_3CH > CH_3-CH_2-CH_3 > CH_3-CH_3 > CH_4$
- Reactivity of halogen towards free radical substitution
  $F_2 > Cl_2 > Br_2 > I_2$
- Knocking tendency of petroleum as fuel decrease with increase in side chain.
  Straight chain > Branched chain
  Knocking tendency is in the order
  Olefin > cycloalkane > aromatic
  Boiling point decrease with increase in number of side chain.

n > iso > neo $\quad$ C–C–C–C–C >  >

Alkene

- Order of reactivity of olefins for hydrogenation
  $CH_2=CH_2 > R-CH=CH_2$ (Reverse of stability)
- Order of reactivity of alkene towards hydration



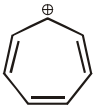
Alcohol

- Solubility of alcohol increase with increase in branching
  n < iso < neo (isomeric)
- Relative order of reactivity
  (i) $1^o > 2^o > 3^o$ (O–H bond fission)
  (ii) $3^o > 2^o > 1^o$ (C–O bond fission)
  (iii) $3^o > 2^o > 1^o$ (Dehydration)

Reaction mechanism

1. All the +ve charge species are electrophile except H_3O^+ and NH_4^+
2. Relative electron withdrawing order (–I order)
   $-NO_2 > -CN > -COOH > -F > -OR > -OH > -C_6H_5 > -CH=CH_2$
3. +I order
   $-NH^- > -O^- > -COO^- > 3^o$ alkyl $> 2^o$ alkyl $> 1^o$ alkyl
4. Greater the number of α-Hydrogen, more stable is carbocation and free radical due to hyperconjugation.

(A) Carbocation



$> (Ph)_3\overset{\oplus}{C} > (Ph)_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2$

$(CH)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

(B) Free radical

$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H >$

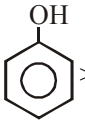
$CH_3\dot{C}H_2$

(C) Carbanion

$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

Acidic Strength:

(i) $H_2O > CH\equiv CH > NH_3$
(ii) $CH\equiv CH > CH_2=CH_2 > CH_3-CH_3$

(iii) $R–SO_3H > R–COOH >$  $> R–OH$

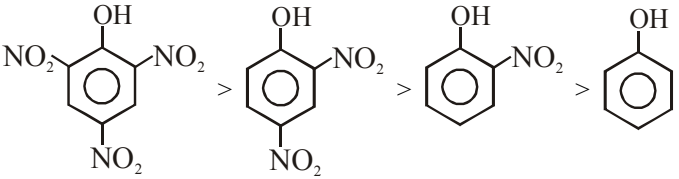
(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

(v) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

(vi) $CH_3–\underset{F}{CH}–COOH > CH_3–\underset{F}{CH}–CH_2COOH > \underset{F}{CH_2}–CH_2CH_2COOH$

(vii) $C_6H_4\begin{matrix}OH\\CH_3\end{matrix}$ Phenol > m > p > o

(viii) $C_6H_4\begin{matrix}OH\\NO_2\end{matrix}$ p > o > m > Phenol

(ix) 

(x) $C_6H_4\begin{matrix}COOH\\NO_2\end{matrix}$ o > p > m > benzoic acid

(xi) $C_6H_4\begin{matrix}COOH\\CH_3\end{matrix}$ o > benzoic acid > m > p

(xii) $C_6H_4\begin{matrix}COOH\\OCH_3\end{matrix}$ o > m > benzoic acid > p

(xiii) $C_6H_4\begin{matrix}COOH\\Cl\end{matrix}$ o > m > p > benzoic acid

27 Practical Organic Chemistry

Quantitative analysis of organic compounds:

- Estimation of carbon and hydrogen-Leebig's method

$$C_xH_y + \left(\frac{x+y}{4}\right)O_2 \longrightarrow xCO_2 + y/2H_2O$$

$$\%\text{ of } C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of Organic compound}} \times 100$$

$$\%\text{ of } H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of Organic compound}} \times 100$$

Note :

This method is suitable for estimation of organic compound C and H only. In case if other elements e.g. N,S, halogens are also present in organic compound will also give their oxides which on being absorbed in KOH will increase the percentage of carbon and therefore following modification should be made.

- **Estimation of nitrogen :**

Duma's method : In this method a nitrogen containing compound is strongly heated with CuO in the atmosphere of CO_2 to get free nitrogen along with CO_2 and water.

$$\%\text{ of } N = \frac{28}{22400} \times \frac{\text{vol. of } N_2 \text{ collected at NTP}}{\text{wt. of Organic compound}} \times 100$$

Note: This method can be used to estimate nitrogen in all types of organic compounds.

Kjeldahl's method : In this method nitrogen containing compound is heated with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is

$$\%\text{ of } N = \frac{14 \times \text{vol. of acid used in ml} \times \text{normality of acid}}{\text{wt. of Organic compound}} \times 100$$

Note :

This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, oil, fertilizers and various agricultural products. This method cannot be used for compound having nitrogroups, azo group (–N=N–) and nitrogen in the ring (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

- **Determination of molecular formula :**
- **Empirical :** It is the simplest formula which expresses the simple whole number ratio of the atoms of constituent elements present in the molecule.
- **Molecular Formula :** The formula which gives the actual number of atoms of various elements present in the molecule of the substance is termed as the molecular formula.
- Molecular Formula = n × [empirical formula]

  $$\text{Where } n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

- **An alternate method of molecular formula determination :** In this method molecular formula can be determined without determining empirical formula.

  Number of moles of element

  $$= \frac{\%\text{ of element}}{100} \times \frac{\text{mol. mass}}{\text{atomic mass of element}}$$

28 Distinction Between Pairs of Compounds

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

- **Unsaturation test :**

Double/Triple bonded compounds + Br_2 in CCl_4 ⟶ Colourless compound
(C=C) / (C≡C) (Brown colour)

$$R\text{–}CH{=}CH\text{–}R + Br_2 \xrightarrow{CCl_4} R\text{–}\underset{Br}{\overset{Br}{CH}}\text{–}\underset{Br}{\overset{Br}{CH}}\text{–}R$$
(Alkene) (Brown) (Colourless)

$$R\text{–}C{\equiv}C\text{–}R + Br_2 \xrightarrow{CCl_4} R\text{–}\underset{Br}{\overset{Br}{C}}\text{–}\underset{Br}{\overset{Br}{C}}\text{–}R$$
(Alkyne) (Brown) (Colourless)

Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) ⟶ Brown precipitate

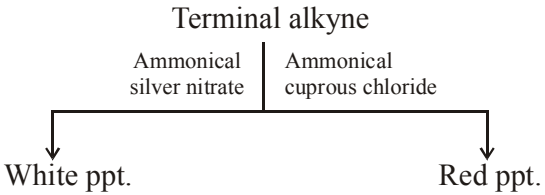
$$R\text{–}CH{=}CH\text{–}R + \text{(Cold, dilute) } KMnO_4 \longrightarrow R\text{–}\underset{OH}{\overset{OH}{CH}}\text{–}\underset{OH}{\overset{OH}{CH}}\text{–}R + MnO_2$$
(Alkene) (Colourless) Brown ppt.

$$R\text{–}C{\equiv}C\text{–}R' + \text{(Hot, dilute)}KMnO_4 \longrightarrow \underset{\text{Brown ppt.}}{MnO_2} + RCOOH + R'COOH$$

$$R\text{–}C{\equiv}C\text{–}H + \text{(Hot, dilute)}KMnO_4 \longrightarrow \underset{\text{Brown ppt.}}{MnO_2} + RCOOH + \underset{\text{(Colourless)}}{CO_2} + H_2O$$
(Alkyne)

Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.
Note: The above test are not given by Benzen. Although it has unsaturation.

- **Test for terminal alkyne**



$NH_4NO_3 + H_2O + R{-}C{\equiv}C{-}Ag$ (White ppt.) $\xleftarrow{AgNO_3 + NH_4OH}$ $R{-}C{\equiv}CH$ (Terminal ppt)

$NH_4Cl + H_2O + R{-}C{\equiv}C{-}Cu$ (Red ppt.) $\xleftarrow{Cu_2Cl_2 + NH_4OH}$ $R{-}C{\equiv}CH$ (Terminal ppt)

- **Nature of X-group in C-X bond**

$$R{-}X + \text{aquesous KOH} \longrightarrow R{-}OH + KX \xrightarrow[AgNO_3]{HNO_3} \underset{\text{Precipitate}}{AgX\ \downarrow}$$

If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

- **Distinction between 1º, 2º and 3º alcohols**

$$\underset{\text{Tertiary alcohol}}{R{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}{-}OH} \xrightarrow[\text{Room temperature}]{\text{Lucas agent}} \underset{\text{Cloudiness appears immediately}}{R{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}{-}Cl}$$

$$\underset{\text{Secondary alcohol}}{R{-}\overset{\overset{R}{|}}{CH}{-}OH} \xrightarrow[\text{Room temperature}]{\text{Lucas agent}} \underset{\text{Cloudiness appears within five minutes}}{R{-}\overset{\overset{R}{|}}{CH}{-}Cl}$$

$$\underset{\text{Primary alcohol}}{R{-}CH_2{-}OH} \xrightarrow[\text{Heat}]{\text{Lucas agent}} \underset{\text{Cloudiness appears after 30 minute}}{R{-}CH_2{-}Cl}$$

Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl

$\overset{\overset{OH}{|}}{H_3C{-}CH{-}R}$ type of alcohols give iodo form test.

$$\overset{\overset{OH}{|}}{H_3C{-}CH{-}R} + I_2 \xrightarrow[\text{Iodoform test}]{NaOH} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + RCOONa$$

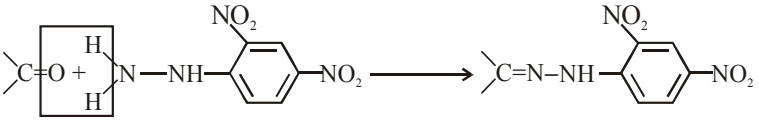
- **Phenol**

$$\text{Phenol + ferric chloride} \longrightarrow \underset{\text{(neutral)}}{\text{Violet colouration}}$$

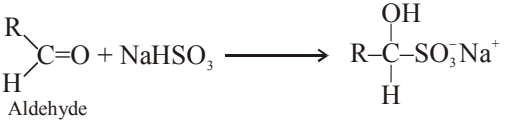
$$6\,\text{C}_6\text{H}_5\text{OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{3H^+ + [Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

- **Carbonyl group**

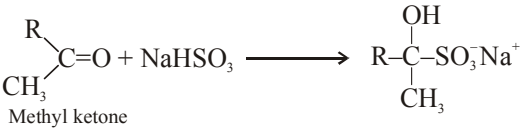
Carbonyl compound + 2,4-Dinitrophenylhydrazine
(Bredy's reagent) ⟶ Yellow/Orange Crystal



(All aldehydes and only aliphatic methyl ketones) + $NaHSO_4$ ⟶ White crystalline bisulphite.



