

* Solution = Solute + Solvent, not original ref.

phase of solⁿ = phase of solvent

* Vapour Pressure :- (Pure liquid)

→ Initially rate of evaporation is maximum and rate of condensation is zero.

→ At equilibrium rate of evaporation = rate of condensation.

→ Vapour Pressure: Pressure exerted by the saturated vapour at equilibrium, on the surface of liquid or on the walls of the container is the vapour pressure at that temperature.

at equilibrium

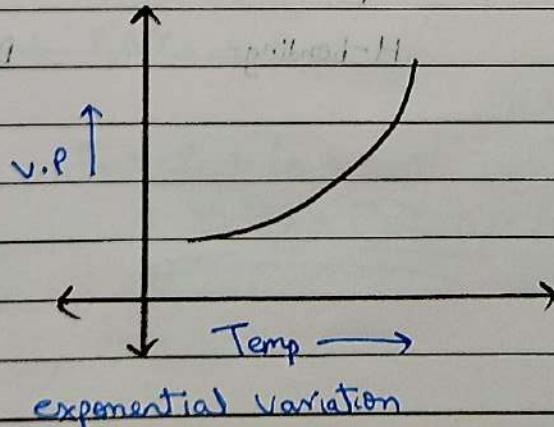
$$K_p = P_{\text{app}}$$

on temperature (t)

dependent

* * * Irrespective of amount of liquid and shape of container, the vapour pressure remains constant at particular temperature provided liquid is sufficient to make liquid-vapour equilibrium.

* $PV = nRT$



→ on changing temperature, moles of vapors also change.

$\text{P}_{\text{vap}} \propto \frac{1}{T}$ only $\Rightarrow \text{P}_{\text{vap}} \propto \text{e}^{-\Delta H_{\text{vap}}/RT}$

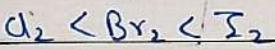
→ V.P. does not depend on 'T' linearly because eq. constant ' K_p ' has; exponential variation with T.

$$\log \frac{P_{T_2}}{P_{T_1}} = \frac{\Delta H_{\text{vap}}}{2.302} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

→ Force of attraction $\propto \frac{1}{\text{Vapour pressure}}$

Hydrogen bond $>$ dipole-dipole $>$ Vander Waal's

* For Vander Waal's forces more the molecular mass, more will be the force of attraction.



(V.P.)_{polar} $<$ (V.P.)_{non-polar} [at temp. T]

(Force of attraction)_{polar} $>$ (Force of attraction)_{non polar}

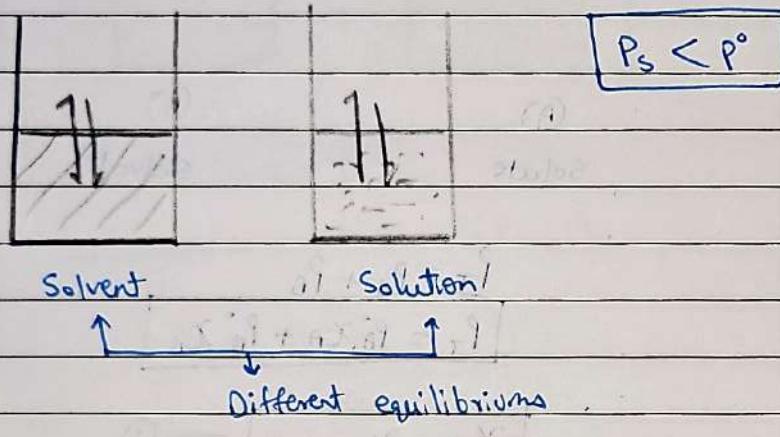
e.g. V.P. of H_2O is less than CH_3Cl

\uparrow
H-bonding

\uparrow $\text{DP} - \text{DP}$

\star [Case - I] : Solution of non-volatile solute in volatile solvent.

→ Vapour pressure of solution is less than vapour pressure of solvent.



\star Raoult's law:-

→ For any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.

$$P_s = P^\circ \chi_{\text{solvent}}$$

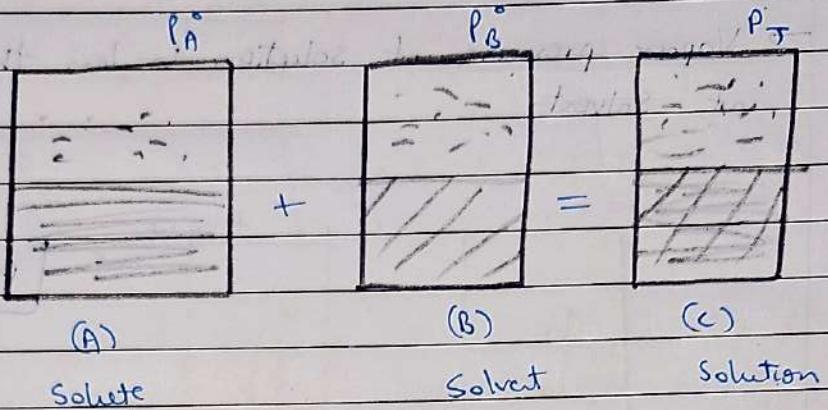
$$\chi_A = \frac{n_A}{n_A + n_B}$$

$$P_T = P_A \chi_A + P_B \chi_B$$

$$P_T = P_A + P_B + \dots$$

$$= P_A^\circ \chi_A + P_B^\circ \chi_B + \dots$$

(Case II): Solution of a volatile solute in a volatile solvent.



$$P_T = P_A + P_B$$

$$\boxed{P_T = P_A^{\circ} \chi_A + P_B^{\circ} \chi_B}$$

$$\boxed{\chi_A + \chi_B = 1} - ①$$

$$\therefore P_T = P_A^{\circ} (\chi_A) + P_B^{\circ} (1 - \chi_A)$$

$$\therefore P_T = (P_A^{\circ} - P_B^{\circ}) \chi_A + P_B^{\circ}$$

* Composition of Vapour Phase :-

Mole fraction

$$Y_A = \frac{V.P. \text{ of } A}{V.P. \text{ of } A + V.P. \text{ of } B} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Vapour phase}$$

$$Y_B = \frac{V.P. \text{ of } B}{V.P. \text{ of } A + V.P. \text{ of } B} \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$\chi_A = \frac{V.P. \text{ of } A}{P_T} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{Liquid phase}$$

$$\chi_B = \frac{V.P. \text{ of } B}{P_T}$$

$$P_T = P_A^\circ \chi_A + P_B^\circ \chi_B$$

→ Composition of A in vapour phase:-

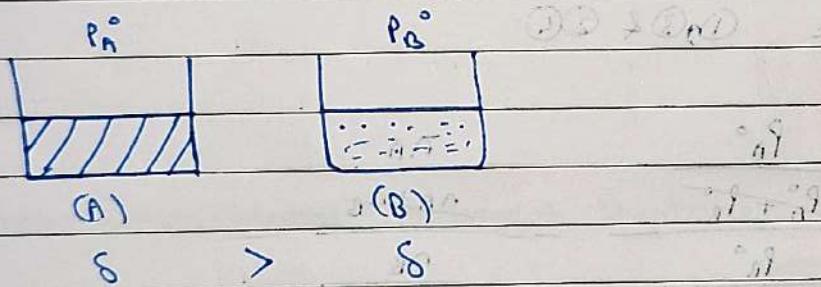
⇒ Pressure of A in V.P.
Total V.P.

$$\frac{P_A}{P_T} = \frac{P_A^\circ \chi_A}{P_A^\circ \chi_A + P_B^\circ \chi_B} = Y_A$$

$$\therefore Y_A = \frac{P_A^\circ \chi_A}{P_A^\circ \chi_A + P_B^\circ \chi_B}$$

$$Y_B = \frac{P_B^\circ \chi_B}{P_A^\circ \chi_A + P_B^\circ \chi_B}$$

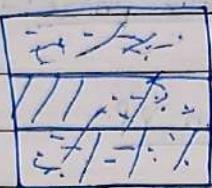
★ Mixture of two volatile liquids both are immiscible



Case 1: (no agitation)

s_2	$\dots \dots \dots$	$P_T = P_B$ only
s_1	$\dots \dots \dots$	

(case 2: agitation occurred)



$$P_T = P_A + P_B$$

$$P_A^\circ \chi_A + P_B^\circ \chi_B$$

$$\therefore P_T = P_A^\circ + P_B^\circ$$

$$\chi_A = \chi_B = 1$$

\because they do not mix

but $\gamma_A \neq \gamma_B \neq 1$. (nothing can stop vapours from mixing)

$$\gamma_A = \frac{P_A^\circ + P_B}{P_A^\circ + P_B^\circ} - ① \quad \text{and} \quad \gamma_A = \frac{n_A + n_B}{n_A + n_B} - ②$$

$$\gamma_B = \frac{P_B^\circ}{P_A^\circ + P_B^\circ} - ③ \quad \text{and} \quad \gamma_B = \frac{n_B}{n_A + n_B} - ④$$

Divide ①③ & ②④

$$\frac{\frac{P_A^\circ}{P_A^\circ + P_B^\circ}}{\frac{P_B^\circ}{P_A^\circ + P_B^\circ}} = \frac{\frac{n_A}{n_A + n_B}}{\frac{n_B}{n_A + n_B}}$$

$$\therefore \frac{n_A}{n_B} = \frac{P_A^\circ}{P_B^\circ}$$

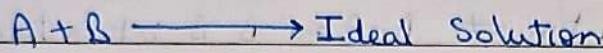
mole ratio

$$\Rightarrow \frac{W_A/M_A}{W_B/M_B} = \frac{P_A^\circ}{P_B^\circ} \quad [W_A \text{ & } W_B \text{ are weights of A & B in vapour phase}]$$

$$\frac{W_A}{W_B} = \frac{P_A^\circ M_A}{P_B^\circ M_B}$$

Hydrogen bonding > Dipole-Dipole > Vanderwaal's

★ Ideal Solution :-



when,

A-A & B-B interactions = A-B interactions

(i) $\Delta H_{\text{mix}} = 0$

(ii) $\Delta V_{\text{mix}} = 0$

(iii) $\Delta G_{\text{mix}} < 0$

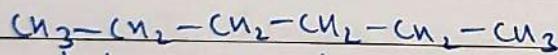
(iv) $\Delta S > 0$

1) When strong interaction replaces weak interaction it gives negative deviation and makes negatively deviated non ideal sol.

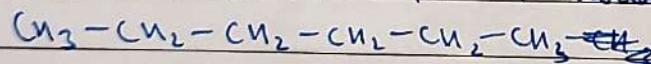
2) When weak interaction replaces strong interaction it gives positive deviation and makes positively deviated non ideal solution.

Eg's :-

(i) ~~Benzene + Toluene~~ Hexane + Heptane

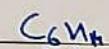


| | | | | . . . | Vander waal (V.W)



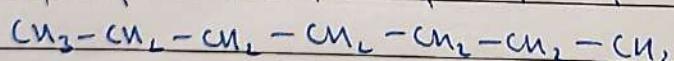
+

→



↑↑↑
C₇H₁₆

(V.W)



$\therefore A - A \text{ & } B - B = A - B \quad \therefore \text{It is ideal solution.}$

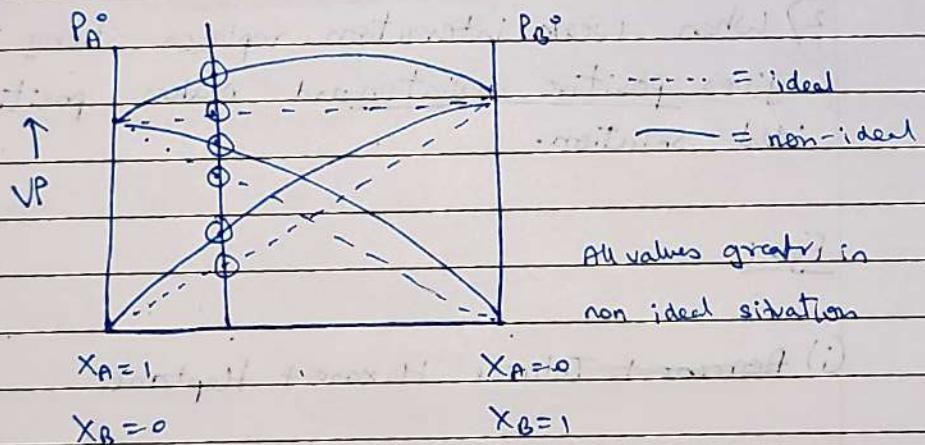
★ Non-Ideal Solution:-

A-B interaction \neq A-A and B-B interaction

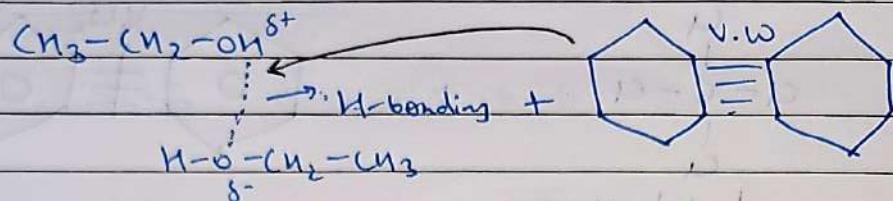
1] Positive deviation:-

A-B interaction $<$ A-A and B-B interaction

- * $\Delta H_{\text{mix}} > 0$ Weaker interaction is replacing
- * $\Delta V_{\text{mix}} > 0$ Stronger interaction
- * $\Delta G_{\text{mix}} < 0$
- * $\Delta S_{\text{mix}} > 0$

