

## JEE FORMULA NOTES

## **DEPTH Notes with Revision**

# CHEMISTRY

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### The Mole Concept

**One Mole =** Avogadro's Number  $[N_A] = 6.023 \times 10^{23}$ . It is the number of atoms present in exactly 12g of C-12 isotope. **Atomic weight** [A]: Atomic weight is the relative weight of one atom of an element with respect to a standard weight weight of one atom of an element.

 $A = \frac{\text{weight of one atom of an element}}{\frac{1}{12} \text{th part by weight of an atom of C-12}}$ 

isotope u (atomic mass unit) weight:

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

- Atomic Weight (A) × u = Absolute atomic weight...
- Atomic weight is a relative weight that indicates the relative heaviness of one atom of an element with respect to amu weight.
- > Atomic weight has no unit because it is the ratio of weights.
- ➢ One mol of an u =1.00 g

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

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

Where, A = conventional atomic weight.

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

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

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

 $M = A u \times Avogadro number = A g$ 

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

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

Molecular formula	Empirical formula
C <sub>6</sub> H <sub>6</sub> (benzene)	СН
$C_6H_{12}O_6$ (glucose)	CH <sub>2</sub> O
H <sub>2</sub> O <sub>2</sub>	НО
$H_2S_2O_8$	$HSO_4$

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

16g 18g

Here  $H_2$  and  $O_2$  combines in a fixed mass ratio of 1:8.

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

(Stoichiometric mass ratio)

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

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

**Concentration Units** 

**Molarity (M):** It is the moles of solute in one litre of solution.  $M = \frac{n}{v}: n = \text{No. of solute in litre.}$   $\implies \text{Molarity (M) \times \text{Volume(V)} = n(\text{moles of solute})$ If volume is in MI; MV = millimoles. If d g/cc is density of a solution and it contains x% of solute of molar mass M, its

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

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

$$\mathbf{M}_1\mathbf{V}_1 = \mathbf{M}_2\mathbf{V}_2$$

(i)

 $(M_1 \text{ and } V_1 \text{ are the molarity and volume before dilution and } M_2 \text{ and } V_2 \text{ are molarity and volumes after dilution})$ **Mixing of two or more solutions of different molarities:** If two or more solutions of molarities  $M_1, M_2, M_3$ ...... are mixed together, molarity of the resulting solution can be worked out as:

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

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

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

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

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

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

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

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

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



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### **ATOMIC STRUCTURE**

**Rutherford's nuclear model of atom:** Through it  $\alpha$ -particle (He<sup>2+</sup>) scattering experiment. Rutherford presented that ::

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

Plank's equation:

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

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

Centrifugal force of orbiting electrons = Coulombic attraction by nucleus.

$$\implies \qquad \frac{\mathrm{mv}^2}{4} = \frac{\mathrm{Ze}^2}{4\pi\varepsilon_0 r^2}$$

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

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

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

$$KE = -TE = \frac{-PE}{2}$$
  
Speed of electron in nth Bohr's orbit

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

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

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

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

(i) For Lyman series : 
$$n_1 = 1, n_2 > 1(2, 3, 4 \dots )$$

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

Wave-Particle Duality (de-Broglie relationship)

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

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

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

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

$$\implies \qquad \Delta x. \, \Delta p \ge \frac{h}{4\pi}$$

Here  $\Delta x$  is uncertainty in position and  $\Delta p$  is the uncertainty in momentum.

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

(i) Principal quantum number (n): This specify position and energy of an electron in the atom. Possible values of n

are 1, 2, 3, 4 .....∞(positive integers).

(ii) Azimuthal (or even subsidiary) quantum number(*l*): This is used to specify subshell (orbital). Possible values of

'l' are 0, 1, 2, ......(n-1). Orbitals with different 'l' values are denoted as : I = 0, s-orbital, I = 1, p-orbital, I = 2, d-orbital,

1 = 3, f-orbital etc. '*I*' also determine shape of orbitals as:

I = 0, s-orbital, spherical shape.

I = 1, p-orbital, dumb-bell shape

I = 2, d-orbital, double dumb-bell shape.

It determines the orbital angular momentum (L) as:

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

It also determine magnitude of magnetic moment as:

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

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

Its possible values are:

$$m = -l.....0.$$

- Total values of m = (2l + 1) = no. of orbitals in a given orbital.

- Spilliting of spectral lines occurs when placed in a magnetic field (Zeeman effect)

Or in an electric field (Stark effect). Total lines from a single line in the normal spectrum = (2l + 1)

- The total number of orbitals in nth orbit =  $n^2\,$
- The total number of electrons in nth orbit =  $2n^2\,$

(iv) Spin quantum number (s): Electrons spin on its own axis like a top, in clockwise and anticlockwise directions.

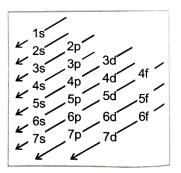
The two directions of spinning are denoted by spin quantum number as:

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

Spin quantum number are also denoted by up-half arrow (1) and down-half arrow (I) but neither the  $+\frac{1}{2}$  and  $-\frac{1}{2}$  nor the 1 l are specific for and direction, they just represent the two opposite directions of spinning of electrons.

#### **Electronic configuration:**

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



(Aufbau principle)

Cr :  $1s^22s^22p^63s^23p^61s^23d^54s^1$ (not  $3d^44s^2$ ) Cu :  $1s^22s^22p^63s^23p^63d^{10}4s^1$ (not  $3d^94s^2$ )

Quantum mechanical model of atom (Schrodinger's equation)

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

"Schrodinger's Equation

Some normalized wave-functions:

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

$$3p_x: \Psi_{2p_x} = \frac{1}{\sqrt{3}} \left(\frac{z}{2a_0}\right)^{\frac{3}{2}} \left(\frac{zr}{a_0}\right) e^{\frac{-Zr}{2a_0}}$$

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

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



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### SOLID STATE

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

C.N.	3	4(T <sub>d</sub> )	4(sp)	6	8
r₊/r_	0.155	0.225	0.414	0.414	0732

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

SC	BCC	FCC	НСР
0.53	0.68	0.74	0.74

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

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

Seven crystal system and cell parameters

System	Parameters	Interaxial angles
Triclinic	a≠b≠c	a ≠ β ≠ γ
Monoclinic	a≠b≠c	a = γ = 90°≠ β
Orthorhombic	a≠b≠c	$a = \beta = \gamma = 90^{\circ}$

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

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

Density(f) = 
$$\frac{NM}{N_{A}\cdot V}$$
  $N_A$  = Avogadro's number, V = volume of unit cell.

**Tetrahedral and octahedral voids:** If there are N particles per unit cell then there will be "2N" tetrahedral voids and "N" octahedral voids.

Point defect:

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

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

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### **CHEMICAL EQUILIBRIUM**

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

 $aA + bB \rightleftharpoons dD + eE$ 

Rate of forward reaction

$$(\mathbf{R}_f) \propto [A]^a [B]^b \implies R_f = k_f [A]^a [B]^b$$

Rate of back ward reaction

 $(\mathbf{R}_b) \propto [D]^d [E]^e \implies R_b = k_b [D]^d [E]^e$ 

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

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

$$\implies \qquad \frac{\mathbf{k}_{\mathbf{f}}}{\mathbf{k}_{\mathbf{b}}} = \frac{[D]^d [E]^e}{[A]^a [B]^b} = \mathbf{K}_{\mathbf{C}}.$$

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

$$K_{p} = \frac{p_{D}^{d} p_{E}^{e}}{p_{A}^{a} p_{B}^{b}}$$

#### Properties of equilibrium constants:

(i) Equilibrium constant ( $K_c$  or  $K_p$ ) is a characteristics constant for a given reaction.

(ii) Equilibrium constant of a reaction does not depend on concentration, pressure, volume, catalyst.(iii) Equilibrium constant depends only on temperature.

(iv) If a reversible reaction is multiplied by a constant factor, equilibrium constant changes as follows:

 $A \rightleftharpoons B K_c \implies aA \rightleftharpoons aB K_c = (K_c)^a$ 

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

$$A \rightleftharpoons B K_c \implies B \rightleftharpoons A K'_c = \frac{1}{K_c}$$

(vi) If reversible reaction are added, equilibrium constants are multiplied:

$$\begin{array}{rcl} A & \rightleftharpoons B & K_1 \\ B & \rightleftharpoons D & K_2 \end{array} \implies A \rightleftharpoons D K = K_1 \cdot K_2 \end{array}$$

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

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

Where,

- $\Delta n = (stoichiometric coefficients of products {stoichiometric coefficients of reactants})$
- eg.  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \Delta n = 0;$   $K_p = K_c = K$   $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g);$  $K_p = K_c = K$

Important: In determining  $\Delta n$ ; species whose active masses are unity, are not considered eg,

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$
  
 $\Delta n = 0 - 2 = -2$ 

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

$$\begin{split} N_2 O_4(g) &\rightleftharpoons 2 N O_2 & \text{Total} \\ 1 - \alpha & 2 \alpha & 1 + \alpha \, ; \\ \alpha &= \text{degree of dissociation} \end{split}$$

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

Partial pressure:  $\frac{1-\alpha}{1+\alpha} p \qquad \frac{2\alpha p}{1+\alpha}$ :

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

$$\implies \qquad \qquad K_{\rm p} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{1-\alpha p}{1+\alpha}\right)} = \frac{4a^2}{1-a^2}$$

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

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g), K = 4$$

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

$$Q = \frac{[HI]^2}{[H_2][I_2]} = 1$$

 $\therefore$  Q < K, reaction will proceed in forward direction to attain the equilibrium.