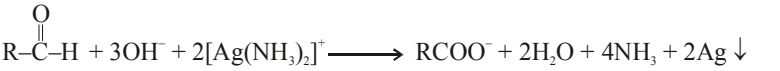
Aldehyde



Methyl ketone

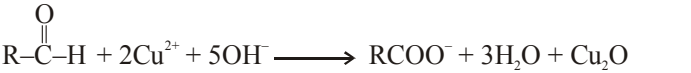
- **Aldehyde group**

Aldehyde + Tollen's reagent ⟶ Silver mirror



(Silver mirror)

Aldehyde + Fehling's solution ⟶ Reddish brown precipitate



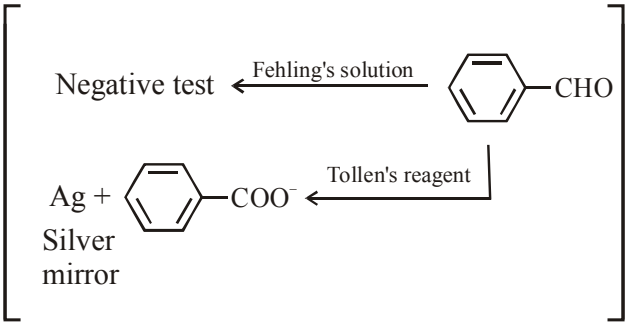
(Reddish brown ppt)

-  group also give iodoform test

$$CH_3-\overset{\overset{O}{\|}}{C}-R + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + RCOONa$$

- **Aromatic aldehyde group**

Aromatic aldehyde + Tollen's reagent ⟶ Silver mirror
Aromatic aldehyde + Fehling's solution ⟶ Negative test



- **Carboxylic group**

Carboxylic acid + Sodium bicarbonate ⟶ effervescence
$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$

- **Amine (1°)**

$$\text{Primary amine} + KOH + CHCl_3 \xrightarrow{\text{Carbylamine reaction}} \underset{\text{(Offensive smell)}}{\text{Isonitrile}}$$

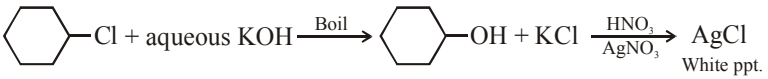
- **Amines (1°, 2° & 3°) (Hinsberg's test)**

Primary amine + Benzenesulphonyl Chloride ⟶ Precipitate $\xrightarrow{KOH}$ Soluble
Secondary amine + Benzenesulphonyl Chloride ⟶ Precipitate $\xrightarrow{KOH}$ Insoluble
Tertiary amine + Benzenesulphonyl Chloride ⟶ No reaction
Note: Benzenesulphonyl Chloride is called Hinsberg's reagent.

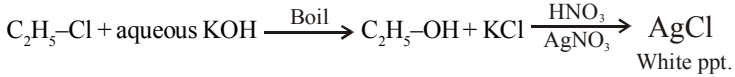
1. Chloroethane and Chlorobenzene

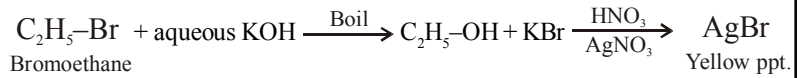
$$C_2H_5-Cl + \text{aqueous } KOH \xrightarrow{\text{Boil}} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} \underset{\text{White ppt.}}{AgCl}$$

2. Chlorocyclohexane and Chlorobenzene

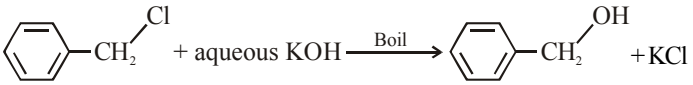


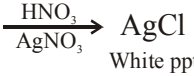
3. Chloroethane and bromoethane



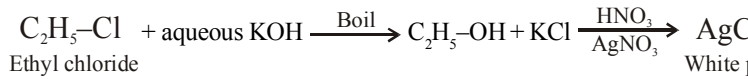


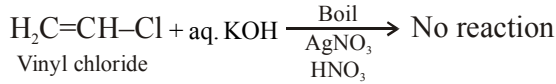
4. Benzylchloride and chlorobenzene



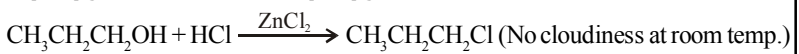


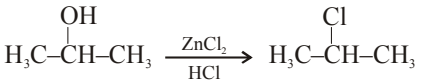
5. Ethyl chloride and vinyl chloride





6. n-propyl alcohol and iso-propyl alcohol





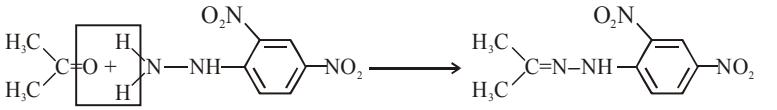
Cloudiness within 5 minutes

7. Ethyl alcohol and methyl alcohol

$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa$$

Yellow ppt.

8. Ethyl alcohol and acetone

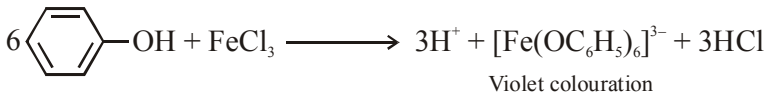


Acetone 2,4-Dinitrophenylhydrazine (Yellow Orange Crystals)

$$C_2H_5OH \longrightarrow \text{No reaction}$$

9. Phenol and ethyl alcohol

Phenol + Neutral ferric chloride $\longrightarrow$ Violet colouration



Violet colouration

CH_3CH_2OH + Neutral ferric chloride $\longrightarrow$ No violet colouration

10. Benzoic acid and Phenol

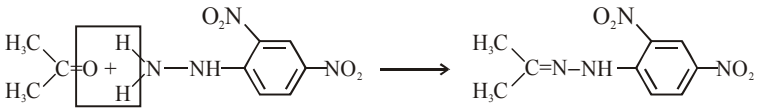
Benzoic acid + Sodium bicarbonate $\longrightarrow$ effervescence

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$$

Phenol + Sodium bicarbonate $\longrightarrow$ No effervescene

(Phenol is less acidic than benzoic acid)

11. Propanone and propanol



2,4-DNP Yellow Orange Crystals

Propanol + 2,4-Dinitrophenylhydrazine $\longrightarrow$ No crystals

12. Propanal and propanone

Propanal + Tollen's reagent $\longrightarrow$ Silver mirror

$$H_3C{-}CH_2{-}\overset{\overset{O}{\|}}{C}H + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3CH_2COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$

(silver mirror)

Propanal + Fehling's solution $\longrightarrow$ Reddish brown precipitate

$$H_3C{-}CH_2{-}\overset{\overset{O}{\|}}{C}H + 2Cu^{2+} + 50H^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$

(Reddish brown ppt)

Propanone — Fehling's solution → Negative test

Propanone — Tollen's reagent → Negative test

13.

$$\underset{\text{Ethanal}}{H_3C{-}\overset{\overset{O}{\|}}{C}{-}H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\(\text{Yellow ppt})}}{CHI_3} + HCOONa$$

$$H_3C{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}H + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \text{No yellow ppt}$$

14. Pentan-2-one and pentan-3-one

$$\underset{\text{Pentan-2-one}}{H_3C{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\(\text{Yellow ppt})}}{CHI_3} + CH_3CH_2CH_2COONa$$

$$\underset{\text{Pentan-3-one}}{H_3C{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_3} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \text{No yellow ppt}$$

15. Propanal and benzaldehyde

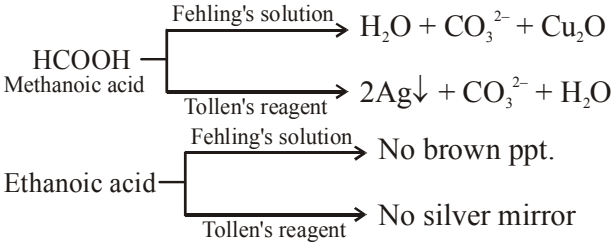
Propanal + Fehling's solution $\longrightarrow$ Reddish brown precipitate

$$\underset{\text{Fehling's solution}}{H_3C{-}CH_2{-}\overset{\overset{O}{\|}}{C}H} + 2Cu^{2+} + 50H^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$

Benzaldehyde + Fehling's solution $\longrightarrow$ No precipitate

$$CHO + 2Cu^{2+} + 50H^- \longrightarrow \text{No reaction}$$

16. Methanoic acid and ethanoic acid



17. Ethanal and methanal

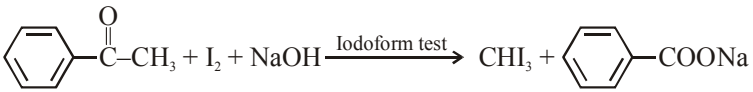
$$CH_3CHO + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt)}}{CHI_3} + HCOONa$$

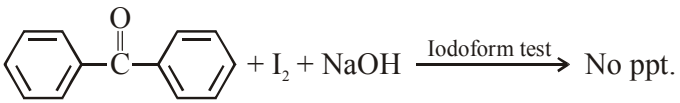
Ethanal

$$HCHO + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$$

Methanal

18. Acetophenone and benzophenone





19. Benzoic acid and ethylbenzoate

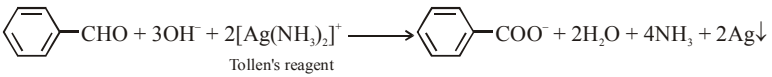
Benzoic acid + Sodium bicarbonate $\longrightarrow$ effervescence

$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$

Ethyl benzoate + Sodium bicarbonate $\longrightarrow$ No effervescence

20. Benzaldehyde and acetophenone

Benzaldehyde + Tollen's reagent $\longrightarrow$ Silver mirror



Acetophenone + Tollen's reagent $\longrightarrow$ No silver mirror

21. Methyl amine and dimethyl amine

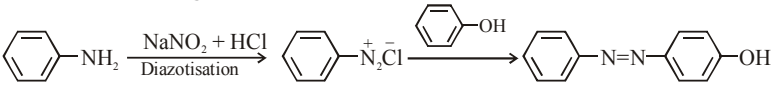
$$CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$$