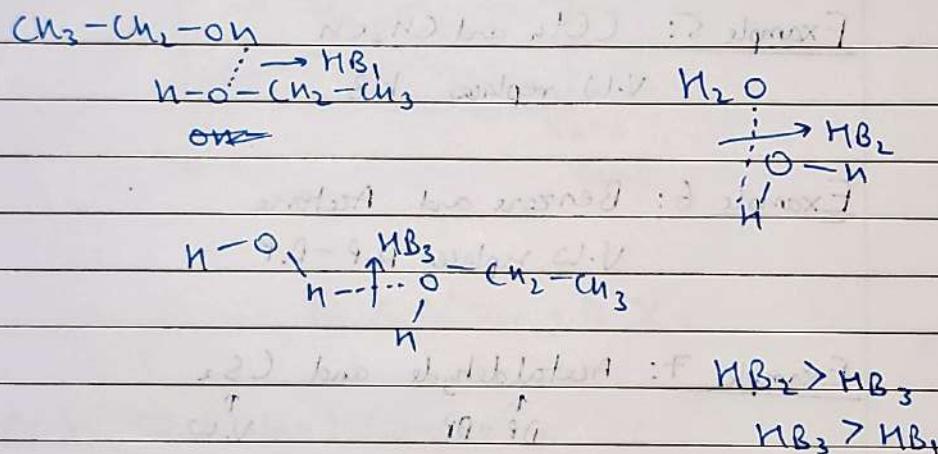
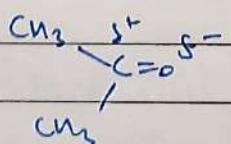
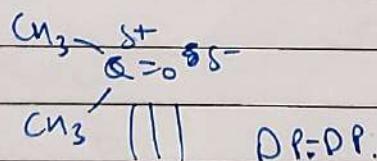


$$\therefore P_T > P_A^\circ X_A + P_B^\circ X_B$$

Example 1: Ethanol + Cyclohexane

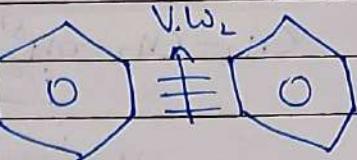
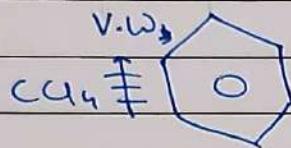
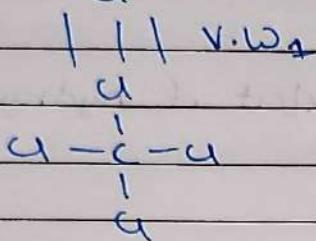
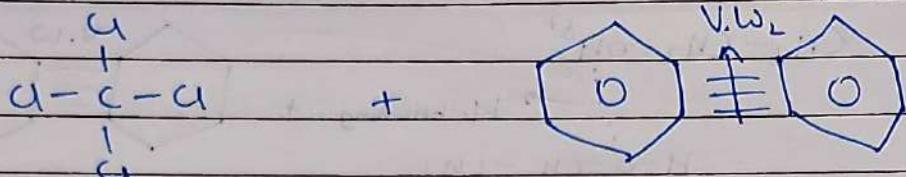
→ Cyclohexane reduces the extent of hydrogen bonding in ethanol.

→ Weaker interaction is replacing stronger interaction.
 (Positive deviation)

Example 2: Ethanol + WaterExample 3: Ethanol + Acetone

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Example 4: CCl_4 and Benzene



$$\begin{aligned} & \therefore \text{V.W}_1 > \text{V.W}_2 \\ & \therefore \text{V.W}_3 < \text{V.W}_1 \\ & \therefore \text{positive deviation} \end{aligned}$$

Example 5: CCl_4 and CH_3ON

V.W replaces HB

Example 6: Benzene and Acetone

V.W replaces P.P - P.P

Example 7: Acetaldehyde and CS_2

$\overset{\uparrow}{\text{DP}}-\overset{\uparrow}{\text{DP}}$ $\overset{\uparrow}{\text{V.W}}$

2] Negative deviation:-

$$A-B > A-A \text{ and } B-B$$

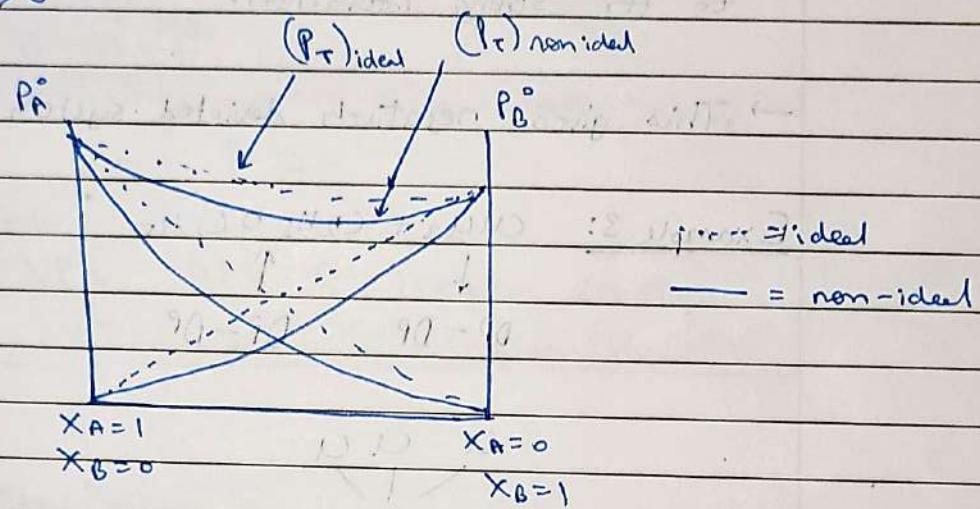
$$\Delta H_{\text{mix}}^{\circ} < 0$$

$$\Delta V_{\text{mix}}^{\circ} < 0$$

$$\Delta G_{\text{mix}}^{\circ} < 0$$

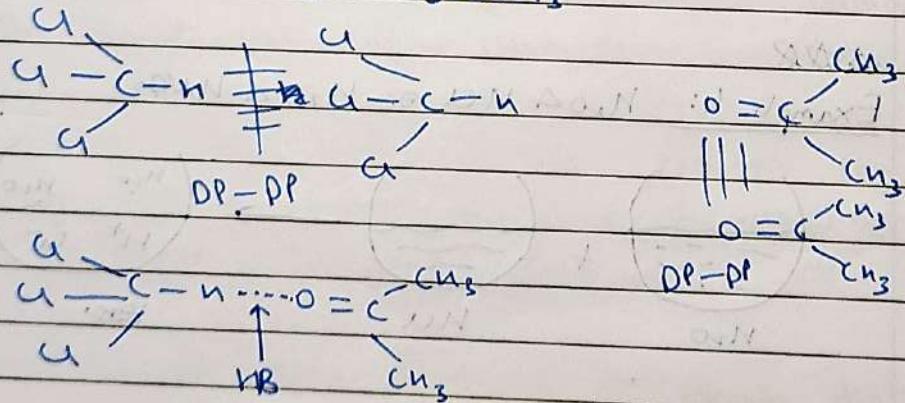
$$\Delta S_{\text{mix}}^{\circ} > 0$$

Strong interaction replaces weak interaction.



$$\therefore P_T < P_A^{\circ} x_A + P_B^{\circ} x_B$$

Example 1: $\text{CH}_3\text{I}_3 + \text{CH}_3\text{COCH}_3$



$$\therefore \text{N-B} > \text{BP-D.P}$$

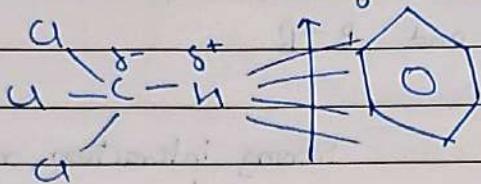
$\therefore -\text{ve deviation}$

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~~Q&A~~

(2) Example 2: $\text{CuCl}_2 + \text{C}_6\text{H}_6$

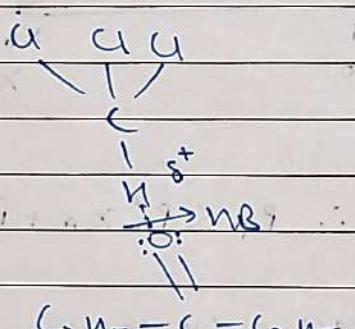
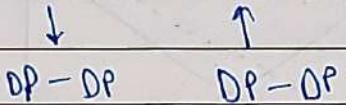
Stronger (sort of n-bond)



→ δ^+ of N of CuN_3 interacts with π bond. of C_6H_6 to form strong interaction.

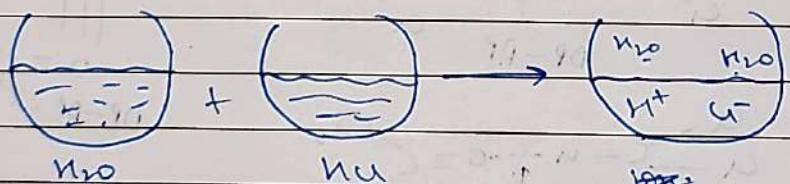
→ This gives negatively deviated system.

Example 3: $\text{CuCl}_2 + \text{C}_2\text{H}_5\text{O}_2\text{C}_2\text{H}_5$



~~Q&A~~

Example 4: $\text{H}_2\text{O}_4\text{NC}$ or $\text{H}_2\text{O}_4\text{NNO}_3$

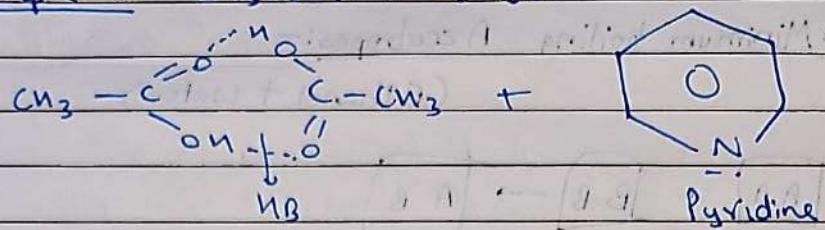


→ ions do not evaporate.

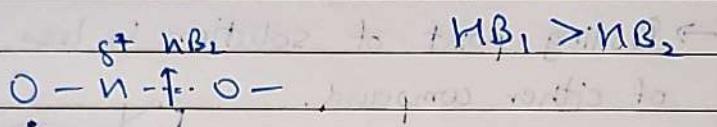
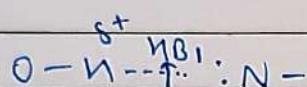
→ ∴ V.P. ↓

→ This gives negatively deviated system.

Example 6: $\text{CH}_3\text{COONH}_4 + \text{C}_5\text{H}_5\text{N}$



→ NB between H and N is greater than H and O .
hence negatively deviated system.



★ ★ ★	$\text{VP} \downarrow$	$\text{BP} \uparrow$	(-) negative deviation
	$\text{VP} \uparrow$	$\text{BP} \downarrow$	(+) positive deviation

★ Distillation Process:-

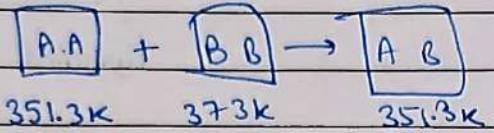
★ Azeotropic mixture:-

→ A binary solution containing two volatile liquids in which both liquid and vapour have same composition.

→ A boiling liquid mixture at the azeotropic composition produces vapors of exactly the same composition as that of the liquid.

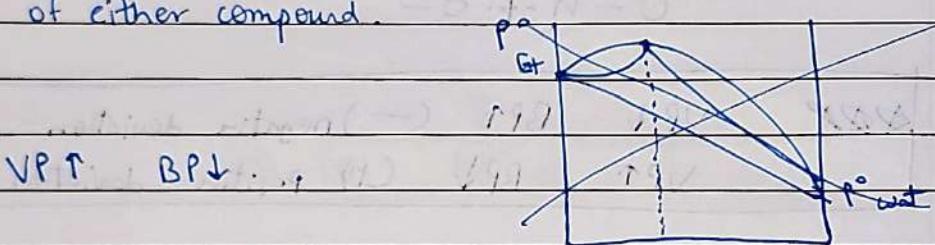
★ → Composition of liquid mixtures at which distillation can not separate the two liquids because the condensate has the same composition as that of the azeotropic liquid.

→ Minimum boiling Azeotropes:—
(Ethanol + Water)

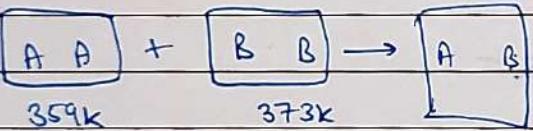


→ These azeotropes are formed by the solutions having large (+ve) deviation.

→ Boiling point of solution is less than Boiling point of either compound.



→ Maximum boiling azeotrope:— (CH₃CO₂H + H₂O)



→ These are formed by the solutions which show (-ve) deviation from Raoult's law.