Similarly if Q < K, reaction will proceed in backward direction to restore equilibrium.

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

(i) Effect of pressure and volume at constant temperature: If for a fixed amount of equilibrium system,

pressure is increased at constant temperature, reaction proceed from more crowded to less crowded side to restore equilibrium.

 $H_2 + I_2 \rightleftharpoons 2HI$   $\Delta n = 0$ ; no effect of pressure

 $2NO_2 \rightleftharpoons N_2O_4 \qquad \Delta n = -1;$ 

Increase in pressure, forward shift.

 $PCl_5 \rightleftharpoons PCl_5 + Cl_2 \Delta n = -1;$ 

Increase in pressure, forward shift. Reverse is true for decreases in pressure.

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

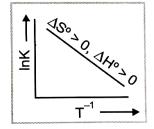
 $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ 

Add  $PCl_5$  —Forward shift Add  $PCl_3$  or Cl2 — Backward shift Remove  $PCl_5$  - Backward shift

Remove  $PCl_3$  or  $Cl_2$  –Forward shift

- (iii) Effect of adding "Inert Gas": If an inert gas is added at constant volume, if does not affect equilibrium composition anyway. If an inert gas is added at constant pressure, it has the same effect as of increasing volume ie, reaction proceeds towards more crowded side.
- (iv) Effect of catalyst: A catalyst has no effect on equilibrium however it speed up both forward and backward reaction and reduces the time required to attain equilibrium.
- (v) Effect of temperature: Increasing temperature increases the equilibrium constant (K) of an endothermic reaction ie, forward reaction is favored. Decreasing temperature increase equilibrium constant (K) of an exothermic reaction and forward reaction is favored.

#### **Equilibrium and Thermodynamics:**



 $\Delta G^{\circ} = -RT \text{ In } K = \Delta H^{\circ} - T\Delta S^{\circ}$  $\implies \text{ In } K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$ 

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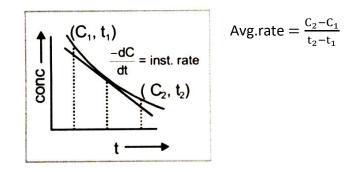
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### **CHEMICAL KINETICS**

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



**Rate law:**  $aA+bB \rightarrow dD + Ee$ Inst – Rate

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

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

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

**First order reaction** :  $A \rightarrow P$ 

 $\frac{-d[A]}{dt} = k[A] = [A] = [A]_{0}e^{-kt}$ Half –life  $(t_{1/2}) = \frac{\ln 2}{k}$  independent of initial amount of reactant.

- (ii) Both concentration (A) and rate decreases exponentially with time.
- (iii) Reaction complete in infinite time.
- (iv) All radioactive process are first order.

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n^{th} order reaction : A \rightarrow P
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$$\frac{-d[A]}{dt} = k[A]^n \implies kt = \frac{1}{(n-1)} \left[ \frac{1}{[A]^{n-1}} - \frac{1}{[A]^{n-1}} \right]$$

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

Effect of temperature on rate: Increasing temperature increases the rate of reaction. Rate constant is related to

Temperature by Arrhenius equation as

$$k = Ae^{-\frac{E_a}{RT}} OR In k = In A - \frac{E_a}{RT}$$

 $E_a = Activation energy$ 

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

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

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

 $k_c =$  rate constant for catalyzed path

 $k_{uc}$  = rate constant for uncatalyzed, path

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

Parallel first order reaction:

$$A \xrightarrow{k_1} B \xrightarrow{d[B]} = k_1[A]$$

$$A \xrightarrow{k_2} C \xrightarrow{-d[A]} = k_3[A]$$

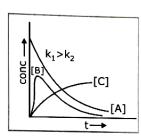
$$B \xrightarrow{d[C]} = k_2[A]$$

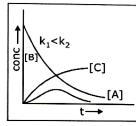
$$B \xrightarrow{d[C]} = k_2[A]$$

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

#### **Consecutive first order reaction:**

 $A \xrightarrow{K_1} B \xrightarrow{K_2} C$  $\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}\mathrm{t}} = \mathrm{k}_1(\mathrm{A}) - \mathrm{k}_2(\mathrm{B})$  $[B] = \frac{k_1[A]_0}{k_2 - k_1} \left[ e^{-k_1 t} - e^{-k_2 t} \right]$  $t_{\max} = \frac{1}{k_2 - k_1} \ln \left( \frac{k_2}{k_1} \right)$  $[B]_{\max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1-k_2}}$  $A \rightleftharpoons P$ a – x x  $\frac{\mathrm{dx}}{\mathrm{dt}} = \mathrm{k}_1(\mathrm{a} - \mathrm{x}) - \mathrm{k}_2 \mathrm{x}$  $\implies$   $t = \frac{1}{k_1 + k_2} \ln \left[ \frac{k_1 a}{k_1 a - (k_1 + k_2)x} \right]$ 





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### COLLIGATIVE PROPERTIES OF DILUTE SOLUTION

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

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

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

**Elevation of boiling point (Ebullioscopy):** Addition of a non-volatile solute to a volatile solvent increases the boiling point of solution and  $\Delta T_{b} = K_{b}$ . m

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

K<sub>b</sub> = molal elevation constant (ebullioscopic constant), a characteristics of solvent and determined as

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

 $T^{o}_{b} = Boiling point of solvent$ 

 $\Delta H_{M_V}$  = Molar enthalpy of vaporization of solvent.

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

$$\Delta T_{\rm f} = T^{\circ}_{\rm f} - T_{\rm f} = K_{\rm f} m$$

 $T_{f}^{o}$  = freezing point of pure solvent,  $T_{f}$  = freezing point of solution, m = molarity of solution and  $K_{f}$  = molal depression (cryos copic) constant, characteristics of solvent.

$$K_f = \frac{M_1 R (T^\circ_f)^2}{\Delta H_{mf}} M_1$$
 = Molar mass of solvent  $\Delta H_{mf}$  = molar enthalpy of fusion of solvent.

Osmosis and osmotic pressure ( $\pi$ ):

 $\pi = CRT = hfg$ 

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

**Binary solution:** When two volatile solvents A and B with their vapour pressures  $p^{\circ}_{A}$  and  $p^{\circ}_{B}$  are mixed, the resulting solution is known as binary solution hose vapour pressure lies between  $p^{\circ}_{A}$  and  $p^{\circ}_{B}$  and determined as

 $p = p_A + p_B = x_A p^{\circ}_A + x_B p^{\circ}_B$  ......(a)

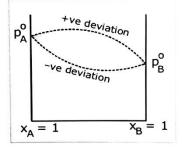
Where,  $x_A$  and  $x_B$  are mole fractions of A and B in solution. The mole fractions of A and B in the vapour phase are  $y_A$  and  $y_B$  then

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

and

**Ideal and non-ideal solution:** It the solution obey Raoult's law ie, equation a, it is called ideal binary solution otherwise non-ideal binary solution.

(i) If the observed vapour pressure is greater than the ideal vapour pressure, it is known as positive (+) deviation.(ii) If the observed vapour pressure approaches to ideal curve on dilution hence dilution decreases the extent of deviation.



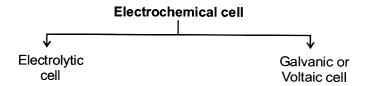


## JEE FORMULA NOTES

## **DEPTH Notes with Revision**

# CHEMISTRY

### **ELECTROCHEMISTRY**



#### Faraday's Law of electrolysis:

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

 $W \propto Q$ , where,  $Q = \frac{I}{t}$ , I =current strength

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

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

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

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

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

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

 $\implies \frac{W_1}{W_2} = \frac{E_1}{E_2} W_1 \text{ and } W_2 \text{ are weight of electrolytes discharged at two different electrodes in two different cells connected in series and E_1 and E_2 are their respective equivalent weights.}$ 

#### Galvanic cell

**EMF:** It is the potential difference across the electrodes.

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

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

 $Ag^+ + e^- \rightarrow Ag \quad E^\circ = 0.80 \text{ V}$  $2Ag^+ + 2e^- \rightarrow 2Ag \quad E^\circ = 0.80 \text{ V}$  Multiplying an equation by a constant

factor do not change E°.