Methyl amine (alc.) Methyl isocyanide (Offensive smell)

$$H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{N}}H + CHCl_3 + 3KOH\ (alc.) \longrightarrow \text{No offensive smell}$$

Di-methyl amine

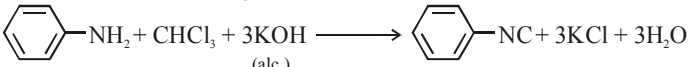
22. Aniline and ethyl amine



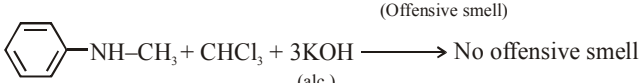
Aniline Orange dye p-hydroxy azobenzene

Ethyl amine

23. Aniline and N-methylaniline

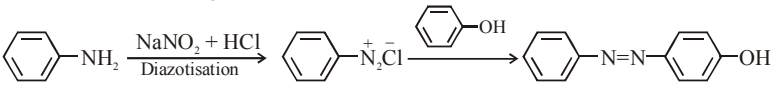


Aniline Phenyl isocyanide (Offensive smell)

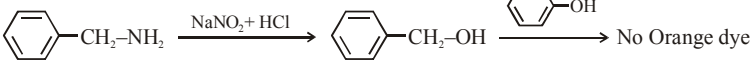


N-Methylaniline

24. Aniline and Benzylamine



Aniline Orange dye



Benzylamine

25. Glucose and fructose

$$\text{Glucose} + Br_2 + H_2O \longrightarrow \text{Gluconic acid} + 2HBr$$

(Brown colour) (Colourless)

$$\text{Fructose} + Br_2 + H_2O \longrightarrow \text{Brown colour}$$

(Brown colour)

26. Glucose and sucrose

Glucose + Tollen's reagent $\longrightarrow$ Silver mirror

Sucrose + Tollen's reagent $\longrightarrow$ No silver mirror

27. Glucose and starch

Glucose + Fehling's reagent $\longrightarrow$ Red ppt.

Starch + Fehling's reagent $\longrightarrow$ No red ppt.

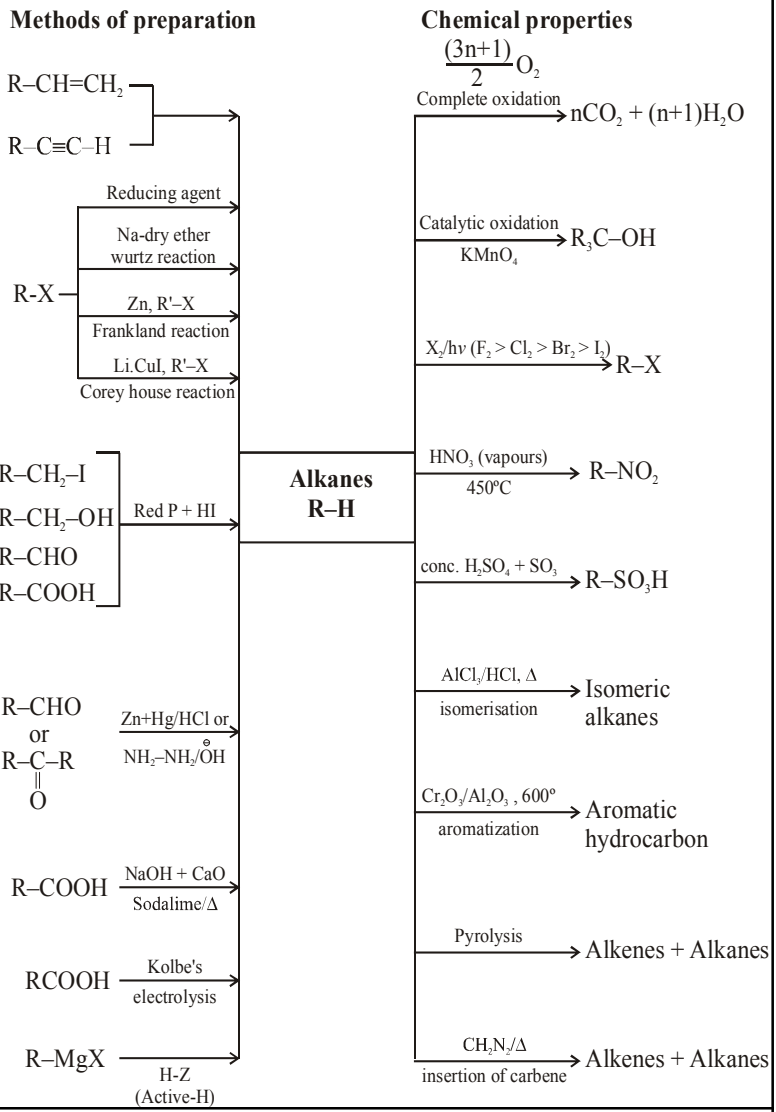
or

Glucose + I_2 Solution $\longrightarrow$ No blue colour

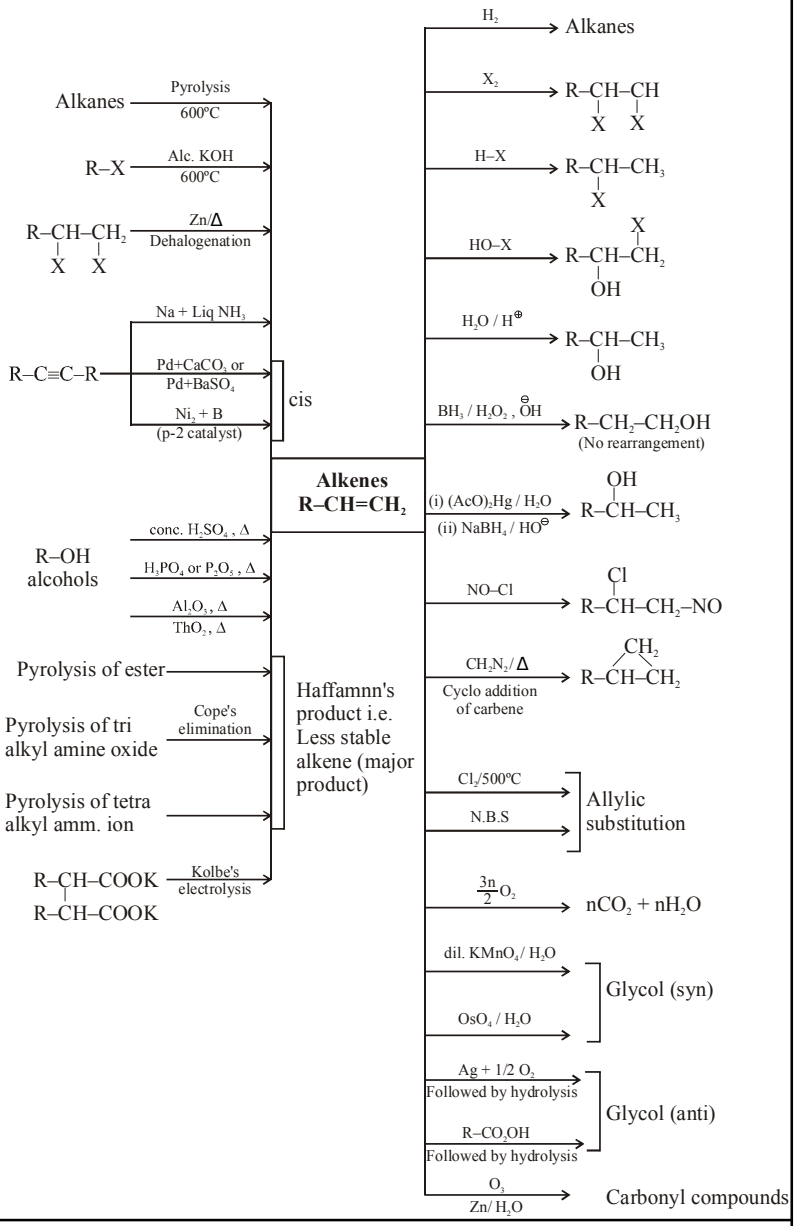
Starch + I_2 Solution $\longrightarrow$ Blue colour