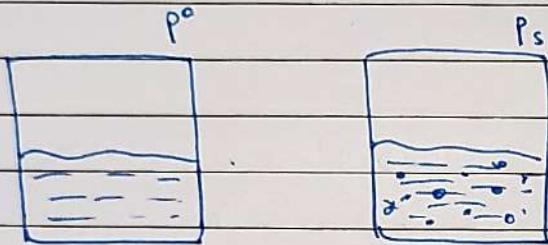
→ Boiling point of this ~~azeotrope~~ solution is more than either component.

V.P.T. B.P.T.

★ Colligative Properties:-

→ Properties of a solution of a non-volatile solute in a volatile solvent, which depends only on the number of solute particles not on the nature of solute particles.

★ Relative Lowering of Vapour Pressure:-



$$P_s = P^\circ \chi_{\text{solute}}$$

$$P_s = P^\circ (1 - \chi_{\text{solute}})$$

$$P^\circ - P_s = P^\circ \chi_{\text{solute}}$$

$$\frac{P^\circ - P_s}{P^\circ} = \chi_{\text{solute}}$$

$$\therefore \frac{(P^\circ - P_s)}{P^\circ} = \chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvant}}}$$

Here, $P^\circ - P_s$ = lowering of vapour pressure

and, $\frac{P^\circ - P_s}{P^\circ}$ = relative lowering of vapour pressure.

$$\therefore RLVP = \frac{P^\circ - P_s}{P^\circ} = \chi_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvant}}}$$

for highly diluted solution $\approx \frac{n_{\text{solute}}}{n_{\text{solvant}}} [n_{\text{solute}} \ll n_{\text{solvant}}]$

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~~RRR~~

$$\text{and, } \frac{P^o - P_s}{P_s} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

this is not RLVP

$$\frac{P^o - P_s}{P_s} = \frac{\omega_1/M_1}{\omega_2/M_2} \rightarrow \text{To find molecular weight}$$

* Position in periodic table:-

d-block element: G-3 to G-12 → $3d \left\{ \begin{array}{l} 4d \\ 5d \end{array} \right.$

* Electronic configuration: $(n-1)d^{1-10} ns^{0-2}$

$(n-1)d^{1-10} ns^{1-2}$ [except Pt $4d^{10} \neq 5s^0$]

3d → Sc Ti V Cr Mn Fe Co Ni Cu Zn

$4d^{10} 5s^0$

4d → Y Zr Nb Mo Tc Ru Rh Pd Ag Cd

5d → La Hf Ta W Re Os Ir Pt Au Hg

Coinage metals

* Exceptional E.C.: - finite oxidation states

→ Nb, Cu; Cr, Mo, Tc, Ru, Rh, Pd, Ag, Pt, Au

Definition of transition elements:-

→ A transition element is defined as the one which has incompletely filled d-orbital in its ground state or in any one of its oxidation state.

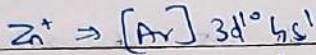
→ Zn, Cd and Hg are not considered transition elements because they do not have incomplete d-orbital in ground state or in any oxidation state.

→ All transition elements are D-block elements but not all D-block elements are transition elements.

Q1 The value of magnetic quantum no. of the outermost e^- of Zn^+ ion is _____

[31 Aug 2021 (shift-II)]

$$Z = 30 \Rightarrow [Ar] 3d^10 4s^2$$



$l=0, m=0$

★ Physical properties :-

→ Nearly all transition elements show metallic properties.

→ With exception Zn, Cd and Ra Mn, Mg have one or more typical metallic structures at normal temperatures.

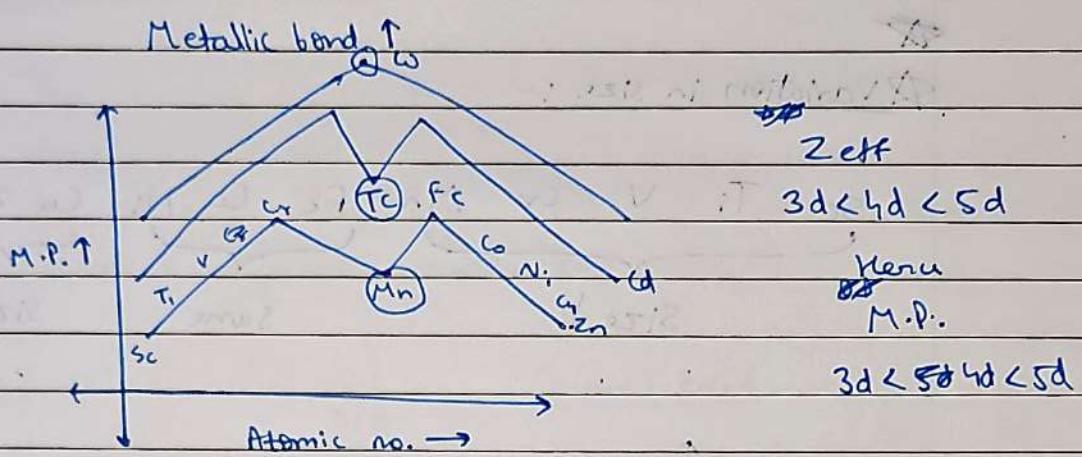
→ The transition metals are very hard and have low volatility. (exceptions: Zn, Cd and Ra)

→ Their melting point and boiling point are high.

I) Melting point :-

→ Melting point is high because more electrons participate in bonding because energy gap is less between d & s orbital.

No. of unpaired $e^- \uparrow$ Melting point ↓
so



→ 3d series has exception Mn, 4d series has exception Tc but 5d series has no exception and has the highest melting point of Tungsten (W).

→ Exceptions 1) $Zn > Cd > Hg$ (liquid)

$\downarrow \quad \downarrow \quad \downarrow$
3d 4d 5d

2) $Cu > Au > Ag$ [coinage metal]

$\downarrow \quad \downarrow \quad \downarrow$

3d 5d 4d

→ They have high enthalpies of atomisation.

$M_{(s)} \rightarrow M_{(g)} \quad \Delta_H \quad * 3d \text{ series:-}$

Min: Zn

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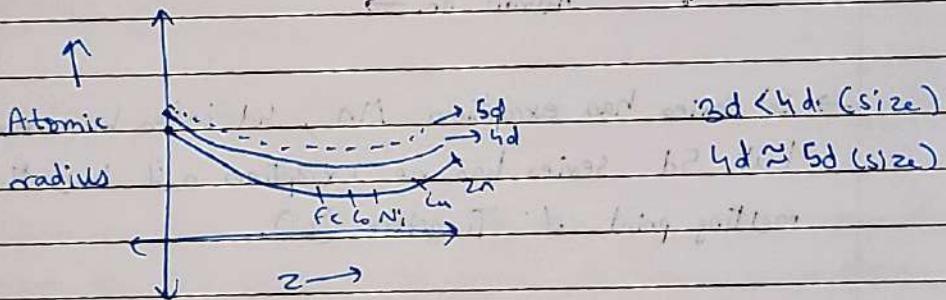
→ Zn has lowest enthalpy of atomisation because

- No unpaired e^-
- Metal-metal bonding ↓
- M.P. ↓
- $\Delta H_f^\circ \downarrow$

~~★~~ Variation in size :-

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Size ↓ Same Size ↑



→ 4d and 5d have almost same size because of: 'Lanthanoid contraction. [poor shielding of e^-]'

$$\therefore 3d < 4d \approx 5d$$

from G-4 to G-12

→ Exception in G-3

$$Sc < Y < La < Ac$$
$$3d < 4d < 5d$$

Q2 The atomic radius of Ag is closest to [7 Jan, 2020 (shift -2)]

Ⓐ Ni

Ⓑ Cu Ans: Au

Ⓒ Au

Ⓓ Mg

Density :-

→ The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from Titanium ($Z=22$) to Copper ($Z=29$) there is significant increase in the density.

$$\frac{D}{M} = \frac{\text{Size}}{\rho}$$

General trend: $\frac{\text{Size}}{M, \rho}$

→ 3d series: Min density: Sc
Max density: Cu ($D_{\text{Sc}} < D_{\text{Cu}}$)

Q3 Correct order of density

Ⓐ $\text{Cr} < \text{Zn} < \text{Fe} < \text{Co} < \text{Cu}$ Cu has highest density

Ⓑ $\text{Cr} < \text{Fe} < \text{Co} < \text{Cu} < \text{Zn}$

Ⓒ $\text{Cr} < \text{Fe} < \text{Co} < \text{Cu} < \text{Zn}$

Ⓓ $\text{Cr} < \text{Zn} < \text{Co} < \text{Cu} < \text{Fe}$

★ Ionisation enthalpies:-

Radius

$$3d < 4d \approx 5d$$

G-4 to G-12

$$3d < 4d < 5d$$

G-3

$$I.E. = \boxed{3d > 4d > 5d} \rightarrow \text{for } G-3$$

from G-4 to G-12

$$3d > 4d \text{ (I.E.)}$$

$$4d < 5d \text{ (I.E.)}$$

$$\therefore \boxed{5s > 3d > 4d} \rightarrow \text{for G-4 to G-12}$$

(with exceptions)

~~→ All~~

for G-5, G-6 and G-10

$$5d > 4d > 3d \quad Ta > Nb > V$$

$$W > Mo > Cr$$

$$\nabla Pt > Pd > Ni$$

$$\rightarrow Sc < Ti < V < Cr < Mn < Fe > Co \xrightarrow{\text{Co}} Ni < Cu < Zn$$

→ Cr and Cu have high value of IE, because of the extra stability of half filled and completely filled d-orbitals.

→ Mn and Zn have high value of IE, because of extra stability of half filled and completely filled s-orbitals. Zn & Cu do not show +3 oxidation

Magnetic Properties :-

1) Paramagnetic: At least 1 unpaired e^-

2) Diamagnetic: No unpaired e^-

$$\text{Magnetic moment} = \sqrt{n(n+2)} BM$$

↓
no. of unpaired e^-

Oxidation state :-

→ Elements show variable oxidation states because energy levels of 3d, 4d and 5d orbitals are fairly closed to that of 4s, 5s, 6s respectively

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2	+2	+2	+2	+2	+2	+2	+1	
+3	+3	+3	+3	+3	+3	+3	+3	+2	+2
+4	+4	+4	+4	+4	+4	+4	+4	+4	
+5		+5	+5	+5	+5	+5	+5	+2	+2
					+6	+6			
						+7			

→ upto Mn (O.S.) = $n s + (n-1)d$

e.g.: - Mn $1s^2 3d^5$

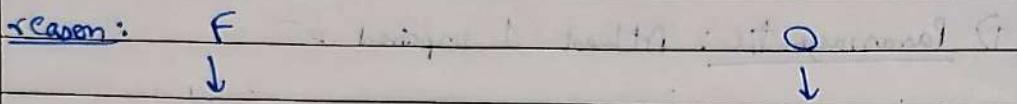
$$\text{O.S.} = 2 + 5$$

$$= 7$$

→ Ru and Os have a maximum oxidation state (+8) which is highest oxidation state shown by any element.

Date: / /

→ Maximum oxidation state is ~~not~~, satisfied by 'F' and 'O'



→ Small size

→ Strong bond formation

→ Multiple bond formation.

e.g.: IF_7 , Cl_2O_7 , SF_6

→ Higher O.S. of 4d and 5d series are more stable than Higher O.S. of 3d series.

e.g.: $\text{Cr}^{+6} < \text{Mo}^{+6} < \text{W}^{+6}$ (stability)

$\text{Cr}^{+6} > \text{Mo}^{+6} > \text{W}^{+6}$ (oxidizing power)

→ Low oxidation states are found when a complex compound has ligands capable of pi acceptor character in addition to the sigma bonding.

e.g.: $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$

★ Alloy Formation :-

- Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.
- Such alloys are formed by atoms with metallic radii that are within about 15% of each other.
- The alloys so formed are hard and have often high melting points.
- Alloys of transition metals with non-transition metals such as brass ($Cu-Zn$) and bronze ($Cu-Tin$)

e.g.: -

- 1) Brass ($Cu + Zn$)
- 2) Bronze ($Cu - Tin$)
- 3) Gun metal [$Cu(87\%) + Sn(10\%) + Zn(3\%)$]
- 4) German silver [$Cu(50\%) + Sn(20\%) + Zn(25\%) + Ni(5\%)$]
- 5) Stainless Steel [Fe + Cr + Ni]
- 6) Bell metal [$Cu(20\%) + Sn(20\%)$]

★ Formation of Complex Compounds :-

- The transition metals form a large number of Co. Co.
- This is due to smaller sizes of the metal ions, high ionic charges and the availability of d -orbitals for bond formation.

*Formation of Interstitial Compounds :-

- They are formed when small atoms like H, C or N are trapped inside the crystal lattice of metals.
- They are usually non-stoichiometric and are neither ionic nor covalent.