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

(iii) Half-cell with smaller E° constitute anode and half-cell with larger E° constitute cathode eg, in Daniell cell,  $E^{\circ}_{Zn^{2+}/Zn} = -0.76 \text{ V}$  and  $E^{\circ}_{\frac{Cu^{2+}}{Cu}} = 0.34 \text{ V}$ . Hence, Zn electrode is anode and Cu electrode is cathode and  $E^{\circ}_{cell}$  is

1.10 V.

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

Gibbs Free Energy and 'E':  $\Delta G = -nEF$ In standard state,  $\Delta G = -nE^{\circ}F$ The Nernst's equation:

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

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### **DEPTH Notes with Revision**

# CHEMISTRY

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## Equivalent Weight and Neutralization Titration

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

$$(EW) = \frac{\text{molar mass}}{\text{net positive (or negative )valency}}$$
eg, EW : CaCl<sub>2</sub> =  $\frac{M}{2}$ , AlCl<sub>3</sub> =  $\frac{M}{3}$ , Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> =  $\frac{M}{6}$   
Equivalent weights of acids and bases:  
EW of acids =  $\frac{\text{molar mass}}{\text{basicity}}$   
eg, EW : HCl = M(basicity = 1);  
H<sub>2</sub>SO<sub>4</sub> =  $\frac{M}{2}$ (basicity = 2)  
H<sub>3</sub>PO<sub>4</sub> =  $\frac{M}{3}$ (basicity = 3)  
EW of bases =  $\frac{\text{molar mass}}{\text{acidity}}$   
Eg, EW : NaOH = M, Ca(OH)<sub>2</sub> =  $\frac{M}{2}$ ; Al(OH)<sub>3</sub> =  $\frac{M}{3}$   
The number of gram-equivalents (Eq):  
Eq =  $\frac{\text{weight of compound}}{\text{equivalent weight}} = \frac{W}{EW}$ 

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

 $n = \frac{w}{M}$  and  $Eq = \frac{w}{EW} \implies \frac{Eq}{n} = \frac{M}{EW} = n - factor$ 

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

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

Normality /Molarity relationship:

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

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

Gram equivalent of acid = Gram equivalent of base

**Titration of a mixture of NaOH/Na** $_2$ **CO** $_3$ **:** The mixture is analyzed by titrating against a standard acid in presence of phenolphthalein and methyl orange indicators. Phenolphthalein end point occur when the following neutralization is complete.

 $\begin{array}{l} \text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} \\ \text{Na}_2\text{CO}_3 + \text{HCl} \longrightarrow \text{NaHCO}_3 + \text{NaCl} \end{array} \} \text{ mmol (HCl)} = \text{mmol(NaOH} + \text{Na}_2\text{CO}_3) \end{array}$ 

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

$$\begin{split} & \text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} \\ & \text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \ \} \text{ methyl orange end point, mmol (HCl)} \\ & = \text{mmol} \ (\text{NaOH}) + 2\text{mmol of} \ (\text{Na}_2\text{CO}_3) \end{split}$$

**Titration of a mixture of NaHCO\_3/Na\_2CO\_3:** The mixture is analyzed by titrating against a standard acid in presence of phenolphthalein and methyl orange indicators.

Phenolphthalein end point occur when the following neutralization is complete:

 $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl \}mmol (HCl)$ = mmol(Na<sub>2</sub>CO<sub>3</sub>) Methyl orange end point occur when the following neutralization is complete:

 $\begin{array}{l} Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2 \\ NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2 \end{array} \} \text{ methyl orange end point, mmol (HCl) = } \\ mmol (NaHCO_3) + 2mmol of (Na_2CO_3) \end{array}$ 

Percentage strength of oleum: It is the mass of  $H_2SO_4$  obtained on hydrolysis of 100 g of oleum as :

 $\begin{array}{c} H_2S_2O_7 + H_2O \longrightarrow H_2SO_4\\ \text{The net reaction is :}\\ SO_3 + H_2O \longrightarrow H_2SO_4\\ 80 \quad 18 \quad 98\\ \Rightarrow \% \text{ of free SO}_3 \text{ in oleum} = \frac{80}{18} \ (\% \text{ strength} - 10) \end{array}$ 



## **DEPTH Notes with Revision**

# CHEMISTRY

#### **GASEOUS STATE**

Pressure(p) =  $\frac{\text{Force}}{\text{Area}}$ Nm<sup>-2</sup> 1.0 Nm<sup>-2</sup> = 1 Pa (Pascal) 1.0 atmosphere = 101325 Pa = 10<sup>5</sup>Pa = 76cm of Hg column = 760 mm of Hg = 760 torr ( $\therefore$  1 mm of Hg = 1 torr) **Temperature (T)** : Absolute temperature (or Kelvin temperature) = ( $t^{0}$ C + 273)K **Boyle's law**: At constant temperature, for a definite amount of gas pV = constant (p vs V follow a rectangular

hyperbolic path)

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

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

Avogadro's hypothesis: At same temperature and pressure:

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

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

$$= 2 \text{ cal } \text{K}^{-1} \text{ mol}^{-1}$$

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

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

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

Where,  $p_1$ ,  $p_2$ ,  $p_3$  ...... etc. are the partial pressure of various components of the mixture.

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

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

Here  $x_i$  =mole fraction of the component

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

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

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

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

 $(M_1 \text{ and } M_2 \text{ are molar masses})$  If mixture contains different moles of gases then:

$$\frac{\mathbf{r}_1}{\mathbf{r}_2} = \frac{\mathbf{n}_1}{\mathbf{n}_2} \sqrt{\frac{\mathbf{M}_2}{\mathbf{M}_1}}$$

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

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

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

#### Kinetic gas equation:

 $pV = \frac{1}{3} mNC^{-2} \qquad (C^{-2} \text{ is mean square speed})$ Average translational kinetic energy E =  $\frac{3}{2}K_bT$ (K<sub>b</sub> = Boltzmann's constant = 1.38 × 10<sup>-23</sup>)

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

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

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

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

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

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

**Real gas :** Gases that to not obey pV = nRT equation of state. Compression (compressibility) factor (Z)

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

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

If Z < 1, net-intermolecular attraction exist and if Z > 1, net intermolecular repulsion exist. Vander Walls's equation :

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

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

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

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

**Boyle's temperature:**  $T_B = \frac{a}{Rb}$  (At Boyle temperature, a non-ideal gas becomes an ideal gas) **Critical points:** Critical volume (V<sub>c</sub>) = 3b Critical temperature (T<sub>c</sub>) =  $\frac{8a}{27Rb}$  (temperature above which only gaseous state exist) Critical pressure (p<sub>c</sub>) =  $\frac{a}{27b^2}$ At critical point  $Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8}$ 



## **DEPTH Notes with Revision**

# CHEMISTRY

#### **IONIC EQUILIBRIUM**

pH and pOH of acids and bases  $pH = -log[H^+]$  and  $pOH = -log[OH^-]$ for any solution; pH + pOH = 14 at 25° C

 $\begin{array}{ll} \mbox{Weak acid HA} \ensuremath{\approx} & \mbox{H}^+ + \mbox{A}^- & \mbox{\alpha} \mbox{K}_a = \frac{\mbox{C} \ \alpha^2}{1-\alpha} \\ \mbox{C}(1-\alpha) & \mbox{C} \alpha & \mbox{C} \alpha \end{array}$ 

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

$$\implies \quad \alpha = \sqrt{\frac{k_a}{c}} \,\, \text{Ostwald's law}$$

According to the Ostwald's, degree of ionization of weak electrolyte increases with dilution. As C ightarrow 0, lpha 
ightarrow 1

$$\begin{split} &\text{If } 1 - \alpha \approx 1, \text{K}_{a} = \frac{[\text{H}^{+}]^{2}}{\text{C}} \implies [\text{H}^{+}]\sqrt{\text{K}_{a}\text{C}} \\ &\text{In case of weak base:} \\ &\text{B(OH)} \ \rightleftharpoons \ \text{B}^{+} + \text{OH}^{-}, \ \text{K}_{b} = \frac{\text{C}\alpha^{2}}{1 - \alpha} \end{split}$$

$$\begin{split} K_{h} &= \frac{K_{w}}{K_{a}} = \frac{C\alpha^{2}}{1-\alpha} \\ \text{If "a" is small,} [OH^{-}] &= \sqrt{K_{h}C} \\ \text{(iii) Salt of strong acid and weak base eg, NH_{4}Cl --acidic salt} \\ NH_{4}^{+} + H_{2}O &\rightleftharpoons NH_{4}OH + H^{+} \\ C(1-\alpha) & C\alpha & C\alpha \\ \\ K_{h} &= \frac{K_{w}}{K_{b}} = \frac{C\alpha^{2}}{1-\alpha} \end{split}$$

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

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

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

(Independent of salt concentration)