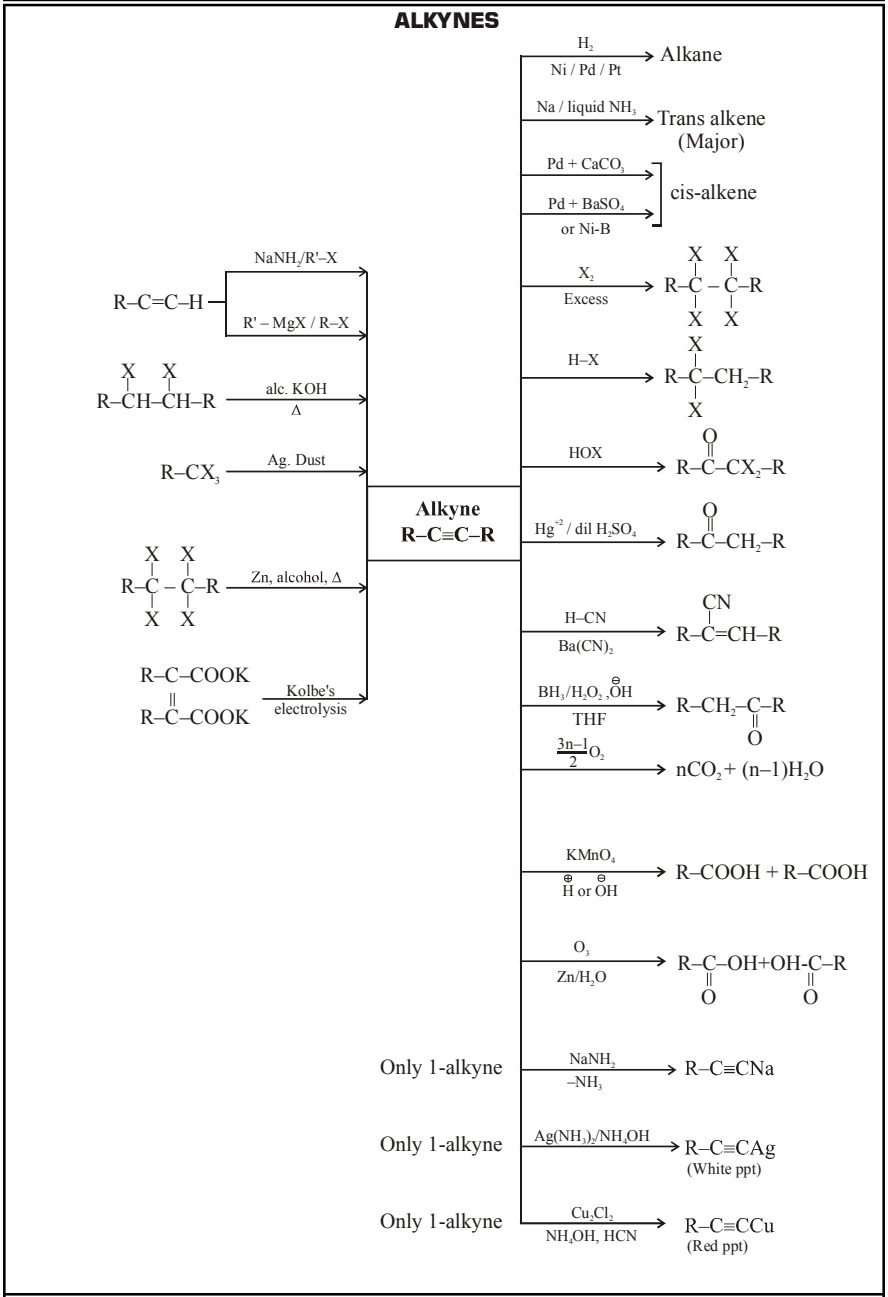
29 Reactions of Organic Chemistry

Alkane

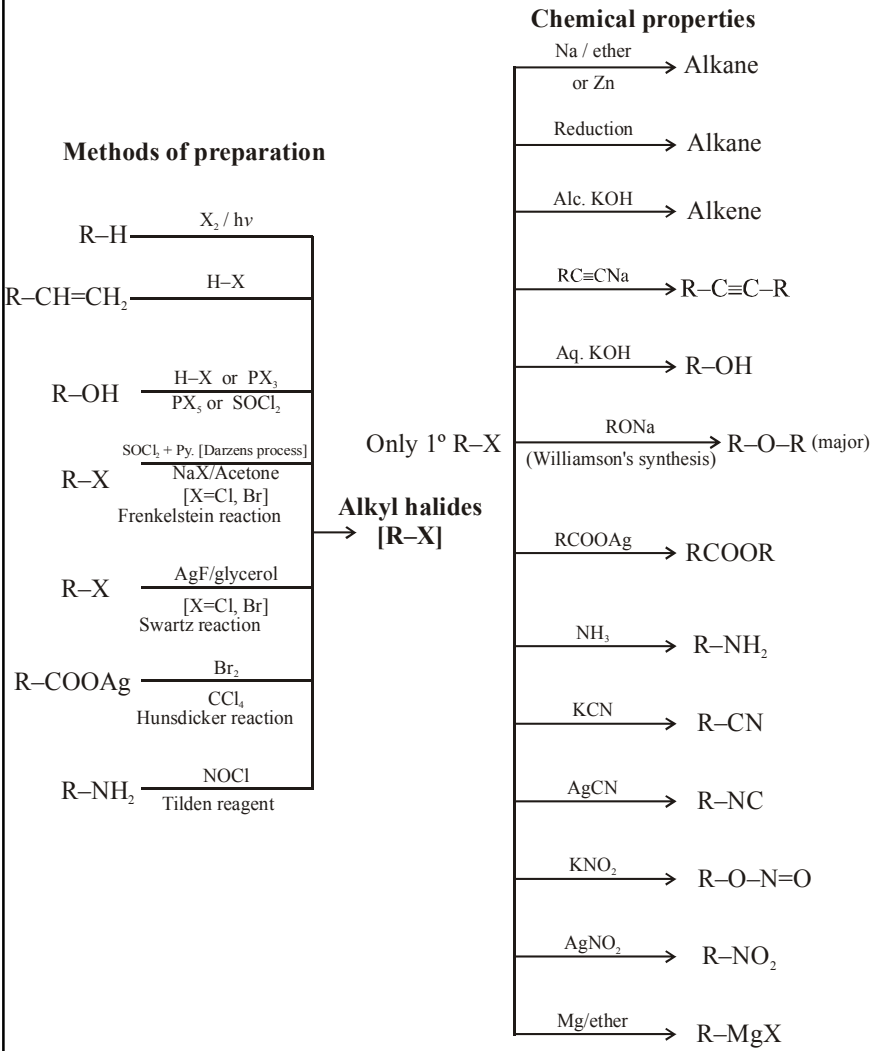


ALKENES

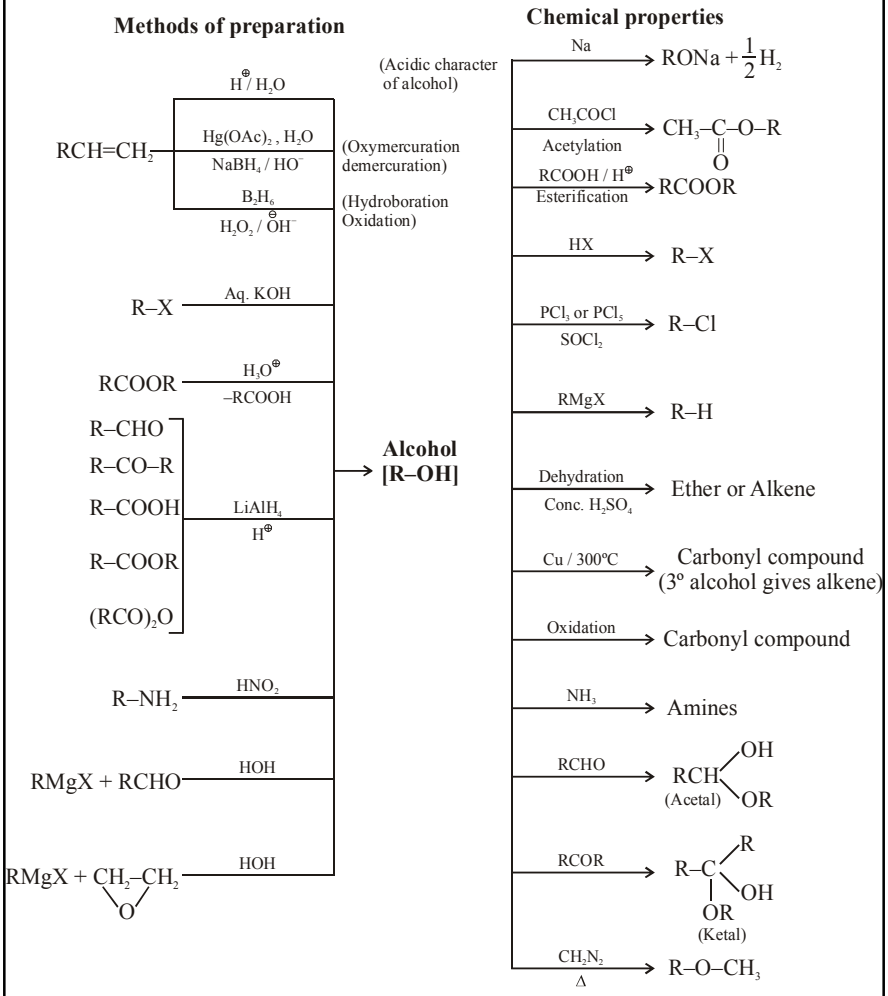

Alkanes
Pyrolysis
600°C
R–X
Alc. KOH
600°C
R–CH–CH2
X X
Zn/Δ
Dehalogenation
R–C≡C–R
Na + Liq NH3
Pd+CaCO3 or
Pd+BaSO4
Ni2 + B
(p-2 catalyst)
cis
R–OH
alcohols
conc. H2SO4 , Δ
H3PO4 or P2O5 , Δ
Al2O3 , Δ
ThO2 , Δ
Pyrolysis of ester
Pyrolysis of tri
alkyl amine oxide
Cope's
elimination
Pyrolysis of tetra
alkyl amm. ion
R–CH–COOK
R–CH–COOK
Kolbe's
electrolysis
Haffamnn's
product i.e.
Less stable
alkene (major
product)
Alkenes
R–CH=CH2
H2
Alkanes
X2
R–CH–CH
X X
H–X
R–CH–CH3
X
HO–X
X
R–CH–CH2
OH
H2O / H⊕
R–CH–CH3
OH
BH3 / H2O2 , ⊖OH
R–CH2–CH2OH
(No rearrangement)
(i) (AcO)2Hg / H2O
(ii) NaBH4 / HO⊖
OH
R–CH–CH3
NO–Cl
Cl
R–CH–CH2–NO
CH2N2 / Δ
Cyclo addition
of carbene
CH2
R–CH–CH2
Cl2/500°C
N.B.S
Allylic
substitution
3n/2 O2
nCO2 + nH2O
dil. KMnO4 / H2O
OsO4 / H2O
Glycol (syn)
Ag + 1/2 O2
Followed by hydrolysis
R–CO3OH
Followed by hydrolysis
Glycol (anti)
O3
Zn/ H2O
Carbonyl compounds