Characteristics:-

- (i) High M.P., higher than pure metals.
- (ii) They are very hard, some borides approach diamond in hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

*Trends in M^{2+}/M Standard Electrode Potentials :-

* ~~S.R.P. ↓~~

Standard reduction potential \downarrow Reducing agent \uparrow

- The general trend towards less $-ve E^\circ$ values across the series is related to the general increase in the sum of the first and second IE's.
- The unique behaviour of Cu, having the E° , accounts for its inability to liberate H_2 from acids. Only oxidising acids react with Cu.
- The high energy to transform $Cu(s)$ to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

Q4 In 3d series highest M^{2+}/M SEP

Ans. Cu

112

112

112

112

112

Catalytic Properties:-

→ Fe: Haber's process (Mo - promoter)

→ V_2O_5 : Contact process ($SO_2 + O_2 \rightarrow SO_3$)

→ MnO_2 : Thermal decomposition of $KClO_3$

→ $TiCl_4 + (C_2H_5)_2Al$ (Ziegler-Natta catalyst) : Production of polythene

→ Ni/Ir : Hydrogenation

→ Pt/PtO (Adams catalyst) : Used in reduction.

→ The transition elements and their compounds are known for their ability to adopt multiple oxidation state and to form complexes.

Formation of coloured Ions:-

→ When an electron from a lower energy d-orbital is excited to a higher energy d-orbital the energy of excitation corresponds to the frequency of light absorbed.

→ This frequency generally lies in the visible region. The color observed corresponds to the complementary color of the light absorbed.

Date: / /

Configuration	Example	Colour
3d ⁰	Sc ³⁺	Colourless
3d ⁰	Ti ⁴⁺	Colourless
3d ¹	Ti ³⁺	Purple
3d ¹	V ⁴⁺	Blue
3d ²	V ³⁺	Green
3d ³	V ²⁺	Violet
3d ³	Cr ³⁺	Violet
3d ⁴	Mn ²⁺	Violet
3d ⁴	Cr ²⁺	Blue
3d ⁵	Mn ²⁺	Pink
3d ⁵	Fe ³⁺	Yellow
3d ⁶	Fe ⁴⁺	Green
3d ⁶ 3d ⁷	Co ³⁺ Co ²⁺	Blue Pink
3d ⁸	Ni ²⁺	Green
3d ⁷	Cu ²⁺	Blue
3d ¹⁰	Zn ²⁺	Colourless

Some important Compounds of Transition elements -

I] Oxides and oxyanions of Metals:

→ All the metals except Sc form MO oxides which are ionic.

→ Mn₂O₃, CrO₃, V₂O₅ → Acidic in nature.

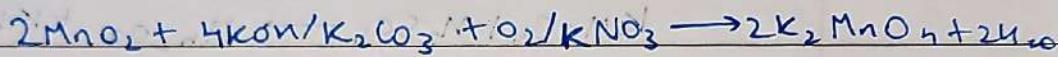
→ CrO is basic and Cr₂O₃ is amphoteric

1) Potassium Permanganate ($KMnO_4$):-

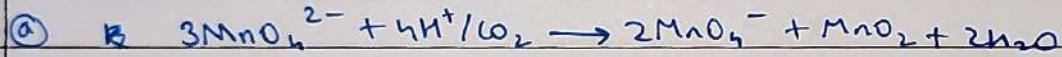
→ It is prepared from pyrolusite (MnO_2) involving the following steps:-

(i) Conversion of MnO_2 into potassium manganate.

→ powdered pyrolusite (black brown) is fused with an alkali metal hydroxide and an oxidising agent like KNO_3 to give green coloured potassium manganate.

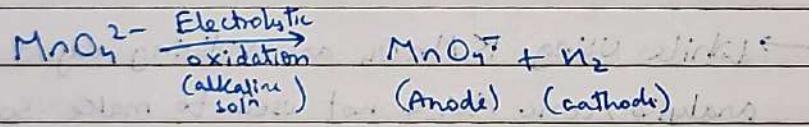


(ii) Conversion of potassium manganate into $KMnO_4$.



→ This $KMnO_4$ is not used as laboratory reagent because of traces of MnO_2 .

(b) Commercial method

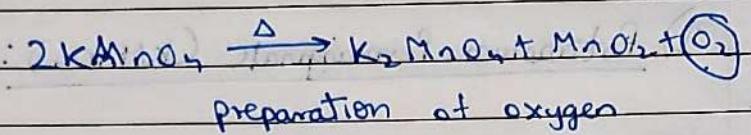


Properties :-

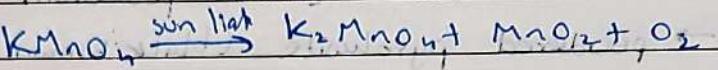
→ It forms dark purple needle like crystals with a metallic lustre. Its melting point is 533K. It is moderately soluble in water giving a purple solution.

→ It is a powerfull oxidising agent in acidic, neutral and alkaline medium.

~~Ques~~ On Heating:-



→ It is unstable in sunlight so it is kept in dark coloured bottles.

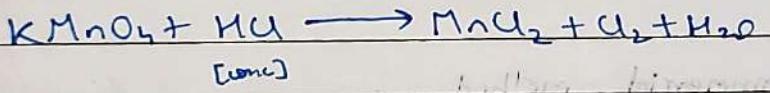


~~Ques~~ Reaction with conc H₂SO₄:



→ This is not a redox reaction.
 → Mn₂O₇ is explosive in nature.

~~Ques~~ Reaction with conc HCl:



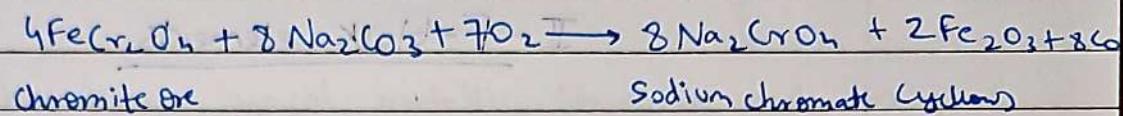
→ While using KMnO₄ as oxidising agent in volumetric analysis, conc HCl is not used to make solution acidic as it is oxidised to Cl₂. Conc NaOH is used instead.

→ In KMnO₄ → Mn⁷⁺

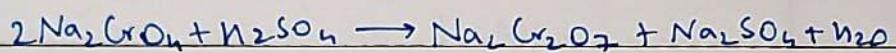
2) Potassium Dichromate ($K_2Cr_2O_7$):-

→ $K_2Cr_2O_7$ is prepared from chromite ore

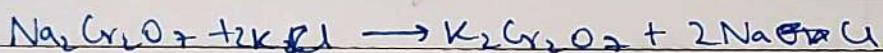
(1) Preparation of sodium chromate:-



(ii) Conversion of sodium chromate into Sodium dichromate :-



(iii) Conversion of sodium dichromate into potassium dichromate:—



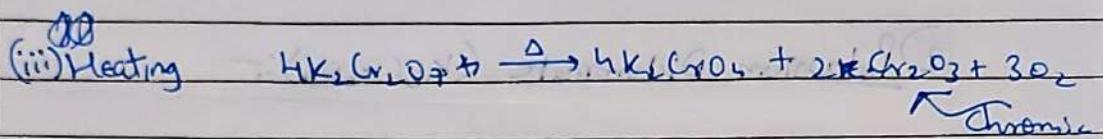
→ $\text{Na}_2\text{Cr}_2\text{O}_7$ is used in organic reactions but not in redox titrations as primary standard because it is hygroscopic in nature. $\text{K}_2\text{Cr}_2\text{O}_7$ is not hygroscopic so it is used.

$$\rightarrow K_{sp}$$



Properties:-

- (i) It is an orange crystalline solid with melting point 670 K
 - (ii) It is appreciably soluble in hot water but moderately soluble in cold water.



→ It acts as oxidizing agent in acidic medium.

II - F-block elements

→ 4f series [Lanthanides] $\Rightarrow z = 58$ to $z = 71 \rightarrow 14$ elements

→ 5f series [Actinides] $\Rightarrow z = 90$ to $z = 103 \rightarrow$ in each

→ They are called Inner transition elements.

Electronic configuration $\Rightarrow (n-2)f^{1-14} (n-1)d^0 \sim ns^2$

→ Because Lanthanum closely resembles the Lanthanides, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used.

→ Similarly, a discussion of the actinoids includes actinium besides the 14 elements.

⇒ E-C lanthanoids $4f^{1-14} 5d^0 \sim 6s^2$

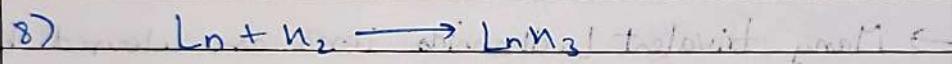
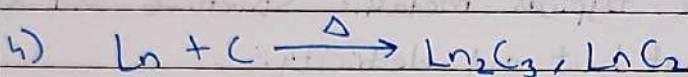
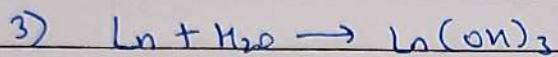
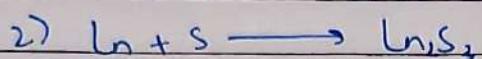
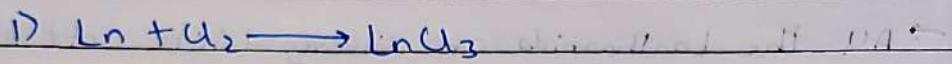
⇒ Atomic radius:-

→ Radius decreases with increasing atomic number because of the poor shielding of 4fⁿ electrons (Lanthanoid contraction). exception: Eu

General Characteristics:-

- All the Lanthanoids are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number.
- They have typical metallic structure and are good conductors of heat and electricity.
- Their melting points range between 1000 to 1200 K but Samarium (Sm) melts at 1623 K.
- Density and other properties change smoothly except for Eu and Yb.
- Many trivalent Lanthanoids ions are coloured both in the solid state and aqueous solutions.
- Colour of these ions may be attributed to the presence of f-electrons.
- Neither La^{3+} nor Lu^{3+} ion shows any color but the rest do so.
- The Lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

General chemical reactions:-



→ They are reactive metals.

→ Basic Strength



Size ↑

Size ↓

B.L. ↑

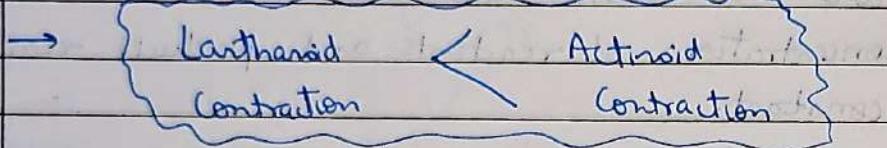
B.L. ↓

Uses :-

- 1) Production of alloy steels for plates and pipes
- 2) Alloy mischmetall ($\text{La}(95\%) \text{ad Fe} (\sim 5\%)$ and $\text{S}, \text{C}, \text{Ca}$ and Al traces). Used with Mg alloy to produce bullets.
- 3) Mixed oxides of La are employed as catalysts in petroleum cracking.

2) Actinoids :-

→ Radius ↓ (Actinoid contraction) [poor shielding of $5f\ e^-$]



General Characteristics :-

→ Silvery in appearance

→ Reactive metals

→ The action of boiling water on them gives a mixture of oxide and hydride and combination with most non-metals takes place at moderate temperatures.

→ HCl attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers.

→ Alkalies have no action.

→ Radioactive in nature.

* Equilibrium: It is a state in which there are no observable changes as time goes by.

→ When a reaction has reached equilibrium state concentrations of reactants and products remains constant.

at equilibrium,

Rate of forward reaction = Rate of backward reaction
concentration of reactant and product is constant

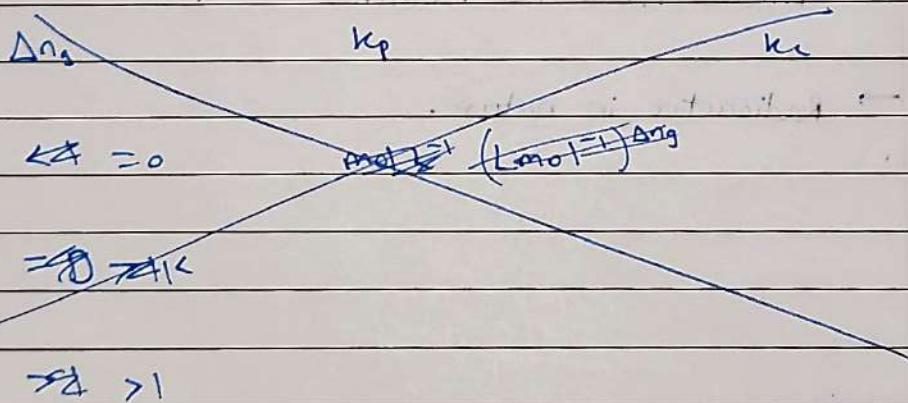
* Law of mass action:-



rate of forward rxn $\propto [A]^a [B]^b$. rate of backward rxn $= [C]^c [D]^d$

$$\frac{k_f}{k_b} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \text{ and } K_p = K_c \times (RT)^{\Delta n_g}$$



★ Special point, if $T = \frac{1}{R}$ then $\underline{k_p = K_c}$ at all times

$$R \approx 0.0821 \cdot \text{LatmK}^{-1}\text{mol}^{-1}$$

$$R \approx \frac{1}{12} \cdot \text{LatmK}^{-1} \therefore T = 12K$$

★ Factors affecting the equilibrium constant :-

① mode of representation of the reaction.

→ if two equations are added their K_c 's are multiplied

② Temperature:

→ In general, the first equilibrium approach is

→ K_c changes with change in temperature.