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

Acid buffer: Formed by mixing weak acid with salt of its conjugate base eg,  $CH_3COO$  and  $CH_3COONa$ , HCN & NaCN, HF and  $CaF_2$  etc.

$$\mathsf{pH} = \mathsf{pK}_\mathsf{a} + \mathsf{log}\frac{[\mathsf{salt}]}{[\mathsf{acid}]}$$

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

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

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

AgCl(s) 
$$\rightleftharpoons$$
 Ag<sup>+</sup> + Cl<sup>-</sup>  
Solubility: S S S  
 $K_c = K_{sp} = [Ag^+][Cl^-] = S^2$   
 $PbCl_2 \rightleftharpoons Pb^{2+} + 2 Cl^-$   
 $S 2S$   
 $K_{sp} = [Pb^{2+}][Cl^-]^2 = S[2S]^2 = 4S^3$   
 $M_xN_y \rightleftharpoons xM + yN$   
 $xS \gamma S$   
 $K_{sp} = (xS)^x(yS)^y = x^xy^y(S)^{x+y}$ 



### **DEPTH Notes with Revision**

# CHEMISTRY

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### REDOX REACTION AND REDOX TITRATION

**Oxidation :** Loss of electron or increases in oxidation number of oxidation.

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

In the above redox reaction, chromium is reduced from + 6 to + 3 and iron is oxidized from + 2 to +3. Hence,  $K_2Cr_2O_7$  is known as oxidizing agent (itself reduced) and FeSO<sub>4</sub> reducing agent (itself oxidized).

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

$$\Delta ON = 1$$

$$K_2 Cr_2 O_7 + Fe^{2+} \rightarrow 2Cr^{3+} + Fe^{3+}$$

$$\Delta ON = 12 - 6$$

on

Hence, multiplying  $Fe^{2+}$  by 6 and  $K_2Cr_2O_7$  by 1 will balance the reaction in terms of OA and RA.

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

$$Br_2 + NaOH \rightarrow NaBr + NaBrO_3$$

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

#### Equivalent weight of OA/RA:

Equivalent weight of

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

eg,  $KMnO_4 + H^+ \rightarrow Mn^{2+}$ ;  $E = \frac{M}{5}$   $K_2Cr_2O_7 + H^+ \rightarrow Cr^{3+}$ ;  $E = \frac{M}{6}$   $2 KI \rightarrow I_2 + 2K^+$ ;  $E = M(\Delta ON \text{ per } I^- = 1)$  $2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2Na^+$ ;  $E = M(\Delta ON \text{ per } Na_2S_2O_3 = 1)$ 

n – factor and normality/molarity relationship:

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

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

Redox titration: At the end point:

Gram equivalents of OA = Gram equivalent of RA.



## **DEPTH Notes with Revision**

# CHEMISTRY

### THERMOCHEMISTRY

**Standard molar enthalpy of formation**  $(\Delta H_{fm}^0)$ : It is the enthalpy change associated with the formation of one mole of a substance in the standard state from the constituent elements in their standard state. It can be either positive or negative.

**Standard molar enthalpy of combustion**  $(\Delta H^0_{comb})$ : It is the heat evolved when one mole of a substance in the standard state is oxidized completely.  $\Delta H^0_{comb}$  is always negative.

**Standard enthalpy of a reaction**  $(\Delta H^0_{rxn})$ : It is the net enthalpy change associated with a reaction. It is determined with the help of  $\Delta H^0_f$  of reactants and products or from  $\Delta H^0_{comb}$  of reactants and products

 $\Delta H_{rxn}^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$ 

or  $\Delta H_{rxn}^0 = \sum \Delta H_{comb}^0$  (reactants)  $-\sum \Delta H_{comb}^0$  (products)

Also,  $\Delta H_f^0$  of pure element in its standard state is zero.

#### Some properties of enthalpy change:

(i) It is an extensive property ie, when a reaction is multiplied by a constant factor, enthalpy is also multiplied by the same factor.

(ii) It is a state function, ie. It does not depend on path it depends on initial and final stage of system.

(iii) Reversing a chemical reaction reverse the sign of enthalpy change.

(iv) Hess's law of constant heat of summation:

$$\Delta H_1 \stackrel{B}{\stackrel{\Delta H_2}{\stackrel{}}} \xrightarrow{C} \Delta H_3$$

$$A \stackrel{\Delta H}{\stackrel{}} \xrightarrow{P} P$$

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

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

 $q = ms\Delta T$ 

Where, m = mass of calorimeter content

S = specific heat of calorimeter content

 $\Delta T$  = change temperature of calorimeter

#### Bond dissociation energy and bond-enthalpy:

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

**Bond enthalpy of a compound:** It is the total energy required to convert one mole of a gaseous substance into their constituent atoms. In term of bond-enthalpy,

 $\Delta H_{rxn}^0$  can be determined as:

 $\Delta H_{rxn}^0 = \sum BE(reactants) - \sum BE(products)$ 

**Resonance energy:** It is the difference in enthalpy change ( $\Delta H$ ) between one determined experimentally

(calorimetrically) and other calculated theoretically.

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

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

Enthalpy of hydration  $(\Delta H_{hyd}^0)$ : It is the heat evolved when one mole of a substance is hydrated to a certain specific degree of hydration eg.

 $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)\Delta H^0$ 

Hence,  $\Delta H^0$  above is enthalpy of hydration of anhydrous  $CuSO_4(s)$  to its pentahydrate.

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

 $Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \Delta H = U_0$ 



## **DEPTH Notes with Revision**

# CHEMISTRY

### THERMODYNAMICS

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

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

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

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

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

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

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

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

#### **Reversible an Irreversible processes**

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

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

#### Intensive and extensive properties

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

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

**State function:** Those functions which do not depend on the path followed during the change. It depends only on the initial and the final state of system eg, internal energy, enthalpy, entropy Gibb's free energy, standard state emf etc. Properties like heat, work etc depends on path and they are non-state (path) functions.

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

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

where,  $\Delta E = Change$  in internal energy

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

In irreversible isothermal expansion:

 $q = -W = P_{ext} \Delta V (\Delta E = 0)$ 

In reversible isothermal expansion:

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

In adiabatic process:

$$-W = -\Delta E = -nC_{\nu}\Delta T = nC_{\nu}(T_1 - T_2)$$

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

$$TV^{\lambda-1} = constant$$
 and  $p^{1-\lambda}T^{\lambda} = constant$ 

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

$$T_{f} = \left[\frac{C_{v} + (P_{ext}/p_{1})R}{C_{v} + (p_{ext}/p_{2})R}\right] T_{i}$$

Where,  $T_{i}=\mbox{initial temperature,}$ 

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

$$T_f = \left[\frac{C_v + (P_2/p_1)R}{C_v + R}\right] T_i = \left[\frac{C_v + (P_2/p_1)R}{C_p}\right] T_i$$
Enthalpy:  $H = E + pV$   
 $\Rightarrow$   $dH = dE + pdV + Vdp$   
At constant pressure:  $dH$ .  $dE + pdV = Q_p = C_p dT$   
 $\Rightarrow$   $\Delta H = \Delta E + p\Delta V + C_p \Delta T$   
Entropy:  $S = \frac{q_{rev}}{T}$ 

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

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

Gibb's free energy (G):

G = H - TS $\Delta G = \Delta H - T\Delta S$ AlsodG = Vdp - SdTAt constant temperature:  $\Delta G = nRt \ln \left(\frac{p_1}{p_2}\right)$ 

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

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

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

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

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



## **DEPTH Notes with Revision**

# CHEMISTRY

#### CHEMICAL BONDING

Summary of molecular geometry and hybridization

Total no. of independent electron pairs	No. of independent bonding electron pair	No. of Nonbonding electron pair	Orbital geometry	Molecular gemetry	Distortion?	Hybridization	Bond angles	Examples
2	2	0	linear	linear	never	sp	180°	CO2, BeCl2
3	3	0	trigonal planer	trigonal planar	possible	sp	1200	HgCl <sub>2</sub> , Znl <sub>2</sub> , CS
3	2	1	trigonal planer	bent	always	sp <sup>2</sup>	120°	NO_2, SO2, SnCl
4	4	0	tetrahedral	tetrahedral	possible*	sp <sup>3</sup>	109.5°	CH4, SO4
4	3	1	tetrahedral	trigonal pryamidal	always	sp3	109.50	NH3, SO4
4	2	2	tetrahedral	bent	always	sp <sup>3</sup>	109.5°	H,O, NH, SeCl
5	5	0	trigonal bipyramidal	trigonal bipyramidal	possible*	sp³d	90° and 120°	PFs
5	4	1	trigonal bipyramidal	distorted square pyramidal (see-saw)	always	sp³d	90° and 120°	SF <sub>4</sub> , TeCl <sub>4</sub>
5	3	2	trigonal bipyramidal	T-shaped	always	sp³d	900	IF,
5	2	3	trigonal bipyramidal	linear	never	sp'd	1800	1,, ICI,
6	6	0	octahedral (square bipyramidal)	octahedral	possible*	sp³d²	900	SF, PF
6	5	1	octahedral (square bipyramidal)	square pyramidal	always	sp³d²	900	IF, BrF,
6	4	2	octahedral (square bipyramidal)	square planar	possible**	sp³d²	900	XeF <sub>4</sub> , ICl <sub>4</sub> , BrF <sub>4</sub>

**Note:** Under distortion, "possible" means that the bond angles will be distorted when the outer atoms are not identical eg, tetrahedral  $CH_4$  (all outer atoms are H) has no distortion (all bond angles are exactly 109.5°). But in tetrahedral  $CH_3F$  (three H and one F) the bonds angles are slightly distorted form 109.5°.