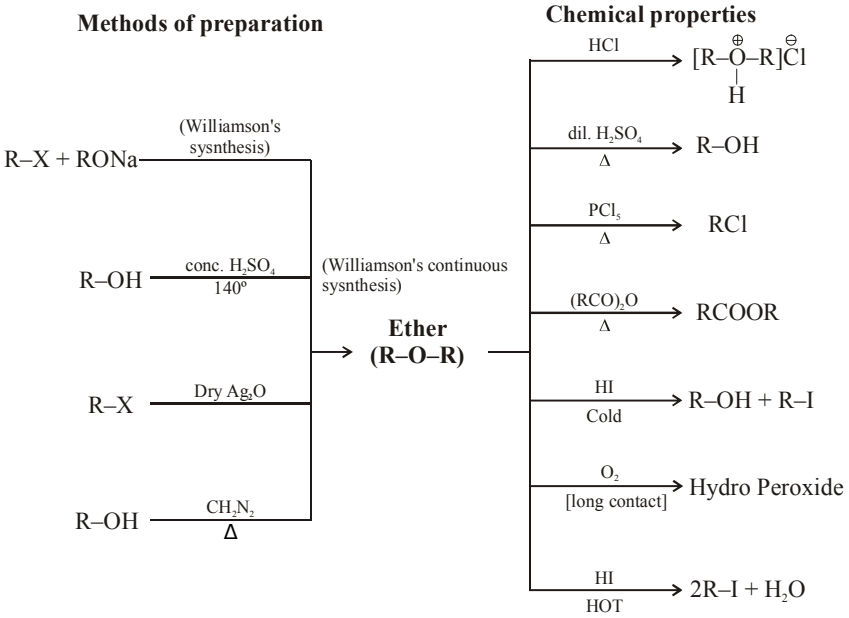
ALKYL HALIDES



ALCOHOL

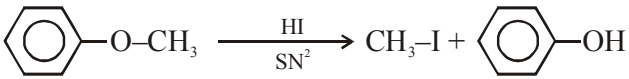


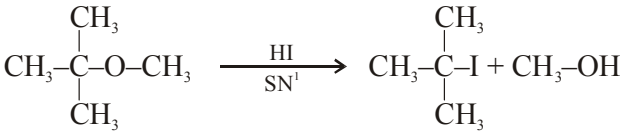
ETHER

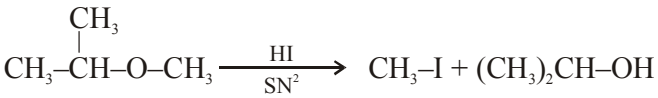


Reaction with cold HI

$$CH_3-O-CH_2-CH_3 \xrightarrow[SN^2]{HI} CH_3-I + CH_3CH_2OH$$

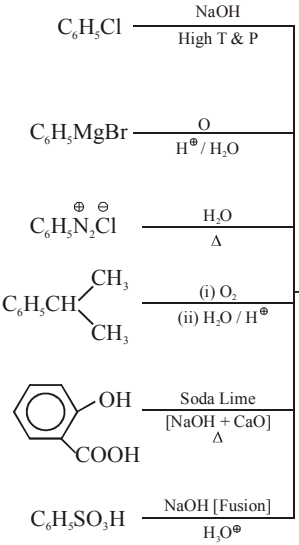






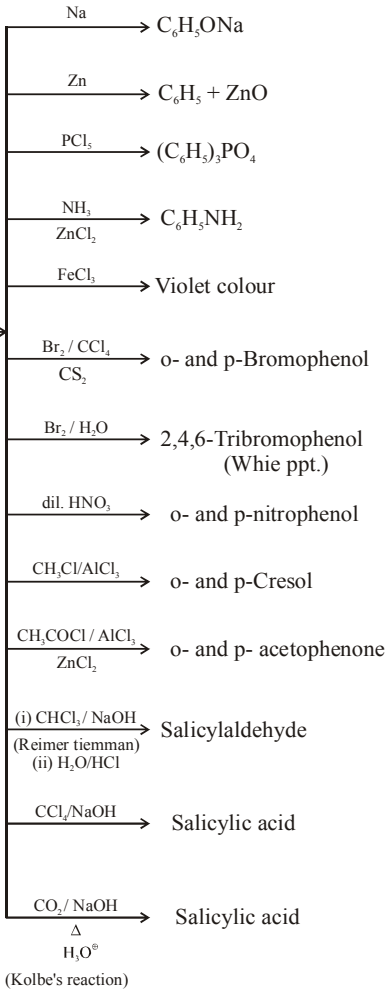
PHENOL

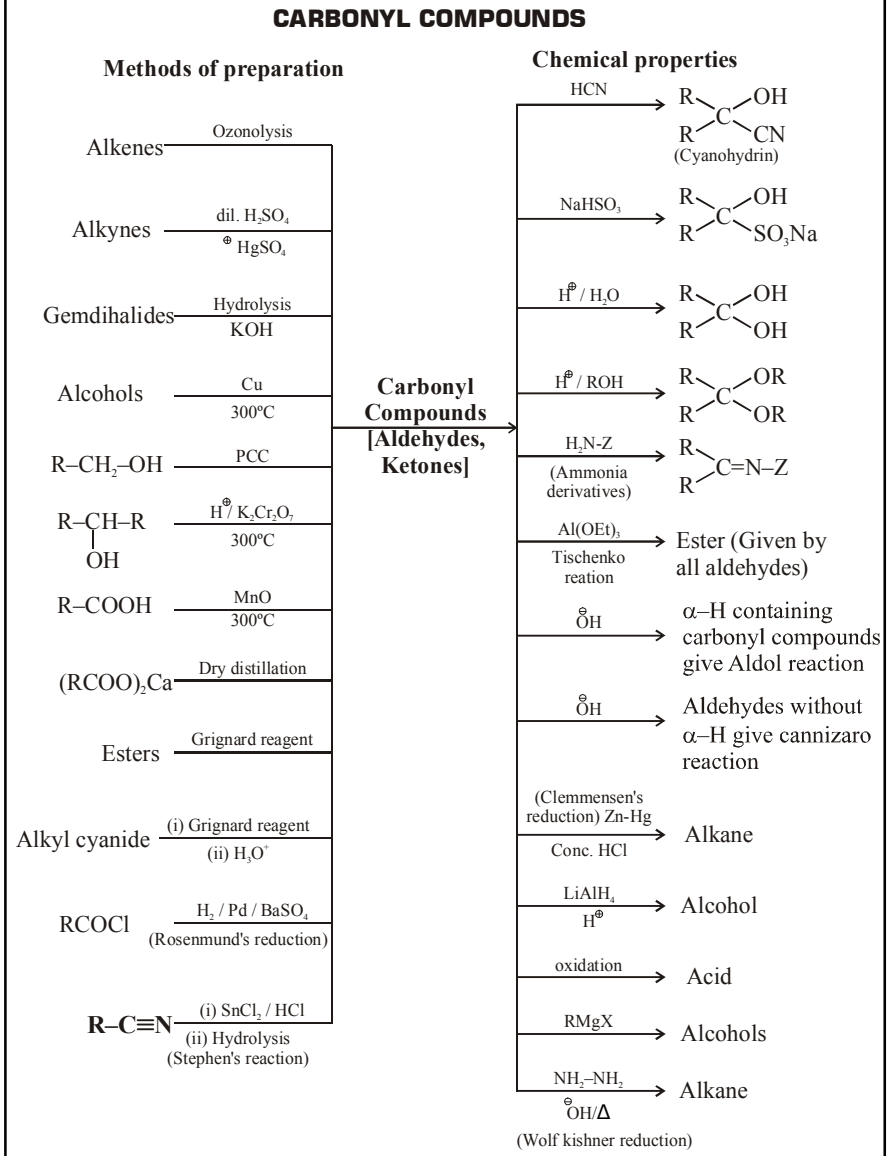
Methods of preparation



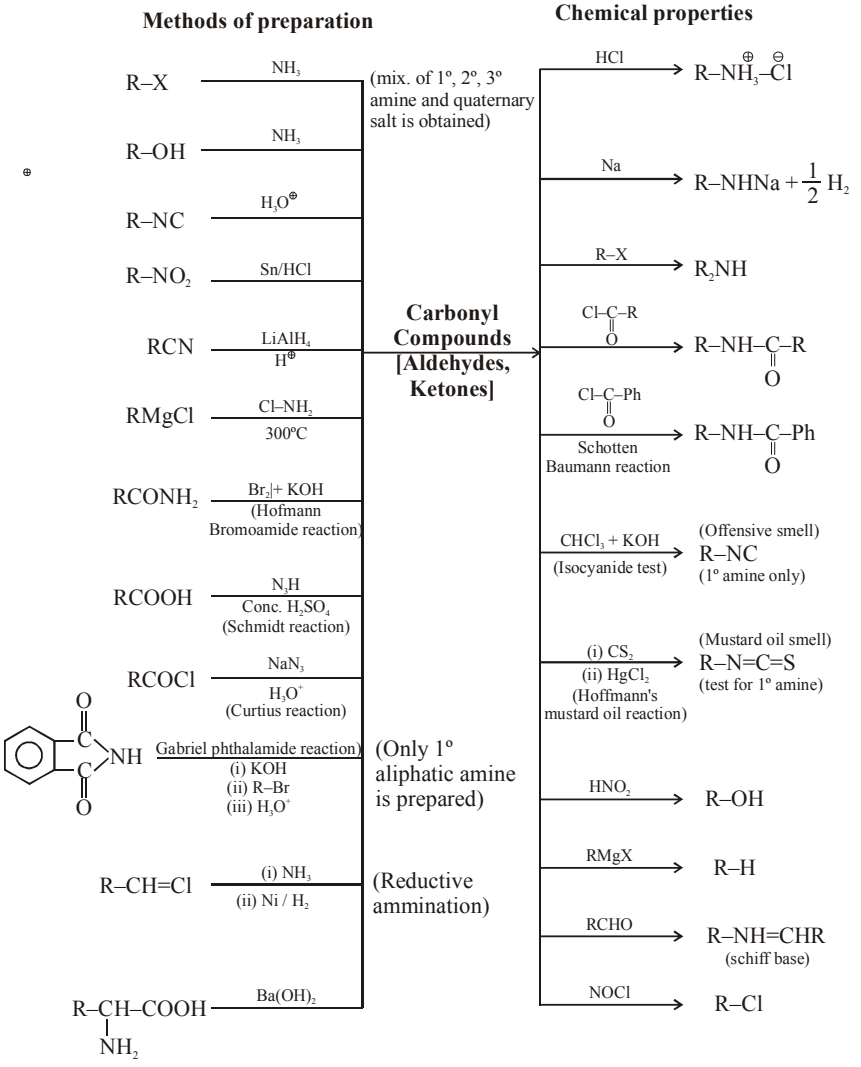
Phenol [C_6H_5OH]

Chemical properties




CARBONYL COMPOUNDS
Methods of preparation
Chemical properties
Alkenes
Ozonolysis
Alkynes
dil. H_2SO_4
$\oplus$ $HgSO_4$
Gemdihalides
Hydrolysis
KOH
Alcohols
Cu
300°C
$R–CH_2–OH$
PCC
$R–\underset{OH}{CH}–R$
$H^{\oplus}$/ $K_2Cr_2O_7$
300°C
R–COOH
MnO
300°C
$(RCOO)_2Ca$
Dry distillation
Esters
Grignard reagent
Alkyl cyanide
(i) Grignard reagent
(ii) H_3O^+
RCOCl
H_2 / Pd / $BaSO_4$
(Rosenmund's reduction)
R–C≡N
(i) $SnCl_2$ / HCl
(ii) Hydrolysis
(Stephen's reaction)
Carbonyl Compounds [Aldehydes, Ketones]
HCN
(Cyanohydrin)
$NaHSO_3$
$H^{\oplus}$ / H_2O
$H^{\oplus}$ / ROH
H_2N-Z
(Ammonia derivatives)
Al(OEt)$_3$
Tischenko reation
Ester (Given by all aldehydes)
$\ominus OH$
α–H containing carbonyl compounds give Aldol reaction
$\ominus OH$
Aldehydes without α–H give cannizaro reaction
(Clemmensen's reduction) Zn-Hg
Conc. HCl
Alkane
$LiAlH_4$
$H^{\oplus}$
Alcohol
oxidation
Acid
RMgX
Alcohols
$NH_2–NH_2$
$\ominus OH/\Delta$
Alkane
(Wolf kishner reduction)