$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

(i) When ΔH° is +ve (endothermic reaction) $K_c \propto T$

(ii) When ΔH° is -ve (exothermic reaction) $K_c \propto \frac{1}{T}$

★ Reaction Quotient (Q_c):-

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

→ It can be written at any point in reaction.

(i) $Q_c > K_c$: Forward reaction

(ii) $Q_c = K_c$: Equilibrium

(iii) $Q_c < K_c$: Backward reaction

Degrees of Dissociation:-

→ It is the fraction of a mole to the reactant that underwent dissociation. It is represented by 'd'.

$d = \frac{\text{no. of moles of the reactant dissociated}}{\text{no. of moles of the reactant present initially}}$

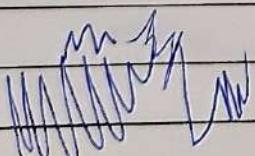
$$\% \text{ dissociation} = d \times 100\%$$

Homogeneous equilibrium: Reactant and product are same phase or are miscible.

Heterogeneous equilibrium: Reactant and product are different phase or are immiscible.

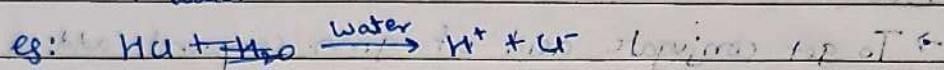
Le Chatelier principle:-

→ If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a substance, there will be a tendency for a net reaction in the direction that tends to reduce the effect of this change.



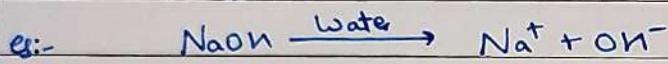
Acids and BasesI] Arrhenius concept:-

1) Acid: Acid is a substance which gives H^+ ions when dissolved in water.



exception / prob wrong: Acidity of CO_2 , SO_2 , $AlCl_3$ at $T = 0^\circ C$

2) Base: Base is a substance which gives OH^- ions when dissolved in water.



exception: Basicity of Na_2CO_3 , NH_3 etc.

Limitations:-

→ Can not explain behaviour of acids and bases in absence of water

→ Does not explain nature of H^+ and OH^- ions in water.

→ It is not able to predict acidic or basic character of a substance.

II] Brønsted-Lowry Concept:-

1) Acid: A substance which can give/donate a H^+ (proton).

2) Base: A substance which can take/accept a H^+ (proton).

→ Water is amphoteric/amphiprotic. i.e.: it can donate as well as accept H^+ ions.

→ This is also called protonic theory of acids and bases.

* Conjugate acid base pair :-

→ An acid base pair that differs only by one proton is called conjugate acid-base pair.

Note:

→ To get conjugate acid of given compound add a H^+ .

→ To get conjugate base of given compound remove a H^+ .

→ Stronger the Brønsted Acid/Base weaker the conjugate base/acid.

→ When two acids are added together the weaker acid acts as the base.



III] Lewis concept :-

1) Acid: A substance which can accept a pair of e^- .

2) Base: A substance which can donate a pair of e^- .

* Species that can act as acid:-

→ All simple cations, e.g: H^+ , Mg^{2+} , Co^{3+} , Ag^+ , Fe^{3+} , etc

→ Molecules having multiple bonds with different electronegativity

e.g: SO_3 , CO_2 etc

→ In coordinate complex, metal is Lewis acid.

→ Molecules having a central atom with different d-orbitals
e.g SF_6 , SiF_4 , SnCl_4

* Species that can act as base:-

- Electron rich neutral compounds
- All negatively charged ions.
- Ligands in coordination compounds.
- All Brønsted bases are Lewis bases because it they have a tendency to donate e^- they can accept H^+ .

~~★~~ Ionisation of Acids and Bases:-

- Ionisation constant / Ionic product of water,

$$K_w = 10^{-14} \text{ at } 298\text{K} \quad [K_w \uparrow \text{when } T \uparrow]$$

- ~~pH~~ pH: Measure of acidity of solution.

$$\rightarrow pH = -\log_{10}[H^+] \quad \text{and} \quad pOH = -\log_{10}[OH^-]$$

$$\rightarrow \boxed{pH + pOH = 14} \quad \text{at } 298\text{K}$$

$$\rightarrow \text{for acid, } K_a = \frac{[H^+][A^-]}{(\text{dissociation constant})[HA]} \quad \alpha = \sqrt{\frac{K_a}{C}}$$

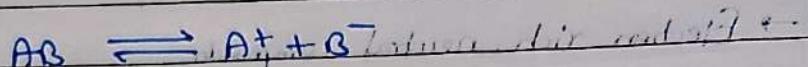
→ for base,

$$K_b = \frac{[OH^-][B^+]}{[BOH]} \quad \alpha = \sqrt{\frac{K_b}{C}}$$

→ $\alpha = \text{dissociation constant degree of dissociation}$

∴ dissociation = $\alpha \times 100\%$.

Ortewald's dilution law :- In case of dilution of strong acid or base



C initial concentration of AB

((1-d)) Cd concentration of dissociated

or, concentration of dissociated AB

1-n fraction of dissociation

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}$$

$$K_a = \alpha^2 c \quad [\text{if } \alpha \leq 0.05]$$

Or, $\alpha \approx \sqrt{K_a c}$

$$\alpha = \sqrt{K_a V} \quad \Rightarrow V = \text{Volume containing 1 mole}$$

$$K_a = \frac{\alpha^2 c}{1-\alpha} \quad [\alpha \geq 0.05]$$

(weak electrolyte)

$$pK_a = -\log_{10} K_a$$

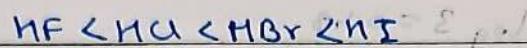
$$pK_b = -\log_{10} K_b$$

$$pK_a + pK_b = pK_w = 14$$

★ Factors affecting acid strength :-

↳ \rightarrow $\text{H-A bond} \rightarrow \text{Strength} \rightarrow \text{F} \rightarrow \text{FSM}$

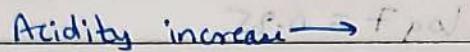
\rightarrow Strength of an acid depends on Strength and polarity of H-A bond.



Electronegativity increase \rightarrow



$\text{CH}_3 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$



Acidity increase \rightarrow

★ Common ion effect :-

\rightarrow The addition of a substance that suppresses the dissociation of weak electrolyte due to the presence of common ion is called common ion effect.

Salt	Hydrolysis	Sol ⁿ⁺¹	Hydrolysis const	Degree of hydrolysis
(i) WA + SB	Anionic	Alkaline $\text{pH} > 7$	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$
(ii) SA + WB	Cationic	Acidic $\text{pH} < 7$	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$
(iii) WA + WB	Anionic and Cationic both	Neutral if $K_a \approx K_b$	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$

$$(i) \text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$$

Note: In salt of WA + WB
pH is determined by values of K_a and K_b

$$(ii) \text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$$

$$(iii) \text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$$

$$\frac{1}{2} \text{p}K_w = 7$$

Date: / /

~~Ques~~ $\text{pH} = \text{pOH}$: neutral \Leftrightarrow $\text{pH} + \text{pOH} = 14$

$\text{pH} > 7$ or $\text{pOH} < 7$ Basic \Leftrightarrow at 298K only

$\text{pH} < 7$ or $\text{pOH} > 7$ Acidic \Leftrightarrow $\text{pH} + \text{pOH} = 14$

$$\text{imp values: } \log 2 = 0.3$$

$$\log 3 = 0.48$$

$$\log 5 = 0.7$$

$$\log 7 = 0.85$$

$$\log 3.2 = 0.5$$

~~Ques~~ pH scale: 0 to 14 at 298K (25°C)

0 to 13.6 at 310K (37°C)

~~Ques~~ Formulae:-

I] Monobasic weak acid

$$1) K_a = \alpha^2 C$$

$$2) [\text{H}^+] = \alpha C = \sqrt{K_a \times C}$$

$$3) \text{pH} = -\log_{10} [\text{H}^+]$$

$$4) \text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C$$

II] Monoacidic base

$$1) K_b = \alpha^2 C$$

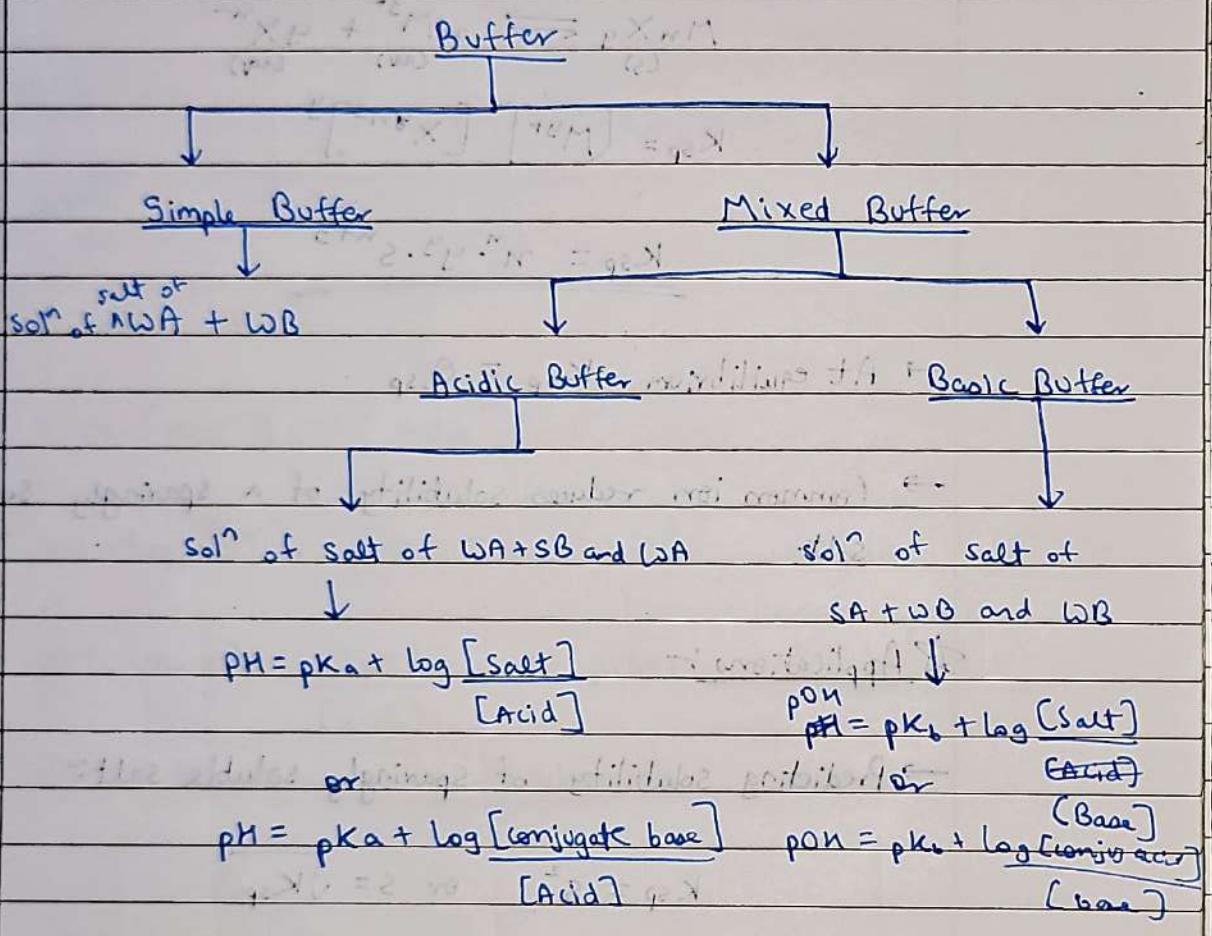
$$2) [\text{OH}^-] = \alpha C = \sqrt{K_b \times C}$$

$$3) \text{pOH} = -\log [\text{OH}^-]$$

$$4) \text{pOH} = \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

★ Buffer Solution:-

→ Solutions which resist change in pH on dilution or with addition of small amounts of acid or alkali are called buffer solutions.



→ Buffer capacity = no. of moles of acid or base / mass of buffer
or
= $\frac{\text{mass of acid}}{\text{mass of buffer}} \times \frac{\text{mass of base}}{\text{mass of buffer}}$ (change in pH)

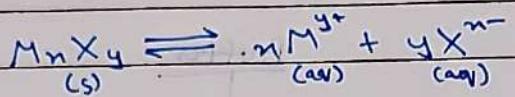
→ The range of pH over which the buffer solution remains effective is called buffer range.

Acidic $\quad \text{pK}_a \pm 1$

Basic $\quad \text{pK}_w - \text{pK}_a \pm 1$

Solubility product:-

→ A solid salt M_nX_y with molar solubility s in the equilibrium with its saturated solution may be represented by the equation.



$$K_{sp} = [M^{y+}]^n [X^{n-}]^y$$

$$\underline{K_{sp} = n^n \cdot y^y \cdot s^{inty}}$$

→ At equilibrium $K_{sp} = Q_{sp}$

→ Common ion reduces solubility of a sparingly soluble salt.

Applications:-

→ Predicting solubility of sparingly soluble salt:-

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

→ Predicting precipitation formation:-

$$\text{Ionic product } \Rightarrow \text{e.g. } NaCl = [Na^+] \cdot [Cl^-]$$

$$H_2O = 10^{-11} T^2$$

Super saturated if Ionic product $> K_{sp}$ precipitation.