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

**Note on molecular polarity:** The following types of molecules are nonpolar; linear  $AB_2$  trigonal planer  $AB_3$ , tetrahedral  $AB_4$ , trigonal bipyramidal  $AB_5$ , octahedral  $AB_6$ , square planer $AB_4$ , and symmetric square planer  $AB_2C_2$ . Any other molecule having a single "central atom" will be polar, as long as the electronegativity's of the elements that make it up are not equal. This includes molecules that have the above geometries but which have dissimilar outer atoms (such as tetrahedral  $CH_3F$  and linear O = C = S).

#### Molecular Orbital Theory (MOT)

	Li₂	Be <sub>2</sub>	B₂	C2	N₂	02	F <sub>2</sub>	Ne₂ ↑↓
	$\sigma_{2p}^{*}$	$\overline{\sigma_{2p}^{*}}$	$\sigma_{2p}^{*}$	$\overline{\sigma_{2p}^{*}}$	$\overline{\sigma_{2p}^{*}}$	σ <sub>2</sub> , ↑ ↑	σ <sub>2</sub> , ↑↓ ↑↓	$ \frac{1}{\sigma_{2}} $ $ \uparrow\downarrow $ $ \uparrow\downarrow $
	$\pi_{2p}^{*}$ $\pi_{2p}^{*}$	$\pi_{2p}^{*}$ $\pi_{2p}^{*}$	$\pi_{2p}^{*}$ $\pi_{2p}^{*}$	$\pi_{2p}^{*}$ $\pi_{2p}^{*}$	π <sup>*</sup> <sub>2p</sub> π <sup>*</sup> <sub>2p</sub> ↑↓	$ \begin{array}{c} \pi_{2p}^{*} & \pi_{2p}^{*} \\ \uparrow \downarrow & \uparrow \downarrow \end{array} $	$\begin{array}{c c} \hline 1 \\ \hline \pi_{2p}^{*} \\ \hline \pi_{2p}^{*} \\ \hline \end{array} \begin{array}{c} \hline 1 \\ \hline 1 \\ \hline \end{array}$	$\begin{array}{c c} \hline \\ \hline \\ \pi_{2}^{*} \\ \hline \\ $
Energy	$\overline{\sigma_{_{2p}}}$	$\overline{\sigma_{2p}}$	 ↑ ↑		$ \frac{1}{\sigma_{2p}} $	$\frac{1}{\pi_{2p}} \frac{1}{\pi_{2p}}$ $\underline{\uparrow\downarrow}$	$\pi_{2}, \pi_{2}, \frac{\uparrow \downarrow}{\uparrow \downarrow}$	$\pi_{2}, \pi_{2}, \uparrow \downarrow$
ш	$\pi_{2p} \pi_{2p}$	$\pi_{2p}$ $\pi_{2p}$	$\pi_{2p} \pi_{2p}$	$\pi_{2p}$ $\pi_{2p}$	$\pi_{2p}$ $\pi_{2p}$	$\sigma_{_{2p}}$	$\sigma_{_{2p}}$	σ2,
		<u><u> </u></u>	<u> </u>	<u>↑↓</u>	<u>↑↓</u>	$\uparrow\downarrow$	<u> </u>	$\uparrow\downarrow$
	$\sigma_{2s}^{*}$	$\sigma_{2s}^{*}$	$\sigma_{2s}^{*}$	$\sigma^*_{2s}$	$\sigma_{2s}^{*}$	$\sigma_{2s}^{*}$	$\sigma_{2s}^*$	$\sigma_{2s}^{\bullet}$
	<u>↑↓</u>		<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>	$\uparrow\downarrow$	<u>↑↓</u>	$\uparrow\downarrow$
	$\sigma_{\rm 2s}$	$\sigma_{2s}$	$\sigma_{\text{2s}}$	$\sigma_{zs}$	$\sigma_{\text{2s}}$	$\sigma_{2s}$	$\sigma_{2s}$	$\sigma_{2}$

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

**Bond order:**  $\frac{\text{No.of bonding electrons} - \text{No.of antibonding electrons}}{2}$ eg,  $N_2$ : Bond order =  $\frac{8-2}{2}$  (one sigma and two pibonds)

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

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

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

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

#### **Highlights of MOT**

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

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

(iii) If there is any unpaired electron in MO, the system will be paramagnetic with s in only magnetic moment ( $\mu_s$ ) =  $\sqrt{n(n+2)}$ 

BM where , 'n' is the number of unpaired electrons.



## **DEPTH Notes with Revision**

# CHEMISTRY

#### **COORDINATION COMPOUND**

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

(i) The positive ion is named first followed by negative ion.

(ii) When writing the name of complex, the ligands are written in alphabetical order, regardless of their charge followed by metal.

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

 $F^- =$ fluoro  $H^- =$ hydrido  $HS^- =$ mercapto  $Cl^- =$ chloro  $HO^- =$ hydroxo  $S^- =$ thio  $Br^- =$ bromo  $O^{2-} =$ oxo  $CN^- =$ cyano  $I^- =$ iodo  $O_2^{2-} =$ peroxo  $NO_2^- =$ nitro

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

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

(III)

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

(v) If complex is negative, metal name ends in ate (with original name of metal eg, ferrate, argentite, aurate, plambate etc.)

Complex cation	Name		
[CO(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	Heaammine cobalt (III) chloride		
[CO(NO <sub>2</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ]Cl	Tetraamminedinitro cobalt(III) chloride		
[Cu(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub>	Tetraammine copper(II)		
[Cr(en) <sub>3</sub> ]Cl <sub>3</sub>	Tris (ethylenediammnine) cobalt (III) chlorid		
Complex Anion			
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	Potassium hexacycnoferrate (II)		
$K_2[Cr(CN)_2O_2(O_2)NH_3]$	Potassium amminedicyanodioxoperoxo chromate (VI)		
Li[AlH <sub>4</sub> ]	Lithium tetrahydrido aluminate (III)		
[Ni(NH <sub>3</sub> ) <sub>4</sub> ][NiCN) <sub>4</sub> ]	Tetraammine nicke(II) tetracyanonickelate(II)		

#### **Isomerism in Complexes**

(i) Ionization isomerism: Complexes having same molecular formula but giving different ions in solution are known as

ionization isomers. This type of isomerism arises due to exchange of groups between the complex ion and the ions outside it.

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

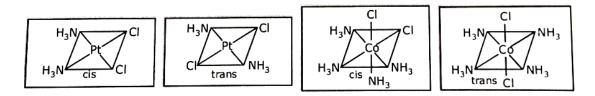
#### $[\rm Cr(H_2O)_6]\rm Cl_3, [\rm Cr(H_2O)_5\rm Cl]\rm Cl_2, \rm H_2O$ and $[\rm Cr(H_2O)_4\rm Cl_2]\rm Cl. 2\rm H_2O$

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

[Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>NC]Cl<sub>2</sub>

Are linkage isomers.

(iv) Gometric isomers:

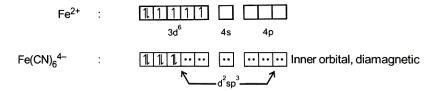


Structure and Bonding in Complexes

The "Valence Bond Theory": According to valence bond theory, a strong legend field force the d-electrons of central metal to pair up against Hund's rule.

The strong ligands which causes this are, CO, NO,  $CN^-$ ,  $NO_2$ ,  $NH_3$ , en (ethylene diamine) and some common weak lighands are  $H_2O, X^-$ ,  $NO_3^-$ , ROH etc.

Example:  $K_4[Fe(CN)_6]$  and  $K_4[FeF_6]$  both have iron in +2 state.



Complex, octahedral in shape



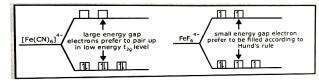
An outer orbital complex, paramagnetic, octahedral in shape

**Spin only magnetic moment**  $(\mu_s) = \sqrt{n(n+2)}BM n = no of unpaired "e". Spire only magnetic moment of$ 

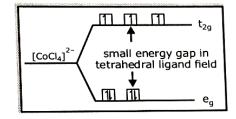
 $K_4[Fe(CN)_6]$  is zero because it has no unpaired electron while the same for  $K_4[FeF_6]$  is  $\sqrt{24}$  BM.