ALIPHATIC COMPOUNDS



ANILINE

Methods of preparation

- $Ph–Cl + NH_3$ —(Cu_2O, high T and P)→ $Ph–NH_2$
- $Ph–OH + NH_3$ —($ZnCl_2$, 300°C)→ $Ph–NH_2$
- $Ph–NC$ —($H_3O^{\oplus}$)→ $Ph–NH_2$
- $Ph–NO_2$ —(Sn/HCl)→ $Ph–NH_2$
- $PhCONH_2$ —(Br_2/KOH)→ $Ph–NH_2$
- $PhCOOH$ —(N_3H, conc. H_2SO_4)→ $Ph–NH_2$
- $PhCOCl + NaN_3$ —($H^{\oplus}/\Delta$)→ $Ph–NH_2$
- $Ph–Mg–Cl + Cl–NH_2$ → $Ph–NH_2$
- $Ph–N=N–Ph$ —(Reduction)→ $Ph–NH_2$

Chemical properties

- $Ph–NH_2$ + HCl → $PhNH_3^{\oplus}Cl^{\ominus}$
- $Ph–NH_2$ + $HAuCl_4$ → $PhNH_3^{\oplus}AuCl_4^{\ominus}$
- $Ph–NH_2$ + Na → $PhNHNa + \frac{1}{2}H_2$
- $Ph–NH_2$ + CH_3I → $Ph–NH–CH_3$
- $Ph–NH_2$ + $Cl–COCH_3$ → $Ph–NH–COCH_3$
- $Ph–NH_2$ + $CHCl_3$–KOH → $Ph–NC$
- $Ph–NH_2$ + CH_3MgCl → $CH_3–H$
- $Ph–NH_2$ + O=CH–R → $Ph–N=CH–R$
- $Ph–NH_2$ + HNO_2 ($[NaNO_2 + HCl]$, 5°C) → $PhN_2^{\oplus}Cl^{\ominus}$
- $Ph–NH_2$ + Br_2/H_2O → 2,4,6-tribromoaniline (white ppt)
- $Ph–NH_2$ + (i) CH_3COCl (ii) Br_2 (iii) H_3O^+ → p-bromoaniline + aniline
- $Ph–NH_2$ + (i) CH_3COCl (ii) NO_2^+ (iii) H_3O^+ → p-nitroaniline + aniline
- $Ph–NH_2$ + HNO_2 ($[NaNO_2 + HCl]$, 10°C) → Phenol
- $Ph–NH_2$ —($CH_3Cl/AlCl_3$)→ No FCR
- $Ph–NH_2$ + conc. H_2SO_4 → sulphanilic acid ⇌ zwitter acid

30 REAGENTS

Nutshell Review and Preview of Organic Reagents

1. Alcoholic KOH

$R–X \longrightarrow$ Alkene;
Elimination

2. Aluminium Ethoxide (Tischenko Reaction)

Aldehyde $\longrightarrow$ Ester

$$RCH{=}O \longrightarrow R–\underset{\underset{O}{\|}}{C}–O–CH_2R$$

3. Aqueous KOH/NaOH

Nucleophillic substitution reaction also used for Cannizzaro reaction
$R–X \longrightarrow ROH$

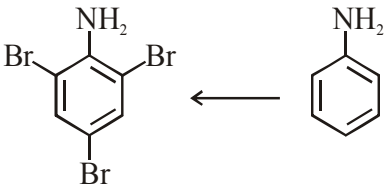
4. Baeyer's Reagent (Alkaline cold dilute $KMnO_4$)
(used to detect unsaturation)
Alkene $\longrightarrow$ 1,2 diol

$$RCH{=}CHR' \longrightarrow RCH(OH)–CHR'(OH)$$

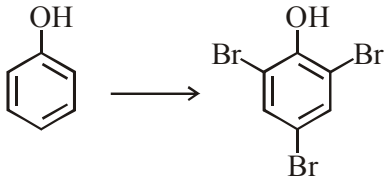
(Syn)

5. Bromine water

(i)



2,4,6-tribromoaniline

(ii) 

2,4,6-tribromophenol

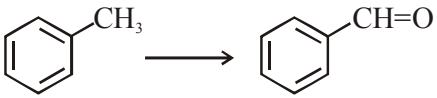
6. **Benedict's solution**
Used to detect aldehyde group

$$RCHO \longrightarrow RCO_2^-$$

[Ketone gives –ve test]

7. **$Cu_2Cl_2 + NH_4OH$ (Used to Detect Terminal Alkyne)**
Red Precipitate observed

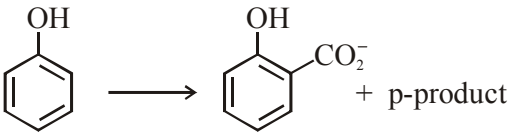
8. **CrO_2Cl_2**
Etard Reaction



9. **CrO_3**

(i) $RCH_2OH \longrightarrow RCHO$
(ii) $R_2CHOH \longrightarrow R_2C{=}O$
(iii) $R_3COH \longrightarrow$ no reaction

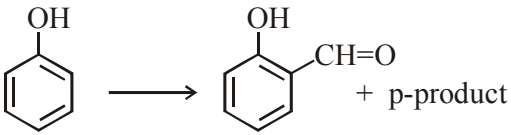
10. **$CCl_4 + \bar{O}H$**



+ p-product

11. $CO + HCl + AlCl_3$

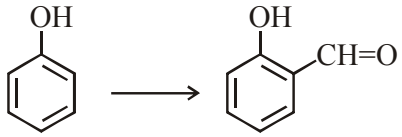
Gattermann Koch reaction



+ p-product

12. $CHCl_3 + KOH$

(i)



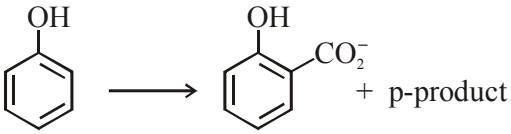
Reimer Tiemann reaction

(ii) $RNH_2 \longrightarrow$ RNC (Carbyl amine reaction)
(used to detect 1° Amine)
(Isocyanide test)

13. $CO_2 + OH^-$

(high temp. + pressure)

Kolbes Reaction

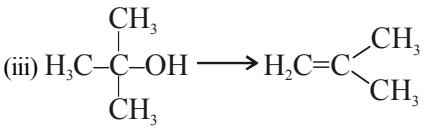


+ p-product

14. **Cu/Δ**

(i) $RCH_2OH \longrightarrow RCHO$

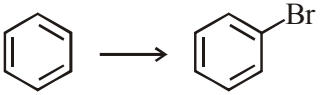
(ii) $R_2CHOH \longrightarrow R_2C{=}O$

(iii) 

15. **2,4 - D.N.P.**
used to detect carbonyl group
(orange ppt observed)

16. **DMSO**
Polar aprotic solvent : favour S_N2 mechanism

17. **$Fe + Br_2/FeBr_3$**

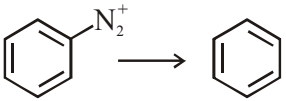


18. **Fehling solution used to identify –CH=O group**
PhCHO gives –ve test
observation: red ppt of Cu_2O formed

19. **Grignard Reagent (Universal reagent)**
Alkane; All types of alcohol;
acids can be prepared

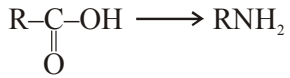
20. **$H_2(Pd/CaCO_3)$ (Lindlar catalyst)**
$R–C\equiv C–R \rightarrow R–CH=CH–R$ (cis)

21. **H_3PO_2**



(Sodium stannite also can be used for this purpose)

22. **$N_3H + H_2SO_4$**



(Schmidt Reaction)

23. **H_3PO_4/Δ**
$H_3PO_4 \Rightarrow$ Same as H_2SO_4/Δ

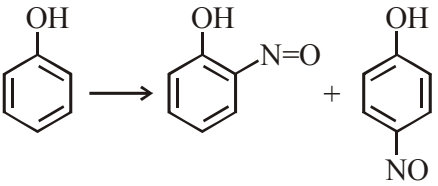
24. **H_2SO_4/Δ**

$$RCH(OH)-CH_3 \longrightarrow RCH=CH_2$$

Saytzeff product; C^+ mechanism;
Rearranged alkene can be formed

25. **$HNO_2(NaNO_2 + HCl)$**

(i) $RNH_2 \longrightarrow R-OH$;
(ii) $PhNH_2 \longrightarrow PhN_2^+$ (0-5ºC)
(iii) $PhNH_2 \longrightarrow PhOH$ (high temperature)

(iv) 

26. **HIO_4 (Periodic acid)**

$$RCH(OH)-CH(OH)-R' \longrightarrow RCH=O + R'CH=O$$

Oxidative cleavage of diol

27. **H_2(Ni) can reduce**

(i) $R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R_2CHOH$

(ii) $R-\underset{\underset{O}{\|}}{C}-H \longrightarrow RCH_2OH$

(iii) $RCN \longrightarrow RCH_2NH_2$,
$-C\equiv C- \longrightarrow -CH_2-CH_2-$,
$-HC\equiv CH- \longrightarrow -CH_2-CH_2-$

28. **$H_2(Pd/BaSO_4)$**
Rosenmund Reduction

$$R-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow RCH=O$$

29. **Jones Reagent** (CrO_3 + dil. H_2SO_4 + acetone)

(i) $RCH_2OH \longrightarrow RCH{=}O$

(ii) $R_2CHOH \longrightarrow R_2C{=}O$

30. **$KHSO_4$**

Dehydrating Reagent

$$CH_2(OH)-CH(OH)-CH_2-OH \longrightarrow CH_2{=}CH-CH{=}O$$

31. **$K_2Cr_2O_7 / H^+$**

(i) $RCH_2OH \longrightarrow RCO_2H$

(i) $R_2CHOH \longrightarrow R_2C{=}O$

32. **MnO_2**

(i) $CH_3-CH{=}CH-CH_2-OH \longrightarrow CH_3-CH{=}CH-CH{=}O$

(ii) $PhCH_2OH \longrightarrow PhCH{=}O$

To oxidise allylic/benzylic hydroxyl group into corresponding carbonyl

33. **$NaHCO_3$**

$$RCO_2H \xrightarrow{NaH^{14}CO_3} RCO_2^-Na^+ + {}^{14}CO_2 \uparrow$$

34. **$NaHSO_3$**

$$R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{OH}{/}}{C}}-SO_3^-Na^+$$

[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

35. **NaOH(aq)**

(i) $R-X \longrightarrow R-OH$

(ii) $$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[(H_2O)]{NaOH} R-\underset{\underset{O}{\|}}{C}-O^- + R'OH$$