Unsaturated

$< K_{sp}$ no precipitation

Saturated

$= K_{sp}$ no precipitation

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Type	Eg	Equation	K _{sp} expression	Molar solubility
1:1	AgCl	$\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$	$K_{\text{sp}} = s^2$	$s = \sqrt{K_{\text{sp}}}$
1:2	PbCl ₂	$\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-$	$K_{\text{sp}} = s \cdot s^3$	$s = \sqrt[3]{K_{\text{sp}}/4}$
2:1	Ag ₂ CrO ₄	$\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$	$K_{\text{sp}} = 2s^2 \cdot s^3$	$s = \sqrt[3]{K_{\text{sp}}/4}$
1:3	AlCl ₃	$\text{AlCl}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{Cl}^-$	$K_{\text{sp}} = 27s^4$	$s = \sqrt[4]{K_{\text{sp}}/27}$
2:3	As ₂ S ₃	$\text{As}_2\text{S}_3 \rightleftharpoons 2\text{As}^{3+} + 3\text{S}^{2-}$	$K_{\text{sp}} = 108s^5$	$s = \sqrt[5]{K_{\text{sp}}/108}$

★ Formulae:-

$$1) d = \frac{K}{C} \quad \text{or} \quad K = d^2 C$$

$$2) d = \sqrt{Kv} \quad \text{or} \quad K = \frac{d^2 v}{V}$$

$$3) K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14} \quad (\text{ionic product})$$

$$4) \text{pH} = -\log_{10} [\text{H}^+], \quad \text{pOH} = -\log_{10} [\text{OH}^-], \quad \text{pH} + \text{pOH} = 14$$

$$5) \text{pH} = \text{pK}_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}, \quad \text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$$

$$6) \text{pK}_a = -\log_{10} K_a, \quad \text{pK}_b = -\log_{10} K_b$$

$$7) K_{\text{sp}} = n^n y^y s^{n+y}$$

$$8) S = \frac{\text{Solubility in g/mol}}{\text{Molar mass in g/mol}}$$

Solubility

Solubility of a salt

Solubility of an acid

Solubility of a base

Solubility of pure materials

Solubility of water

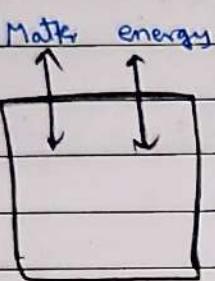
Chemical Thermodynamics

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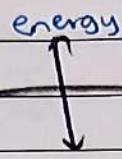
→ System: part of universe under observation.

→ Surrounding: remaining universe.

System + Surrounding = Universe

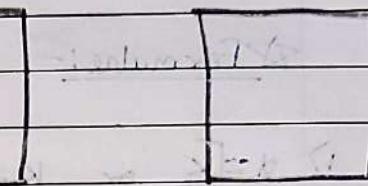


Open system



Closed system

Isolated system



→ Thermodynamic state is a set of measurable properties.

e.g.:-(i) Pressure (P)

(ii) Temperature (T)

(iii) Volume (V)

(iv) Amount (n)

Types of processes

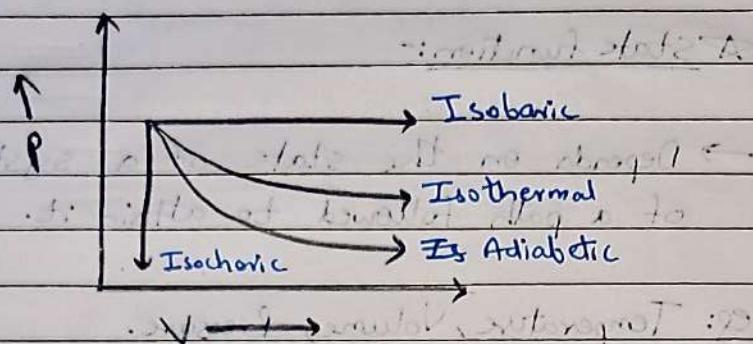
Isothermal $\Delta T = 0$	Adiabatic $\Delta Q = 0$	Isobaric $\Delta P = 0$	Isochoric $\Delta V = 0$

Reversible

→ Direction may be reversed
at any stage.

Irreversible

→ Proceeds in only one
direction and cannot be
reversed.



→ Cyclic process: System returns to original state after a number of steps.

$$\Delta U = 0 \text{ and } \Delta H = 0$$

→ Exothermic process: Heat released by system.

→ Endothermic process: Heat absorbed by system.

* Extensive properties: They depend on the amount of matter present in a system.

Eg: Mass, Volume, internal energy, heat capacity, no. of moles etc.

* Intensive properties: Independent of the amount of matter in a system.

Eg: Pressure, temperature, surface tension, viscosity, M.P., B.P., specific heat etc.

$$\Delta U = Q - W$$

$$\Delta U = nC_V \Delta T$$

$$\Delta U = nC_V \Delta T = nR \Delta T$$

$$\Delta U = nC_V \Delta T = nC_P \Delta T - nR$$

$$\Delta U = nC_V \Delta T$$

$$\Delta U = nC_P \Delta T$$

$$\Delta U = nR$$

*** State function:-**

→ Depends on the state of a system and independent of a path followed to attain it.

e.g: Temperature, Volume, Pressure.

*** Path function:-**

→ Depends on the path followed to reach that state.

e.g: Work and heat

*** Entropy :-**

→ A spontaneous process is an irreversible process and may only be reversed by some external agency.

→ Entropy (S) is the measure of randomness or disorder.

$$\Delta S_{\text{Total}} = \Delta S_{\text{Syst}} + \Delta S_{\text{Sur}} > 0$$

→ Change in entropy for reversible process is,

$$\Delta S = \frac{\alpha V_{\text{sys}}(\text{rev})}{T} \quad T \leftarrow \text{Temperature}$$

→ Entropy change for phase change is,

$$\Delta S_{\text{fus}} = \frac{\Delta f_{\text{fus}} N}{T_m}, \Delta S_{\text{vap}} = \frac{\Delta v_{\text{vap}} N}{T_b}, \Delta s_{\text{sub}} S = \frac{\Delta s_{\text{sub}} N}{T}$$

$$T_m = \text{M.p.} \quad T_b = \text{B.p.} \quad T = \text{S.p.}$$

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$$\rightarrow \Delta_s^\circ = \sum_{\text{products}} S^\circ - \sum_{\text{reactants}} S^\circ$$

$$\Delta_f^\circ H = \Delta U$$

for endo. rxn. $\Delta U > 0$

First law of thermodynamics:-

~~ΔH~~

First law of thermodynamics:-

- It states that is the law of conservation of energy.
- Energy of the universe remains constant.
- ~~The total~~ → Energy is neither created nor destroyed.

$$\Delta U = Q + W$$

Internal energy :- (U)

- It is the total energy within a system. It is the sum of all types of energies of the system.
- It is a state function.
- ~~ΔU~~ Internal energy (U) changes when,
 - Heat is exchanged (enters or leaves)
 - Matter is exchanged (enters or leaves)
 - Work is done on or by the system.

$$\rightarrow \Delta U = Q + W$$

ΔU is a state function but W & Q are not.

\rightarrow Sign convention.

(i) Heat \rightarrow absorbed = +ve

Evolved = -ve

(ii) Work \rightarrow on the system = +ve

by the system = -ve

$$\rightarrow \text{Adiabatic change, } \Delta U = U_2 - U_1 = W_{ad}$$

where, W_{ad} is work when $q=0$ (adiabatic)

~~ΔU = Q + W~~: Adiabatic process $\therefore \Delta U = \cancel{W}$

Isochoric process (no work done, $\Delta V=0$) $\Delta U = q$

Enthalpy:-(H)

\rightarrow Total heat content of the system at constant pressure is known as its enthalpy.

\rightarrow It is an extensive property and a state function.

$$H = U + PV \quad \text{(i)}$$

$$\Delta H = \Delta U + P\Delta V \quad \text{(ii)}$$

exothermic reaction $\Delta H < 0$ -ve

endothermic reaction $\Delta H > 0$ +ve

$$\Delta H = \Delta U + \Delta n g RT \text{ or } q_p = q_v + \Delta n g RT$$

$$q_p = \Delta U + \cancel{\Delta n g RT} PAV \quad \Delta p =$$

$$\Delta n > 0 \quad \Delta n > \Delta v$$

$$\Delta n = 0 \quad \Delta n = \Delta v$$

$$\Delta n < 0 \quad \Delta H < \Delta U$$

→ For a reaction of only solids and liquids or in a closed vessel $\Delta H = \Delta U$

* Types of Enthalpies :-

I) Phase transformation :-

1) Enthalpy of fusion ($\Delta_{\text{fus}}H^\circ$): Enthalpy change when 1 mole of a solid is completely converted into liquid state at its melting point.

2) Enthalpy of Vaporisation ($\Delta_{\text{vap}}H^\circ$): Enthalpy change when 1 mole of a substance liquid is converted into vapour state at its boiling point.

3) Enthalpy of Sublimation ($\Delta_{\text{sub}}H^\circ$): Enthalpy change when 1 mole of a solid is converted into vapour state directly.

BB

$$\Delta_{\text{sub}}H^\circ = \Delta_{\text{fus}}H^\circ + \Delta_{\text{vap}}H^\circ$$

Hess law of constant heat summation:-

→ If a reaction takes place in multiple steps then its standard reaction enthalpy is the sum of all the standard enthalpies of individual steps.

$$\Delta_{\text{rxn}} = \Delta_{\text{H}_1} + \Delta_{\text{H}_2} + \Delta_{\text{H}_3}$$

* Enthalpy of formation: It is the change in enthalpy when one mole of a substance is formed directly from its constituent elements in their most stable state of aggregation.

II) Enthalpies of chemical reactions:-

1) Combustion: Enthalpy change when 1 mole of a substance is completely burnt in oxygen.

2) Enthalpy of atomization: Enthalpy change when 1 mole of bonds are completely broken to get atoms in gas phase.

3) Bond Enthalpy:

4) Lattice enthalpy: Enthalpy change when 1 mole of an ionic compound dissociates into its constituent ions in gas phase.

→ It is calculated using Born Haber cycle.

5) Enthalpy of Solution: Enthalpy change when 1 mole of solid a substance is dissolved in specified amount of solvent.

$$\Delta_{\text{sol}} H^\circ = \Delta_{\text{hydr}} H^\circ + \Delta_{\text{diss}} H^\circ$$

6) Enthalpy of dilution: It is known that enthalpy of a solution is

7) Enthalpy of neutralisation

8) Enthalpy of transition: ~~It is known that enthalpy of transition is~~

9) Enthalpy of hydration.

★ Work (W):- ~~Work done by system is equal to work done by external agent. At given at constant force to move~~

$$\rightarrow W = -P\Delta V$$

$$\rightarrow W = -nRT - 2.303 nR T \log \frac{V_2}{V_1} \text{ or } -2.303 nR T \log \frac{P_1}{P_2}$$

\rightarrow In free expansion of gas ($P_{\text{ext}} = 0$) \therefore no work is done.

\rightarrow No work is done in vacuum

★ Heat capacity :- (C)

\rightarrow Heat capacity (C) of a system is the amount of heat required to raise the temperature of the system by 1°C

$$C = \frac{\alpha Q}{\Delta T} \text{ or } \alpha Q = C \Delta T$$

\rightarrow When value of C is large, i.e. it takes a lot of energy to increase temperature slightly. e.g. Water

* Molar heat capacity (C_m) :- \rightarrow It is the amount of heat required to raise the

\rightarrow It is the amount of heat required to raise the temperature of 1 mole of the substance by 1°C .

$$C_m = \frac{Q}{n \cdot \Delta T} \quad (\text{unit J/g mol } ^\circ\text{C})$$

* Specific heat capacity :- \rightarrow It is the amount of heat required to raise the

\rightarrow Amount of heat required to raise the temperature of 1 gram of the substance by 1°C .

$$\text{or } Q = mc\Delta T$$

\rightarrow Specific heat capacity of water = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ or $1 \text{ cal g}^{-1} \text{ K}^{-1}$

* Relation between C_p & C_v for an ideal gas,

$$C_p - C_v = R, \quad C_p = \frac{\Delta H}{\Delta T}, \quad C_v = \frac{\Delta U}{\Delta T}$$

* Gibbs energy :-

\rightarrow It is the net energy available to do useful work and is a measure of the free energy.

$$G = H - TS$$

→ Standard free energy of a reaction, i.e. reaction

$$\Delta_r G^\circ = \sum \Delta_f G^\circ - \sum \Delta_g G^\circ$$

→ Gibbs-Helmholtz equation,

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

* Gibbs energy change and equilibrium, i.e.