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

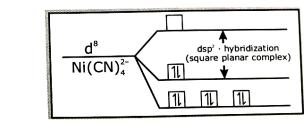
In octahedral ligand field:



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



Square planer complex: When the d-orbitals are unsymmetrically occupied. It gives rise to square planer complex eg,



 $Na_2[Ni(CN)_4]$ 

Au Cu(II)' $d^{9'}$  complex are square planer eg,  $[Cu(NH_3)_4]^{2+}$ ,  $[Cu(CN)_4]^{2-}$  or  $[CuCl_4]^{2-}$ 



## **DEPTH Notes with Revision**

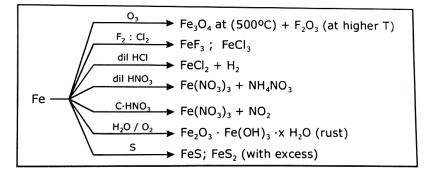
#### METALLURGY

#### **Extraction of Metals**

Metals	Important Ores	Extraction Method	Reactions Involved in Extraction
Fe	Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> . FeS. CuFeS <sub>2</sub> , FeCO <sub>3</sub>	Carbon-reduction method	$C \circ O_{1} \xrightarrow{\text{Blast}} CO$ Furance 3CO + Fe <sub>2</sub> O <sub>1</sub> $\longrightarrow$ 2 Fe + 3CO <sub>2</sub>
Sn	SnO,	Carbon-reduction method	$C + O_{1} \xrightarrow{\text{Blass}} CO_{1}$ Furance $SO_{2} \longrightarrow SO_{2} + 2CO_{2}$
Cu	CuFeS <sub>2</sub> , CuS, CuO, Cu,O	Self-reduction method	$CuS + O_2 \xrightarrow{Partial} CuO + SO_2$ CuS + 2CuO $\longrightarrow$ 3Cu + SO_2
Pb	PbS(Galena) PbO, Pb₃O₄	Self-reduction method	$PbS + O_2 \xrightarrow{Part(a)} PbO + SO_2$ $PbS + 2PbO \longrightarrow 3Pb + SO_2$
Mg	Sea water, MgCl <sub>2</sub> , KCl: 6H <sub>2</sub> O MgCO <sub>3</sub> , CaCO <sub>3</sub>	Electrolytic reduction	MgCl <sub>2</sub> <del>Meit</del> → Mg <sup>2+</sup> + 2Cl Mg <sup>2+</sup> + 2e <u>Electrolysis</u> Mg
AJ	Al <sub>2</sub> O <sub>3</sub> (bauxite)	Electrolytic reduction	$A_i,O_i \xrightarrow{\text{Meit}} A_i^{i*}$ $A_i^{i*} \xrightarrow{\text{Electrolysis}} A_i$
Ag	Ag <sub>2</sub> S (argentite)	Cyanide Process	$\begin{array}{ccc} Ag_{s}S+2NaCN & \longrightarrow & 2AgCN+Na_{s}S\\ AgCN+NaCN & \longrightarrow & Na[Ag(CN)_{s}] \end{array}$
Au	Exist in free state	Cyanide process	$ \begin{array}{ccc} [Ag(CN)_2] + Zn & \longrightarrow & Ag + Na_1[Zn(CN)_1] \\ Au + NaCN & \longrightarrow & Na[Au(CN)_2] \\ [Au(CN)_2] + Zn & \longrightarrow & Au + Na_2[Zn(CN)_1] \end{array} $

#### **Important Reactions**

#### (i) Irons



(ii) Tin

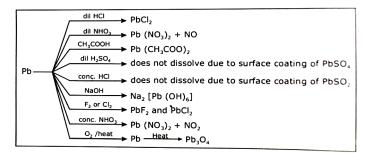
- Stable to water and air at ordinary temperature.
- Does not react with dil HCl or dil H<sub>2</sub>SO<sub>4</sub> but reacts with dil HNO<sub>3</sub>.

 $Sn + HNO_3 \rightarrow Sn(NO_3)_2 + NH_4NO_3$ 

- With hot conc. HCl,  $SnCl_2$  is formed while with hot concentrated  $H_2SO_4$ ,  $SnSO_4$  is formed evolving  $SO_2$ . NaOH + Sn  $\rightarrow Na_2[Sn(OH)_6] + H_2$
- Sn reacts with Cl<sub>2</sub> and Br<sub>2</sub> in cold forming SnCl<sub>4</sub> and SnBr<sub>4</sub>. F<sub>2</sub> and I<sub>2</sub> reacts on warming.
- With hot concentrated  $HNO_3$ , metastannic acid  $H_2 SnO_3$  is formed.

 $Cu + O_2 \xrightarrow{red-heat} CuO \text{ Black} \xrightarrow{Higher \text{ temperature}} Cu_2 O \text{ Red}$ 

(iv) Lead



#### (v) Magnesium

• At highly electropositive metal, displace H<sup>+</sup> from dilute acid.

 $Mg + 2HCl \rightarrow MgCl_2 + H_2$ 

- Reacts with N<sub>2</sub> forming Mg<sub>3</sub>N<sub>2</sub>.
- Reacts with halogens forming MgX<sub>2</sub>
- A strong reducing metal, displaces less active metal from solution.

#### (vi) Aluminium

• A strong electropositive metal, liberate H<sub>2</sub> from solution of dilute acid.

 $Al + HCl \rightarrow AlCl_3 + H_2$ 

- Concentrated HNO<sub>3</sub> render Al passive due to formation of Al<sub>2</sub>O<sub>3</sub> on surface.
- With halogens, AlX<sub>3</sub> is formed.

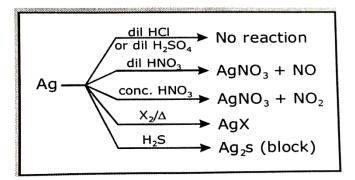
$$Al + NaOH \rightarrow NaAIO_2 + H_2$$

• Thermite welding

 $Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$ 

• Reduces nitrates and nitrites in basic medium to NH<sub>3</sub>.

(vii) Silver



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

• Reacts with aqua regia

 $HCl + HNO_3 + Au \rightarrow AuCl_3 + NOCl + H_2O$ 



## **DEPTH Notes with Revision**

#### **PERIODIC TABLE**

#### Main feature of Modern Periodic Table

(i) The modern Periodic table is divided into two main categories: (i) Vertical columns called groups and (ii) Horizontal columns called Periods.

(ii) There are 18 vertical columns or groups. These are further sub-divided into A and B (group I to VII), VIII group and zero group.

(iii) Member of the same group have similar electronic configuration of the valence shell and thus show same valency.

(iv) Elements of groups IA to VIIA are called groups of typical elements, representative elements or normal elements.

(v) Groups IA and IIA are strongly metallic and called group of 'alkali metals and alkaline earth metals.'

(vi) Groups IB to VIIB and VIII lie in the middle to the table between IIA and IIA groups and are called groups of transition element. They consist of metals

(vii) The zero group consists of 'Noble gasses'.

(viii) There are 7 horizontal rows in the Periodic Table. These are called the periods.

(ix) In a period, the number of valence shell remains the same for all elements. However, the number of electrons in the valence shell increases from left to right.

#### Atomic size and atomic radius

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



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

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

(iv) Conversely, elements in the same group increases in size downward, eg, in group IA, starting from lithium to sodium,

potassium, rubidium and cesium, the atomic size increases because there is a gradual increase in the number of shells.

#### **Ionization Potential**

Ionization potential (or ionization energy) is the amount of energy required to remove one or more electrons form the outermost shell of an isolated atom in the gaseous state. Ionization energy is also called as ionization potential because it is measured as the minimum potential required to remove the most loosely held electron form the rest of the atom. It is

measured in the units of electrons volts (eV) per atom or kilo joules per mole of atoms (KJ mol<sup>-1</sup>), Thus, the ionization energy gives the ease with which the electron can be removed form an atom .

The smaller the value of the ionization energy, the easier it is to remove the electron form the atom. In referring to the Periodic Table of ionization potentials (in electron volts) shown, the following conclusions may be arrived at (i) Metals usually have low ionization potential whereas non-metals have high ionization potential. Metalloids have

intermediate ionization potential.

(ii) The inert gases have very high ionization potential, due to

the stability of the outer shell. Helium has the highest ionization potential.

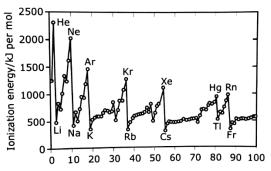
(iii) Within a group, the ionization potential

generally decreases with increasing atomic number.

Increasing atomic number results in increasing atomic radii.

Thus, the electrons of the outer shell are further away

than those of the previous element and can be removed easily.