Basic hydrolysis of ester

(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$

(cannizaro)

(iv) $H_3C-CH{=}O \xrightarrow[\Delta]{OH^-} H_3C-CH{=}CH-CH{=}O$

(Aldol condensation)

36. **Ninhydrin**
Detection of amino acid
Observation : Purple coloured ion

37. **NaOH**
Strong base :

(i) $RCH(X)-CH_2-R \longrightarrow RCH=CH-R$
(Saytzeff Product : E_2 elimination)

(ii) $H_3C-\underset{\underset{O}{\|}}{C}-OEt \longrightarrow H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$
Claisen condensation (keto ester)

38. **NaOH + X_2**

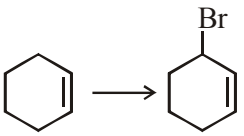
(i) $RC(=O)-CH_3 \xrightarrow[-CHI_3]{} RCO_2^-$
(Haloform reaction)

(ii) $R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow RNH_2$
(Haffman Degradation)

39. **NaOH + CaO (Soda lime)**
$RCO_2H \longrightarrow RH$

40. **NaOX**
Same as NaOH + X_2

41. **NBS (N- bromo succinimide)**

(i) 

(ii) $PhCH_3 \longrightarrow PhCH_2-Br$

42. **$NaNO_2 + HCl$**

$RNH_2 \longrightarrow R\text{–}OH$

43. **$NaNH_2$**

In Paraffin Non-terminal Alkyne $\longrightarrow$ Terminal Alkyne

(2-Butyne $\longrightarrow$ 1-Butyne)

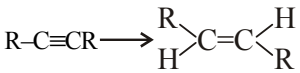
44. **Na/EtOH**

Reduce all except (c = c) double and (C ≡ C) triple bond.

45. **Zn(Hg) + HCl**

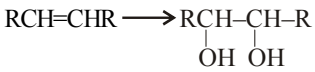
$R\text{–}\underset{\underset{O}{\|}}{C}\text{–}R \longrightarrow R\text{–}CH_2\text{–}R$

46. **Na in liq. NH_3 (Birch Reduction)**



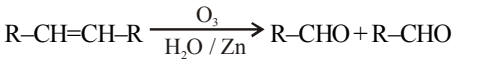
(trans alkene)

47. **$OsO_4 + H_2O$**



(syn addition)

48. **O_3**



(Ozonolysis process)

49. **Oxirane**

followed by H^+ $\quad RMgX \longrightarrow RCH_2\text{–}CH_2\text{–}OH$

50. **PCC** (Mild oxidizing reagent)

(i) $RCH_2OH \longrightarrow RCHO$

(ii) $R_2CHOH \longrightarrow R_2C{=}O$

(iii) $R_3CHO \longrightarrow$ No reaction

51. **P(red) + Br_2**

(i) $CH_3CO_2H \longrightarrow H_2\underset{\underset{Br}{|}}{C}\text{–}CO_2H$

(HVZ reaction)

(ii) $ROH \longrightarrow R\text{–}Br$

52. **P(red) + HI**

(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

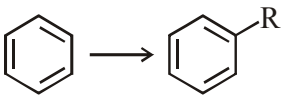
$CH_3CO_2H \longrightarrow CH_3–CH_3$
$CH_3CH{=}O \longrightarrow CH_3–CH_3$
$CH_3CH_2OH \longrightarrow CH_3–CH_3$

53. **Perbenzoic acid** (Baeyer Villiger Oxidation)

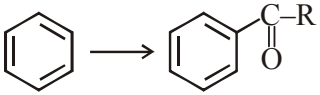
$$R–\underset{\underset{O}{\|}}{C}–R' \longrightarrow R–\underset{\underset{O}{\|}}{C}–OR'$$

R' having more migrating tendency than R

54. $RCl + AlCl_3$ **(Friedel Craft Alkylation Reaction)**



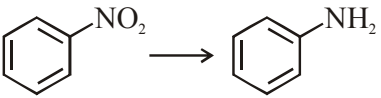
55. $RCOCl + AlCl_3$ **(Friedel Craft Acylation Reaction)**



56. $ROH + R–\underset{\underset{O}{\|}}{C}–OH$ Ester formed

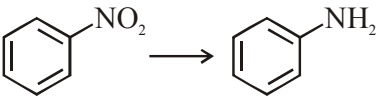
57. $SnCl_2 + HCl$ **(Stephen reduction)**

(i) $R–N{=}N–R' \longrightarrow RNH_2 + R'NH_2$

(ii) 

(iii) $RCN \longrightarrow RCH{=}O$

58. **Sn + HCl**

(i) 

(ii) $RCN \longrightarrow R–CH_2NH_2$

59. Silver salt RCOOAg

$$RCOOAg \xrightarrow[\Delta]{Br_2/CCl_4} RBr + CO_2 + AgBr$$

60. AgOH/moist Ag_2O

$$R_4\overset{+}{N}\overset{-}{X} \longrightarrow R_4\overset{+}{N}\overset{-}{O}H$$

61. $SOCl_2$

$$R-\underset{\underset{O}{\|}}{C}-OH/R-OH \longrightarrow R-\underset{\underset{O}{\|}}{C}-Cl/R-Cl$$

62. Tollens Reagent

$$-CH=O \longrightarrow CO_2^- + Ag$$

(Shining silver mirror)
(I) α-hydroxy ketone,
Ph–NH–OH, HCO_2H gives positive test
(II) Reagent also used to distinguish

(i) $-\overset{\overset{H}{|}}{C}=O$ Vs $-\underset{\underset{O}{\|}}{C}-R$

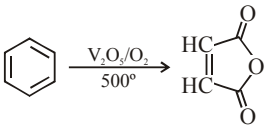
(ii) HCOOH Vs other acid

(iii) ketone gives –ve test

63. Benzene sulphonyl chloride (Hinsberg reagent)
It is used to distinguish and separate 1°, 2° and 3°

64. Tetra ethyl lead
Used as antiknock compound

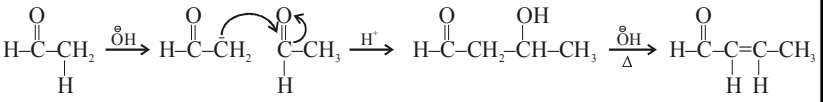
65. V_2O_5



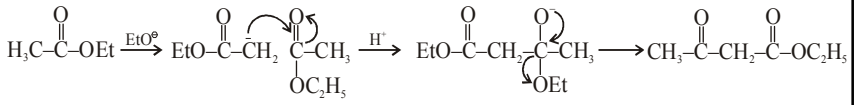
31 Name Reactions

Nutshell Review and Preview of Organic Name Reactions

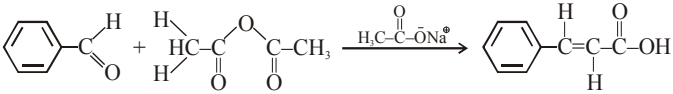
- **Aldol Condensation**



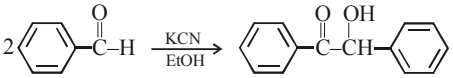
- **Claisen Condensation**



- **Perkin Condensation**

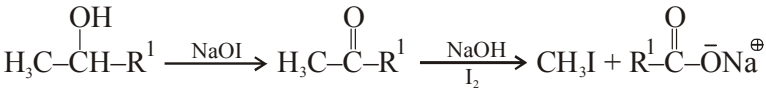


- **Benzoin Condensation**

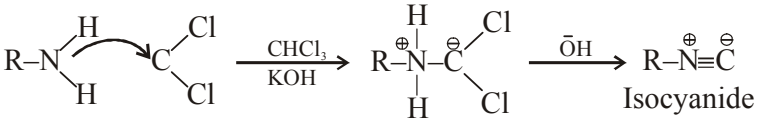


Benzoin

- **Haloform Reaction**

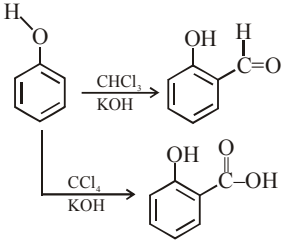


- **Carbylamine Test**

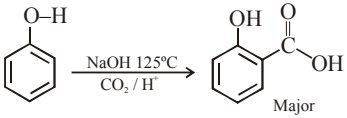


Isocyanide

- **Reimer Tiemman Reaction**



- **Kolbe's Schimdt Reaction**



- **Hoffmann Bromamide Degradation**

$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[KOH]{Br_2} R-NH_2 + K_2CO_3$$

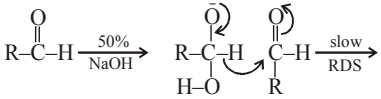
- **Curtius Reaction**

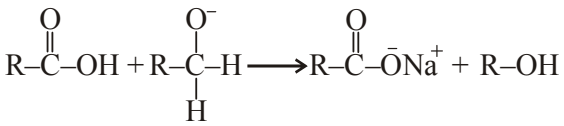
$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\Delta,\ H_3O^+]{NaN_3} R-NH_2$$

- **Schimdt Reaction**

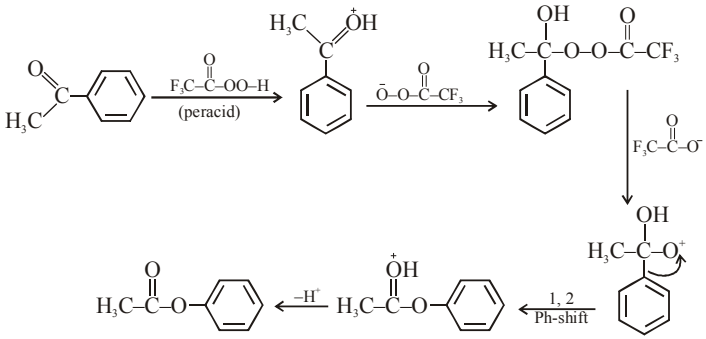
$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[H_2SO_4]{NH_3} R-N=C=O \xrightarrow{H_3O^{\oplus}} R-NH_2$$