→ $\Delta_r G^\circ$ is related to equilibrium constant (K) as,

$$\Delta_r G^\circ = -2.303 RT \log K$$

ΔG°	$\log K$	K	Comment
1) $\Delta G^\circ = 0$	$\log K = 0$ if	($K=1$)	Equilibrium mixture contains comparable amounts of reactants and products.
2) $\Delta G^\circ < 0$	$\log K > 0$	$K > 1$	mixture contains mainly products exothermic
3) $\Delta G^\circ > 0$	$\log K < 0$	$K < 1$	mixture contains mainly reactants endothermic

$$\Delta V = \rho \Delta V$$

$$\Delta V_{\text{max}} = \frac{\rho}{m} \Delta V$$

$$\Delta V_{\text{max}} = \frac{\rho}{m} \Delta V$$

$$(m = 8)$$

Atomic Structure

★ Discovery of electron (Cathode ray experiment)

→ Specific charge of cathode ray = $\frac{\text{charge}}{\text{mass}}$

→ Charge = electronic charge = $1.6 \times 10^{-19} \text{ C}$

→ Mass of $e^- = 9.1 \times 10^{-31} \text{ Kg}$

→ Specific charge of cathode always remains same it will not change on change of gas.

★ Milikan's oil drop experiment:

→ Atomizer converts oil into very tiny droplets.

→ Drop of oil falls from the tiny hole on the positive plate.

→ Beam of electrons or X-rays ionize the air present inside the chamber and released electrons absorbed by oil drops.

→ Potential difference applied such that the net force acting on the oil drop becomes 0.

$$mg = qV$$

$$q = \frac{mg}{e}$$

$$\begin{aligned} q &= -1.6 \times 10^{-19} \text{ C} \\ &= -3.2 \times 10^{-19} \text{ C} \\ &= -4.8 \times 10^{-19} \text{ C} \end{aligned}$$

$$q = ne$$

→ Charge is an integral multiple of 'e', e = minimum charge

- Cathode rays are emitted from the surface of cathode.
- Anode rays are not emitted from surface of Anode.
- Cathode rays = (e^-) , Anode rays = $(+m^+)$

↑

(having mass less than 1) i.e. heavier than hydrogen (1)

- Cathode rays travel in a straight line.

(i.e. no deflection after passing through electric field)

★ Closest distance of approach

$$R_0 = \frac{2Kz(e)}{mv_0^2}$$

$$K = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$$

q = charge of particle (Same as atom to which it is attached)

z = atomic no. of atom which particle is bombarded

R_0 = closest distance of approach coming with NA

v_0 = Velocity through which particle is bombarded

e = electronic charge (the value which we have in)

that values will depend on position etc

(+ve) charged particle \rightarrow ${}_1^1H^+$ (proton)

${}_2^4He^+$ (α -particle)

For proton ($q = e, m = m_p$)

For α -particle ($q = 2e, m = m_\alpha$)

then we can calculate formula for minimum distance

$$R_0 = \frac{2K(z)e}{m_p v_0^2}$$

Hence,	$R_0 = \frac{2Kz e^2}{m_p v_0^2}$
--------	-----------------------------------

$R_0 = \frac{4Kz e^2}{m_\alpha v_0^2}$
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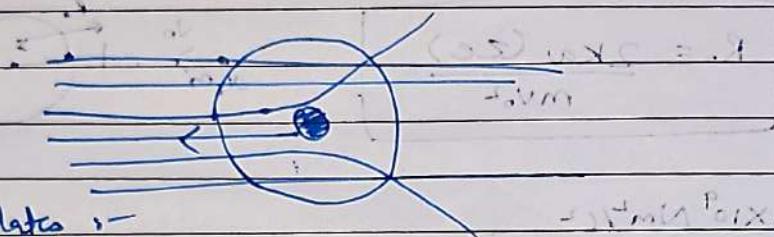
$m_\alpha = 4m_p$

Atomic models

1) Thomson's plum pudding model (Watermelon)

2) Rutherford's Atomic model (Gold foil experiment)

Conclusion: mostly empty with a center called nucleus with concentrated positive charge at center.



Postulates:-

- Size of nucleus is small ($\approx 10^{-15} \text{ m}$)
- most of the space is empty.
- All the positive (+ve) charge is concentrated at the center
- The e^- equal in no. to protons revolve at fast speed in various circular orbit around the nucleus.
- The centrifugal force balances the coulombic attraction between protons and electrons.

Drawbacks:-

- Not according to theory of electromagnetism according to Maxwell (proved theory).

- A charge particle with accelerated motion (change in velocity or direction) in this case of e^- direction the particle radiates energy. When the e^- is losing energy the radius of orbit decreases and the e^- collapses into the nucleus and the atom ends.
- radiates energy in the form of EMR.

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→ It could not explain the line spectrum of Hydrogen atom.

★ Size of the Nucleus:-

$$R = R_0 (A)^{1/3} \text{ cm}$$

R_0 can be ~~1.1~~ 1.1×10^{-13} to 1.44×10^{-13} cm

A = mass no.

R = radius of the nucleus

→ If R_0 is not given in question then find for both 1.1×10^{-13} & 1.44×10^{-13} and mark option in the form range.

★ Electromagnetic radiation:-

→ They are waves.

→ Two vector :- (i) Electric field

(ii) Magnetic field

Important characteristic of waves:-

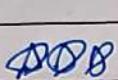
(i) Wavelength (λ): Distance between consecutive crests or troughs

(ii) Frequency (f): Number of waves pass through a point in one second.

(iii) Velocity (c): Linear distance travelled in one second
 $= 3 \times 10^8 \text{ ms}^{-1}$

(iv) Amplitude (a): Height of crests or troughs

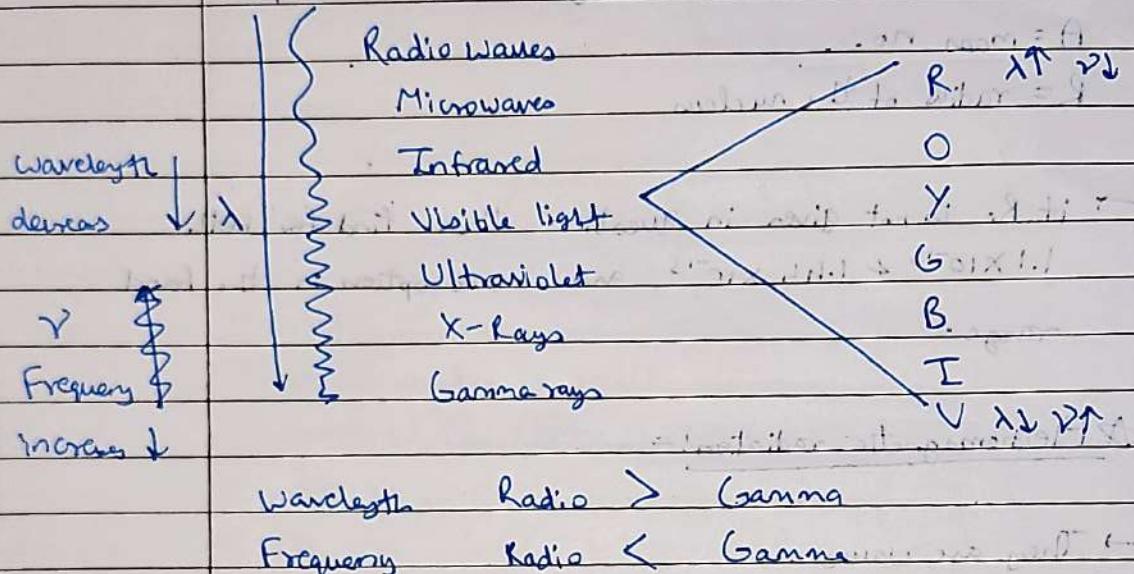
Wave number (ν) = $\frac{1}{\lambda}$: No. of waves present in 1 cm length



$$C = \nu \lambda$$

$$[w^2(A) \rightarrow]$$

★ Electromagnetic Spectrum :-



★ Particle nature of EMR:-

Black body radiation:-

★ Quantum theory of light :-

→ The smallest quantity of light that can be emitted in the form of EMR is called quantum of light

Energy of quanta or photons :

$$E = \frac{h c}{\lambda}$$

$$E = h\nu$$

$$\nu$$

$$c = \frac{\lambda}{\nu}$$

→ Energy of photon (E)

→ $h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J sec}$

→ $c = \text{speed of light } (3 \times 10^8) \text{ m/s}$

→ $\lambda = \text{wavelength of photon}$

$$\lambda_0 = \frac{12400}{E_{\text{ev}}}$$

$$1 \text{ ev} = 1.6 \times 10^{-19} \text{ J}$$

★ Photoelectric effect :-

→ When certain metals (e.g. K, Rubidium, Cesium etc.) were exposed to a beam of light electrons were ejected.

→ Electrons ejected are called photoelectrons.

→ The e^- are ejected as soon as light strikes the surface, i.e. no time lag.

→ No. of e^- ejected is proportional to intensity or brightness of light.

→ For each metal there is a characteristic minimum frequency, v_0 (threshold frequency) below which photoelectric effect does not take place.

→ Kinetic energy of photoelectrons increases with increase in frequency of light used.

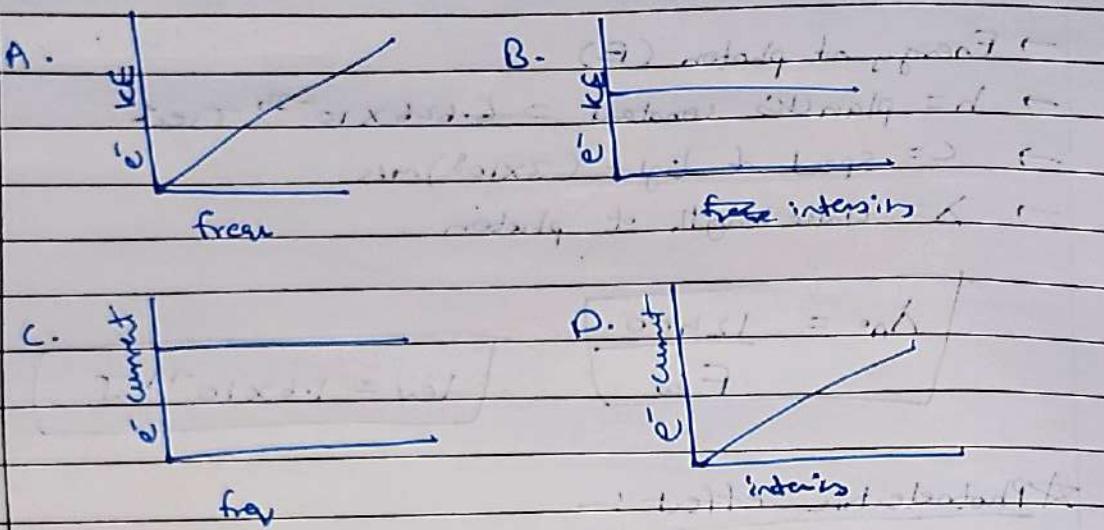
No. photons ↑ No. of photo electrons ↑

(intensity) (current)

Energy of photons ↑ K.E. of electrons ↑

(frequency)

(energy)



* Bohr's Atomic model

Postulates :-

- 1) e^- move in circular orbits around the nucleus in which they do not radiate \rightarrow energy. These orbits are called "Stationary orbits".
- 2) Stationary orbit is the orbit in which the angular momentum of e^- is an integral multiple: $(\frac{nh}{2\pi})$

$$\text{Angular momentum} = mvr = n \frac{h}{2\pi} \quad [n=1, 2, 3, \dots]$$

- 3) If e^- is moving from higher orbit to lower orbit it emits energy in the form of photon. If e^- is moving from lower orbit to higher orbit it emits energy in the form of photons.