#### Atomic number

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

(v) Ionization potential increases across the period because of increase in nuclear charge due to which the atomic size decreases. Thus, more energy is required to pull away the electron from outermost shell of the atom of smaller size.
(vi) Ionization potential decreases down the group because of increase in the number of shells. The effective nuclear charge decreases as atomic size increases. Thus it is easier to pull one electron form the outermost shell of the atom.

#### **Electron Affinity**

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

(ii) Electron affinity depends on

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

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

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

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

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

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

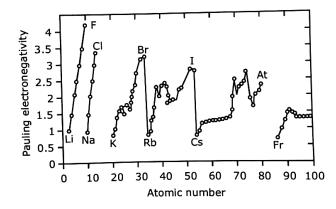
#### Electronegativity

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

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

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

(iv) Fluorine is the most electronegative element.





## **DEPTH Notes with Revision**

#### ALCOLHOLS, ETHERS AND EPOXIDES

#### **Alcohol Preparation**

$$RMgX + R - C - H(R)$$

$$RMgX + R - C - H(R)$$

$$R - CH = CH_2 + B_2H_6 \xrightarrow{(H_2O_2/HO^-)}_{H_2O_2/HO^-} H_2C = CHR$$

$$R - CH = CH_2 + [CoH(CO)_4] \xrightarrow{(CU-Zn/H_2)}_{OXO-Process} H^+/H_2O$$

$$R - X \xrightarrow{aq} AgOH \\ or aq} AgOH \\ R - COOR \xrightarrow{(H^+/H_2O)}_{Or HO^-/H_2O} H_2C = CHR$$

$$R - X \xrightarrow{(A)} AgOH \\ R - COOR \xrightarrow{(H^+/H_2O)}_{Or HO^-/H_2O} H_3O^+R - CN + RMgX$$

$$R - COOR \xrightarrow{(H^+/H_2O)}_{Or HO^-/H_2O} H_3O^+R - CN + RMgX$$

$$R - COOR \xrightarrow{(H^+/H_2O)}_{Or HO^-/H_2O} H_3O^+R - CN + RMgX$$

$$H_2/Ni \text{ or } IIAIH_4 \\ O \\ H^+/H_2O \\ R - O - R$$

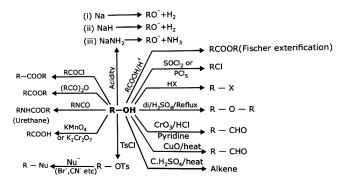
$$R - O - R$$

(i)  $H_2/Ni$  reduces all reducible groups including olefinic bonds.

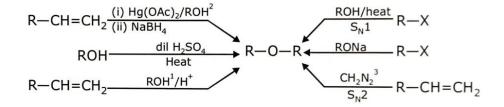
(ii) LiAlH<sub>4</sub> does not reduce olefinic bonds.

- (iii) Reaction proceeds via carbocation, rearrangement may accompany.
- (iv) Avoid rearrangement.
- (v) Anit-Markownikoff's hydration takes place.

#### **Properties**



#### **Ethers Preparation**

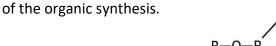


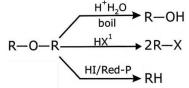
(i) Proceed via carbocation intermediate, rearrangement may take place.

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

(iii) Gives methyl ether (RCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)

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





In case of phenyl ether, one product is phenol:

 $Ph - O - R + HBr \rightarrow PhOH + RBr$ 

Epoxides: The cyclic ether

**Preparation:** 

$$C = C \left( \begin{array}{c} RCO_{3}H \\ \text{or } Ag_{2}O/\Delta \end{array} \right) \left( \begin{array}{c} CH_{1}N_{2}/\Delta \\ \text{or } CH_{1}L_{2}/2n \end{array} \right) C = O$$

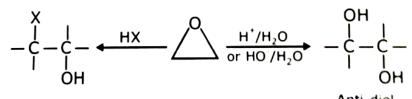
$$C = C \left( \begin{array}{c} RCO_{3}H \\ \text{or } Ag_{2}O/\Delta \end{array} \right) \left( \begin{array}{c} CH_{1}N_{2}/\Delta \\ \text{or } CH_{1}L_{2}/2n \end{array} \right) C = O$$

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$$C = C \left( \begin{array}{c} CH_{1}N_{2}/\Delta \\ \text{or } CH_{1}L_{2}/2n \end{array} \right) C = O$$

**Properties:** 



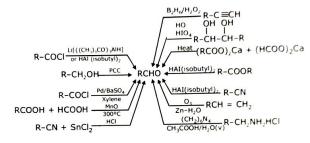
Anti-diol

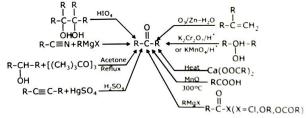


## **DEPTH Notes with Revision**

### ALDEHYDE AND KETONE

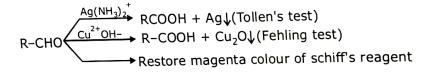
#### **Preparation:**





**Properties:** 

**Reactions given by Aldehyde only:** 



#### Reactions given by ketone only:

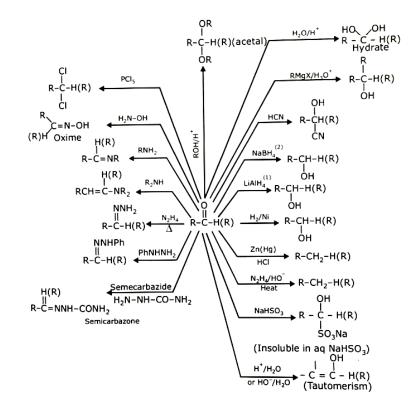
(i) Ketones do not restore magenta color of Schiff's reagent

(ii) Ketones are not oxidized by Tollen's reagent or Fehling solution.

$$R - CO - CH_3 + X_2 \xrightarrow{NaOH} R - COONa + CHX_3$$

(iii) Methyl ketone gives haloform reaction.

#### Reactions common to aldehydes and ketones





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

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

**Aldol condensation:** Aldehydes or ketones containing at least  $\alpha$  —hydrogen on treatment with dilute alkaline or dilute acid undergo condensation to produce  $\beta$  —hydroxy aldehyde or  $\beta$  —hydroxy ketone.

**Cannizaro reaction:** Aldehydes lacking  $\alpha$  —hydrogen, when treated with concentrated solution of strong base, undergo mutual oxidation reaction as:

$$R - C - H + NaOH \rightarrow H-COO^-Na^+ + CH_3OH$$

$$PhCHO + NaOH \rightarrow PhCOONa + PhCH_2OH$$

**Bachmann's rearrangement:** Aldehydes or ketones on treatment with hydroxyl amine gives oximes. Oximes on further treatment with conc.  $H_2SO_4$  or  $PCl_5$  undergoes rearrangement as:

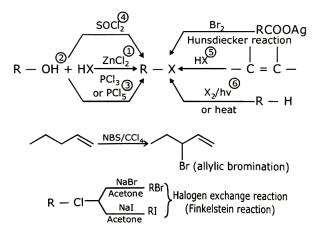
$$R = N \xrightarrow{H_2 SO_4} HO = N \xrightarrow{H - C - NHR} H - C - NHR$$
  
H - C - NHR  
(Anti exchange with HO occur)



## **DEPTH Notes with Revision**

#### **ALKYL HALIDES**

#### Preparation



- (i) Tertiary alcohol react even in absence of a Lewis catalyst.
- (ii) Reaction proceeds via carbocation intermediate, rearrangement may accompany.
- (iii) Primary alcohol react without undergoing rearrangement.
- (iv) Primary alcohol give un-rearranged product, not suitable with 2° or 3° alcohols.
- (v) Addition proceeds through carbocation intermediate, rearrangement may accompany.

(vi) Free radical halogenation, not suitable for fluorination or direct iodination.

lodination can be achieved using an oxidizing agent with  $I_2$ .

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

**Substitution Reaction** 

 $S_N 2$  reaction:

 $R-X + Nu^- \rightarrow R - Nu + X^-$  (HO<sup>-</sup>, CN<sup>-</sup>.....)

Salient features of  $S_N 2$  reaction:

(i) The reaction is an elementary, bimolecular in nature.

(ii) No reactive intermediate and only one transition state is involved.

(iii) Reaction usually require a strong nucleophile.

(iv) The order of leaving ability is  $\rm F^- < Cl^- < Br^- < I^-$ 

(v) The reactivity of different alkyl halides is :  $3^{\circ} < 2^{\circ} < 1^{\circ}$ .

(vi) There occur inversion of configuration at  $\alpha$  –carbon.

(vii) Polar, protic solvents like  $H_2O$ , ROH slow down the reaction.

(viii) Polar, aprotic solvents like DMSO, DMF, THF etc. favour reaction.

(ix) Vinyl and aryl halides are usually inert in this reaction.

**S<sub>N</sub>1 Reaction**:

$$R - X \xrightarrow{\text{Heat}} R^+ + X^- \text{ (slow)(RDS)}$$
$$R^+ + Nu^- \longrightarrow R - NU \text{ (fast)}$$

Salient features of  $S_N 1$  reaction:

(i) It is a two step process as shown above first order in alkyl halide and first order overall.