- **Cannizzaro Reaction**

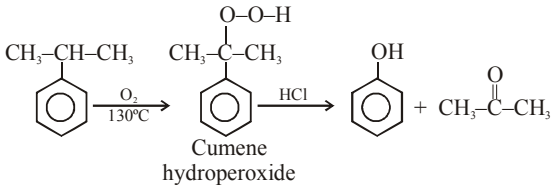




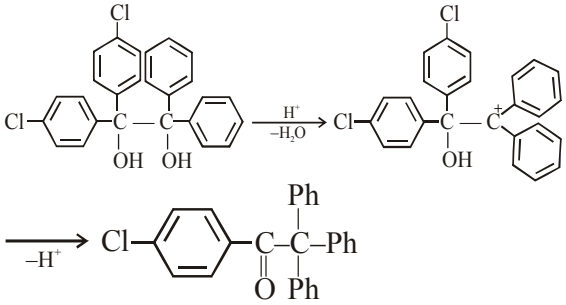
- **Baeyervilliger Oxidation**



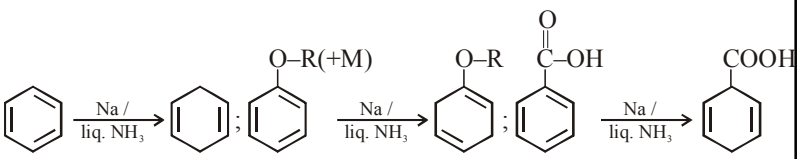
- **Cumene**

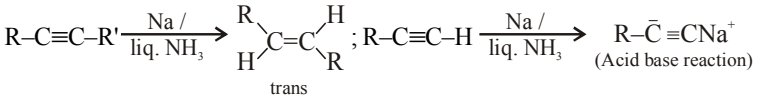


- **Pinacol-Pinacolone rearrangement**

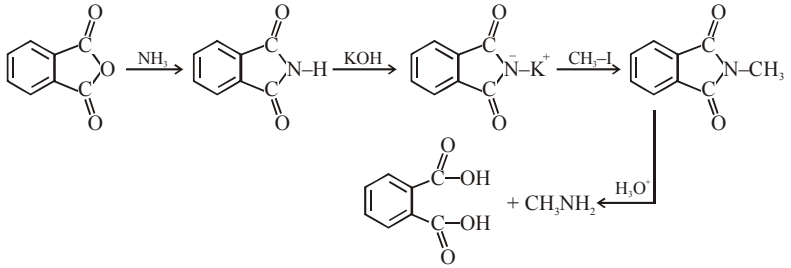


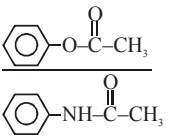
- **Birch Reduction**

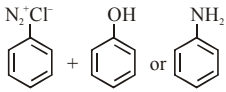
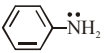
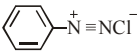
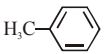
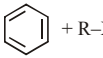
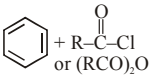




- **Gabriel Synthesis**



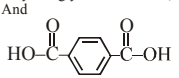
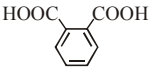
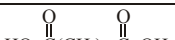
Name	Rectant	Reagent	Product
Sandmeyer reaction	$C_6H_5\overset{+}{N}_2Cl^-$	CuCl/HCl or CuBr/HBr or CuCN/KCN, heat 200-300ºC	Halo or cyanobenzene
Gattermann reaction	$C_6H_5\overset{+}{N}_2Cl^-$	Cu/Hx (HBr/HBr/HBr)	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C_6H_5COCl	
Stephen reaction	alkyl cyanide	$SnCl_2$/HCl	Aldehyde
Williamson synthesis	alkyl halide	Sodium alkoxide or sodium phenoxide	Ether
Wurtz-Fitting reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

Name	Reactant	Reagent	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl.	Alkane
Coupling Reaction		NaOH (phenol) HCl (Aniline)	Azo Dyne (Detection of OH or NH_2 gr)
Diazotization		$NaNO_2$ + HCl 0º-5º C	
Etard Reaction		CrO_2Cl_2/CS_2	 (Benzaldehyde)
Fitting Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation		Anhydrous $AlCl_3$	Alkyl Benzene
Friedel Craft acylation		Anhydrous $AlCl_3$	Acyl Benzene
Gattermann aldehyde synthesis	C_6H_6	HCN + HCl + $ZnCl_2/H_3O^+$	Benzaldehyde
Gattermann-Koch reaction	C_6H_6 (CO + HCl)	anhy $AlCl_3$	Benzaldehyde
Hell-Volhard-Zelinsky reaction	carboxylic acid having α–hydrogen atom	Br_2/red P	α–halogenated carboxylic acid
Hoffmann mustard oil reaction	primary aliphatic amine + CS_2	$HgCl_2/\Delta$	CH_3CH_2– N=C=S + HgS (black)
Hunsdiecker reaction	Ag salt of carboxylic acid	Br_2/CCl_4 , 80ºC	alkyl or aryl bromide
Kolbe electrolytic reaction	alkali metal salt of carboxylic acid	electrolysis	alkane, alkene and alkyne
Mendius reaction	alkyl or aryl cyanide	Na/C_2H_5OH	primary amine
Rosenmund reaction	acid chloride	H_2 , Pd / $BaSO_4$, S, boiling xylene	aldehyde
Sabatier-Senderens reaction	Unsaturated hydrocarbon	Raney Ni/H_2 , 300-400ºC	Alkane

32 Polymers

ADDITION POLYMERS

S.No.	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyolefins			
1.	Polyethylene or Polyethene	$CH_2=CH_2$	Low density homopolymer (Branched chain growth)
2.	Polypropylene or Polypropene	$CH_3CH=CH_2$	Homopolymer, linear, chain growth
3.	Polystyrene or Styron	$C_6H_5CH=CH_2$	Homopolymer, linear, chain growth
II. Polydiences			
1.	Neoprene	$H_2C=CH-\overset{Cl}{\underset{\vert}{C}}=CH_2$ Chloroprene or 2-Chloro-1,3-butadiene	Homopolymer, Chain growth
2.	Buna S (Styrene-Butadiene Rubber SBR or GRS	$H_2C=CH-CH=CH_2$ 1,3-butadiene and $C_6H_5CH=CH_2$ Styrene	Copolymer, chain growth
III. Polyacrylates			
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylite or Perspex PMMA	$H_2C=\overset{CH_3}{\underset{\vert}{C}}-COOCH_3$	Homopolymer
2.	Polyethylacrylate	$H_2C=CH-COOC_2H_5$	Homopolymer
3.	Polyacrylonitrile or Orlon PAN	$CH_2=CH-CN$	Homopolymer
IV. Polyhalofins			
1.	Polyvinyl chloride PVC	$CH_2=CH-Cl$	Homopolymer Chain growth
2.	Polytetrafluoroethylene, or Teflon PTFE	$F_2C=CF_2$	Homopolymer
3.	Polymonochlorotrifluoro ethylene PCTFE	$ClFC=CF_2$	Homopolymer

S.No.	Name of Polymer	Starting Materials	Nature of Polymer
I. Polyolefins			
1.	Terylene or Dacron	$HO–CH_2–CH_2–OH$ Ethylene glycol or Ethane-1,2-diol And  Terephthalic acid or Benzene-1,4-dicarboxylic acid	Copolymer, step growth, linear
2.	Glyptal or Alkyl resin	$HO–CH_2–CH_2–OH$ Ethylene glycol And  Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth
II. Polydiences			
1.	Nylon-6,6	 Adipic acid and $H_2N(CH_2)_6NH_2$ Hexamethylenediamine	Copolymer, linear, step growth
2.	Nylon-6, 10	$H_2N(CH_2)_6NH_2$ Hexamethylene diamine and $HOOC(CH_2)_8COOH$ Sebacic acid	Copolymer, linear, step growth
3.	Nylon-6	 Caprolactum	Homopolymer, linear
Formaldehyde resins			
1.	Phenolformaldehye resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth
2.	Melamine formaldehyde resin	Melamine formaldehyde resin	Copolymer, step growth

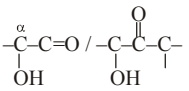
- Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- Monosaccharide ($C_nH_{2n}O_n$) : Single unit, can't be hydrolysed: Glucose and fructose.
- Oligosaccharides gives two to ten monosaccharides on hydrolysis.
- Disaccharides (by glycosydic linkage)

Surcose $\xrightarrow{H_3O^+}$ α-D. Glucose + β-D Fructose

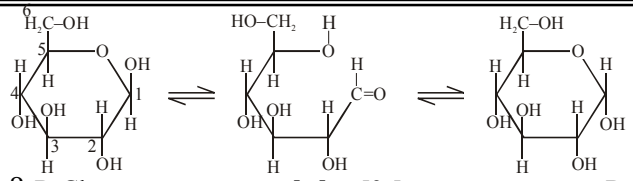
Maltose $\xrightarrow{H_3O^+}$ 2α-D. Glucose unit

Lactose $\xrightarrow{H_3O^+}$ β-D. Glucose unit + β-D. Galactose

- Polysaccharide : Contain more than ten monosaccharide units $(C_6H_{10}O_5)_n$: Starch and Cellulose

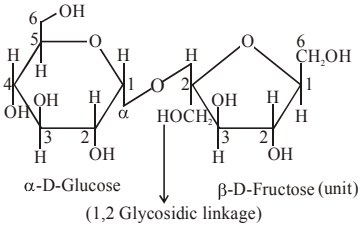
Type of Sugar			
S.No.	**Give Test**	**Reducing**	**Non Reducing**
1.	Tollen's Reagent	+ve test	–ve test
2.	Fehling Reagent	+ve test	–ve test
3.	Benedict Test	+ve test	–ve test
4.	Mutarotation	Yes	No
5.	Functional Unit	  Hemiacetal  Hemiketal	 Acetal  Ketal
6.	Example	All monosaccharides Glucose, Fructose, Mannose, Galactose, Disaccharide, Maltose, Lactose	Disaccharide, Maltose, Polysaccharide, Starch, Cellulose

- **Mutarotation:** When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation ($\pm$ 52.5º) is reached.

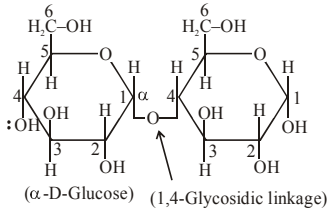


β-D-Glucose $[\alpha]_D = +19°$ | $[\alpha]_0 = 52.5$ $[\alpha]_D = +112°$ | α-D-Glucose

- **Anomer's :** Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new-asymmetric carbon is referred to as Anomeric carbon.
- **Epimer's :** Distereomer's which differ in conformatoin any one chiral carbon.
  eg. D-Glucose and D-monnose
  D-Glucose and D-Galactose
- **Sucrose :**



- **Maltose :**



Two α- D-Glucose unit

- **Lactose :**

(1,4 Glycosidic linkage)

- **Starch :** (Amylose and Amylopectin)
- **Amylose : (Straight Chain):**

(i) Soluble in H_2O and gives blue colour with I_2

- **Amylopectin : (Branch Chain): $(C_6H_{12}O_5)_n$**

(i) Soluble in H_2O.