(ii) Carbocation may undergo rearrangement.

(iii) The order of leaving ability is  $\rm F^- < Cl^- < Br^- < I^-$ 

(iv) Reactivity of alkyl group:

 $1^{\circ} < 2^{\circ} < 3^{\circ} <$ allylic < benzylic.

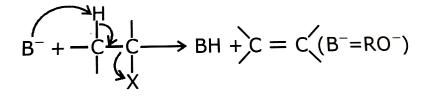
(v) Reaction occur at elevated temperature.

(vi) Strength of nucleophile is unimportant because it is involved in non-rate determining step.

(vii) Polar solvents favour reaction. Presence of Lewis acid catalyst speed-up reaction.

#### **Elimination Reaction**

Bimolecular (E-2) elimination:



Salient Features of E-2 reaction:

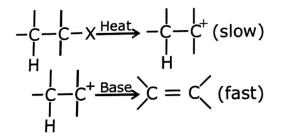
(i) It is single step, bimolecular, concerted reaction, with order of reaction equal to 2.

(ii) Presence of a  $\beta$  –hydrogen anti to leaving group is essential.

(iii) In case of more than one type of  $\beta - H$ , elimination occurs to produce most substituted, most stable product as major product.

- (iv) The order of leaving ability is  $\rm F^- < Cl^- < Br^- < I^-$
- (v) The order of reactivity is :  $1^{\circ} < 2^{\circ} < 3^{\circ}$ .
- (vi) Polar protic solvent slow down the reaction.
- (vii) Presence of a strong base is essential.

**Unimolecular Elimination (E-1)** 



Salient features of E-1 reactions:

(i) It is a two step reaction, proceed via carbocation intermediate. Therefore, carbocation may undergo rearrangement.

- (ii) The order of leaving ability  $\rm F^- < Cl^- < Br^- < l^-$
- (iii) The order of reactivity is:  $1^{\circ} < 2^{\circ} < 3^{\circ}$  (same as  $S_{N}1$ ).
- (iv) Reaction complete with  $S_N 1$ , high temperature favour E-1.
- (v) Strength of base is unimportant.
- (vi) Polar solvent or Lewis acid catalyst favours reaction.



## **DEPTH Notes with Revision**

### AROMATIC COMPOUNDS

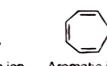
Aromaticity The "Huckel Rule": Factors required for aromaticity are:

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





Naphalene (n = 2)

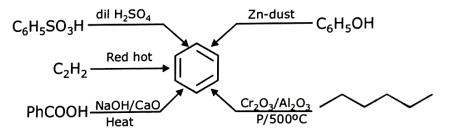


ne Aromatic ion (n = 0)

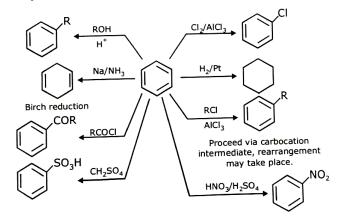
Aromatic ion (n = 1)

Benzene

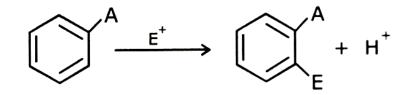
Preparation



#### Preparation



Aromatic electrophilic substitution "Reactivity and Orientation".

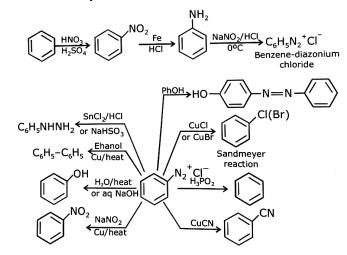


Reactivity: Electron donating A activate the ring towards substitution and electron with drawing A deactivate the

ring towards substitution reaction.

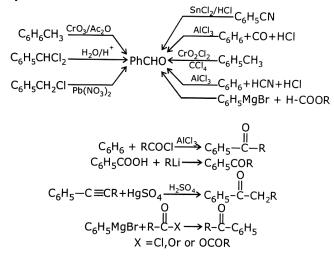
Activating groups	Deactivating groups
R, OR, – OH	$- NO_2, - N^{\dagger}R_3, - SO_3H$
$- OCOR, - NH_2, - NR_2$	$-COOH, -COOR, -CONH_2$
- NHR, $-$ NHCOCH <sub>3</sub>	– CHO, – COR, – CN
$-R_{r}-C_{6}H_{5}$	$-CH = CH - NO_2$
	_

#### **Diazonium synthesis**



#### **Aromatic Aldehydes and Ketones**

#### Preparation



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

**Perkin's reaction:** Reaction of aromatic aldehydes with aliphatic anhydride containing  $\alpha$ -hydrogen

$$Ar - CHO + (CH_3CO)_2O \xrightarrow{RCOONa} Ar - CH = CH - CHO$$

$$R - CH_2CO)_2O \xrightarrow{R} Ar - CH = C - CHO$$

$$Ar-CHO \xrightarrow{CH_{3}CHO/HO^{-}} Ar-CH=CH-CHO(Claisen reaction)$$

$$Ar-CHO \xrightarrow{KCN} Ar-CH(OH)-COC_{6}H_{5}(Benzoin condensation)$$

$$C_{6}H_{5}NR_{2} \xrightarrow{} Ar-CH \xrightarrow{} NMe_{2}$$

Phenol

Preparation

$$C_{6}H_{5}-CH(CH_{3})_{2} \xrightarrow{(i) O_{2}/NaOH}_{(ii) H_{3}O^{+}} PhOH \xrightarrow{O_{2}} PhMgBr$$

$$PhSO_{3}Na \xrightarrow{(i) NaOH/heat}_{(ii) H^{+}/H_{2}O} PhOH \xleftarrow{O_{2}} PhMgBr$$

$$COOH \xrightarrow{O_{2}} PhMgBr$$

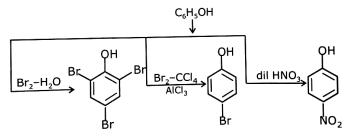
$$H_{2}O/heat} C_{6}H_{5}N_{2}^{+}HSO_{4}^{-}$$

$$NaOH \\ heat} ArX$$

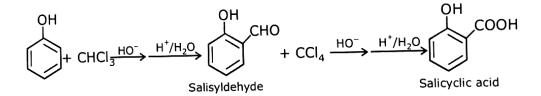
**Properties:** 

(i) Acidity stronger acid than aliphatic alcohols and water but weaker acid than a carboxylic acid.

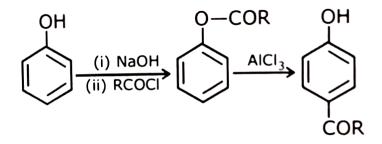
(ii) Highly reactive in aromatic electrophilic substitution reaction if occur in aqueous medium.



**Reimer Tiemann's reaction** 



**Fries rearrangement** 





## **DEPTH Notes with Revision**

#### CARBOXYLIC ACIDS AND DERIVATIVES

**Carboxylic acid** 

Preparation

$$\begin{array}{c} O \\ R - C - X & \frac{H^{+}/H_{2}O}{or HO^{-}/H_{2}O} \\ R - CH_{2}OH & \frac{Na_{2}CrO_{4}/H^{+}}{or KMnO_{4}/H^{+}} \\ R - CH_{2}OH & \frac{Na_{2}CrO_{4}/H^{+}}{or KMnO_{4}/H^{+}} \\ R - CN & \frac{H^{+}/H_{2}O}{or HO^{-}/H_{2}O} \end{array} \xrightarrow{Na_{2}CrO_{4}/H^{+}} \\ R - CN & \frac{H^{+}/H_{2}O}{or HO^{-}/H_{2}O} \\ \end{array}$$

**Properties:** 

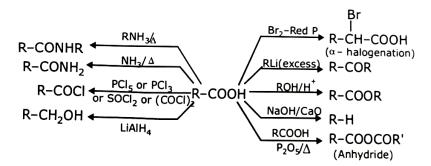
Acidity

$$R - COOH \xrightarrow{Na} RCOONa + H_2$$

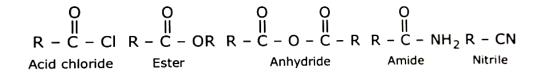
$$R - COOH \xrightarrow{NaOH} RCOONa + H_2O$$

$$\xrightarrow{NaHCO_3} RCOONa + H_2O + CO_2$$

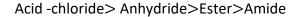
 $NaHCO_3$  can be used to distinguish a carboxylic acid from aliphatic and aromatic alcohols.

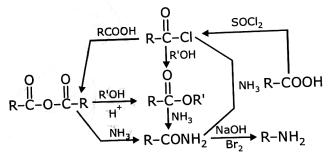


Acid derivatives: Derived from acids



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







## **DEPTH Notes with Revision**

#### **HYDROCARBONS**