To emit photon \rightarrow e^- loses energy
(emission) \rightarrow e^- gains energy
(absorption)

$\diamond \diamond$ All the derived formulae are applicable only for single electron system or H^+ -like system.

e.g.: - H, He^+, Li^{2+}, \dots etc

$$r_n = 0.529 \times \frac{n^2}{Z} \text{ Å} \quad (\text{Anstom } \text{Å})$$

$$v_n = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$$

$n = \text{no. of orbit}$

$Z = \text{atomic no.}$

$$1\omega = 1.6 \times 10^{-19} \text{ J}$$

$$\begin{aligned} TE &= -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom} \\ &= -13.6 \frac{Z^2}{n^2} \text{ eV/atom} \end{aligned}$$

$\diamond \diamond$ Time period (T)

$$T = \frac{\text{distance}}{\text{velocity}} = \frac{2\pi r}{v}$$

$$\therefore T = 2\pi \left(\frac{0.53 \times 10^{-16}}{2.18} \right) \frac{n^3}{Z^2} \text{ sec}$$

$$T \propto \frac{n^3}{Z^2}$$

$\diamond \diamond$ Frequency (F)

$$F = \frac{1}{T}$$

$$F \propto \frac{Z^2}{n^3}$$

$$F = \frac{2.18 \times 10^{-16}}{2\pi(0.53)} \frac{Z^2}{n^2} \text{ sec}^{-1}$$

For a particular atom

$$\frac{F_1}{F_2} = \frac{n_2^3}{n_1^3}$$

\star Acceleration (a)

$$a = \frac{v}{T}$$

$$\boxed{ad \frac{Z^3}{n^5}}$$

$$\frac{a_1}{a_2} = \frac{Z_1^3 n_2^4}{Z_2^3 n_1^5}$$

Energy level diagram

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

$n=7$

$n=6$

$n=5$

$n=4$

$n=3$

$n=2$

$n=1$

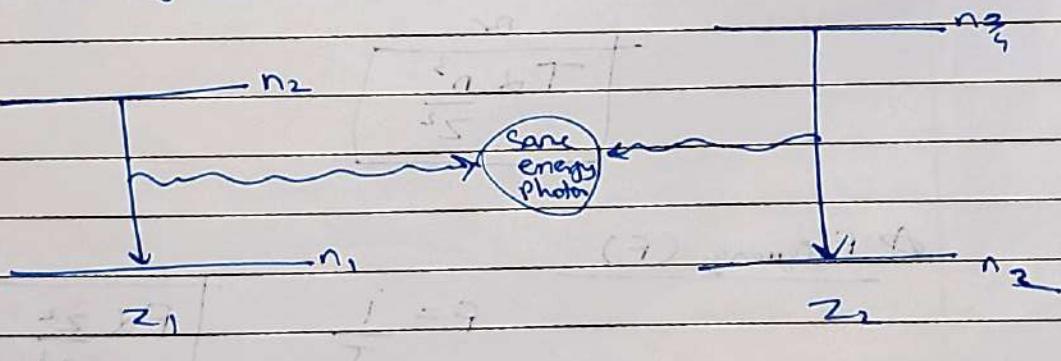
$0.05 Z^2 \text{ eV}$
 $-0.23 Z^2 \text{ eV}$
 $-0.38 Z^2 \text{ eV}$
 $-0.544 Z^2 \text{ eV}$

$-1.51 Z^2 \text{ eV}$

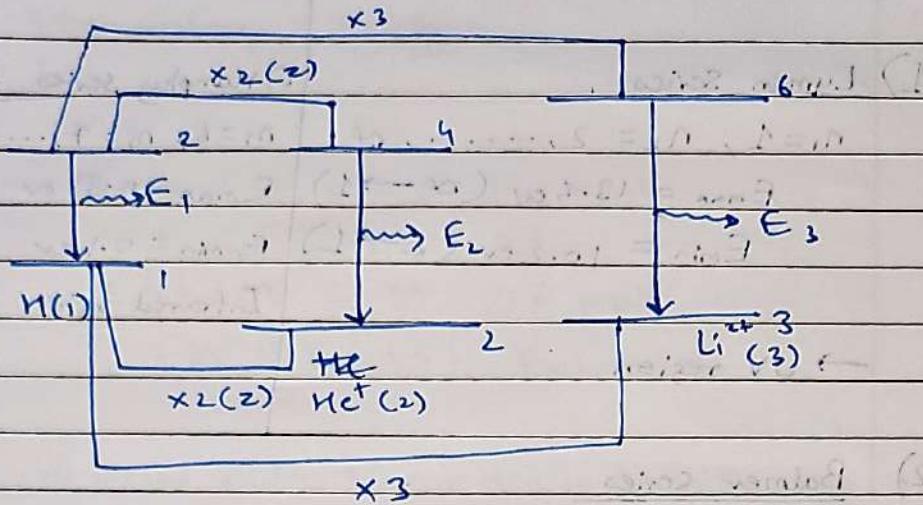
$-3.4 Z^2 \text{ eV}$

$-13.6 Z^2 \text{ eV}$

\star Equi energy transition



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$$\therefore E_1 = E_2 = E_3$$

Corresponding orbit = given orbit \times atomic no. of other atom.

$$e.g.: H \quad 2 \rightarrow 1$$

\therefore in Ne atom corresponding orbit is,

$$2 \times 2 = 4 \rightarrow \text{high orbit}$$

~~Ex:~~

$$1 \times 2 = 2 \rightarrow \text{lower orbit}$$

Emission spectrum of Hydrogen:

→ When hydrogen gas at low pressure is taken in the discharge tube and light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

1) Lyman Series $n_1 = 1, n_2 = 2, \dots, \infty$

$E_{\max} = 13.6 \text{ eV } (\infty \rightarrow 1)$

$E_{\min} = 10.2 \text{ eV } (2 \rightarrow 1)$

 $\rightarrow \text{UV region}$ 2) Humphrey series $n_1 = 6, n_2 = 7, \dots, \infty$

$E_{\max} = 0.38 \text{ eV}$

$E_{\min} = 0.1 \text{ eV}$

Infrared region2) Balmer series $n_1 = 2, n_2 = 3, \dots, \infty$

$E_{\max} = 3.4 \text{ eV } (\infty \rightarrow 2)$

$E_{\min} = 1.99 \text{ eV } (3 \rightarrow 2)$

Visible region3) Paschen series $n_1 = 3, n_2 = 4, \dots, \infty$

$E_{\max} = 1.51 \text{ eV } (\infty \rightarrow 3)$

$E_{\min} = 0.66 \text{ eV } (4 \rightarrow 3)$

Infrared region4) Pfund series Brackett series $n_1 = 4, n_2 = 5, \dots, \infty$

$E_{\max} = 0.85 \text{ eV } (\infty \rightarrow 4)$

$E_{\min} = 0.31 \text{ eV } (5 \rightarrow 4)$

Infrared region5) Pfund series $n_1 = 5, n_2 = 6, \dots, \infty$

$E_{\max} = 0.544 \text{ eV } (\infty \rightarrow 5)$

$E_{\min} = 0.16 \text{ eV } (6 \rightarrow 5)$

Infrared region

~~Q8~~ ~~3 to 5 Energy \rightarrow 10.2 eV~~

4.

$$10.2 \leq E \leq 13.6 \quad \text{Lyman}$$

$$3.4 \cancel{e} < E < 10.2 \quad \text{Not possible}$$

$$1.89 \leq E \leq 3.4 \quad \text{Balmer}$$

$$1.51 < E < 1.89 \quad \text{Not possible}$$

$$0.05 \leq E \leq 1.51 \quad \text{Paschen series}$$

~~Q9~~ no. of unique photons emitted in transition to ground state

$$= \frac{n(n-1)}{2}$$

~~Q10~~ transition from higher orbit to lower orbit

$$= \frac{\Delta n(\Delta n + 1)}{2}, \quad \Delta n = n_2 - n_1$$

→ In single isolated atom ~~if~~ if e^- makes transition from n^{th} state to ground state ($n=1$) then maximum no. of spectral lines observed = $(n-1)$

~~Q11~~ Dual nature of electron (de-Broglie hypothesis)

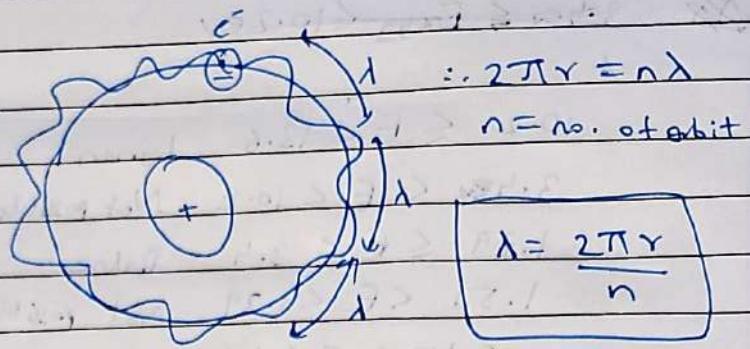
→ Einstein suggested light has dual character.

→ de-Broglie proposed e^- also has dual character.

→ This proposed a new theory, wave mechanical theory of matter. according to this theory the electrons, protons and even atom when in motion possess wave properties.

→ According to de-Broglie, the wavelength λ is given by

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



$$\lambda = \frac{2\pi r}{n}$$

λ = de Broglie wavelength

$$(i) \lambda = \frac{h}{p} = \frac{h}{mv} \quad \begin{array}{l} \text{for small mass only } \lambda \text{ is significant} \\ \text{value.} \end{array}$$

$\uparrow \quad \uparrow$
momentum mass

$$(ii) \lambda = \frac{2\pi r}{n}$$

$$(iii) \lambda = \frac{h}{\sqrt{2mKE}}, KE = \frac{1}{2}mv^2 \Rightarrow v = \sqrt{\frac{2KE}{m}}$$

$$(iv) \lambda = \frac{h}{\sqrt{2m(aV)}} \quad , KE = aV \text{ for charged body accelerating with } V \text{ Volts}$$

$$\lambda_e = \frac{h}{\sqrt{2m(eV)}} = \sqrt{\frac{150}{V}} \text{ Å}$$

$$\lambda_p = \frac{0.286}{\sqrt{V}} \text{ Å}$$

$$\lambda_d = \frac{0.101}{\sqrt{V}} \text{ Å}$$

Heisenberg's Uncertainty Principle:-

→ The exact position and momentum of a fast moving particle cannot be calculated precisely at the same instant of time.

If Δn is the error of measurement of position and Δp is error of measurement of momentum, then,

$$\boxed{\Delta n \cdot \Delta p \geq \frac{h}{4\pi}} \quad \text{or} \quad \boxed{\Delta n \cdot \Delta p m v \geq \frac{h}{4\pi}}$$

$$\boxed{\Delta n \Delta v \geq \frac{h}{4\pi m}}$$

Δn = uncertainty in position

Δp = uncertainty in momentum

Δv = uncertainty in velocity

m = mass of particle

h = Planck's constant

Quantum Mechanical Model :-

→ Based on particle and wave nature of electron.

→ Developed by Erwin Schrodinger

→ Schrodinger wave equation.

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

$$\Psi(\text{sci}) = \psi \text{ in quantum theory}$$

Q Significance of Ψ is:

- Ψ is a wave function.
- It refers to the amplitude of e^- wave.
- It has got no physical significance.
- The Ψ may be +ve or -ve.
- All the information about the electron in an orbit is stored in orbital wave function.

Q Significance of Ψ^2 i.e. (Probability density)

- Ψ^2 is the probability of e^- at a particular point.
- The region within an atom where the probability of finding an e^- is maximum is known as orbital.

Note: The region within an atom where probability of finding an e^- is zero, i.e., $\Psi^2 = 0$.

Radial node



$(n-l-1)$

Angular node / nodal plane



(l)

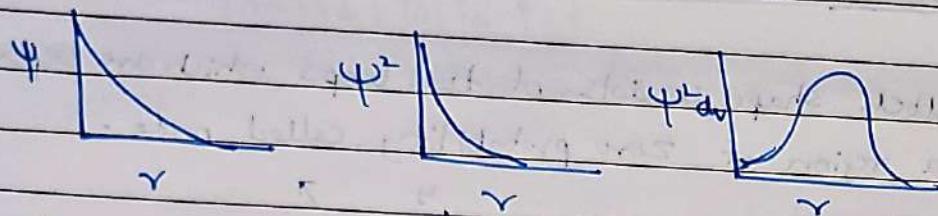
Ψ = wavefunction

Ψ^2 = Probability density

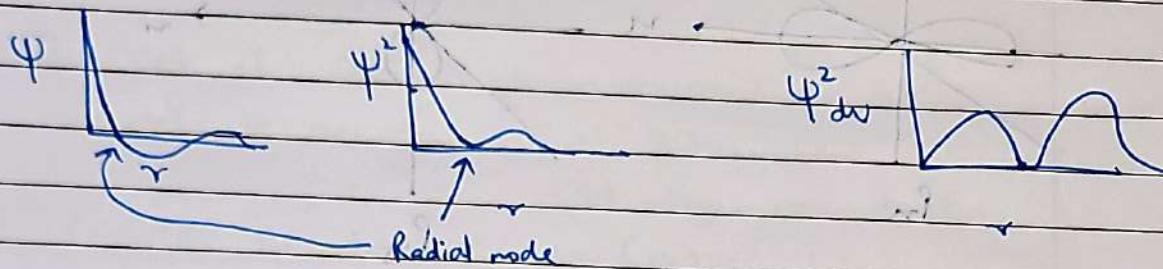
$4\pi r^2 dr \Psi^2$ or $4\pi r^2 dr \Psi^2$ = Probability

Date: / /

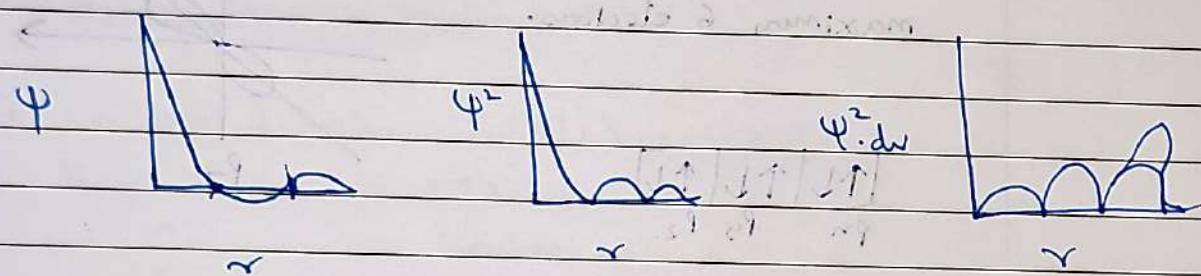
Plots :- for 1s



for 2s



For 3s

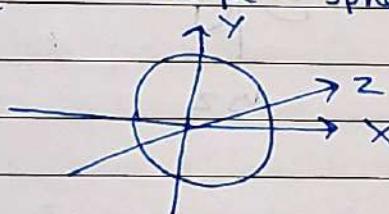


Ψ orbitals:-

→ A region where probability of finding electron is maximum.

D) S-orbital:-

Shape - Spherical



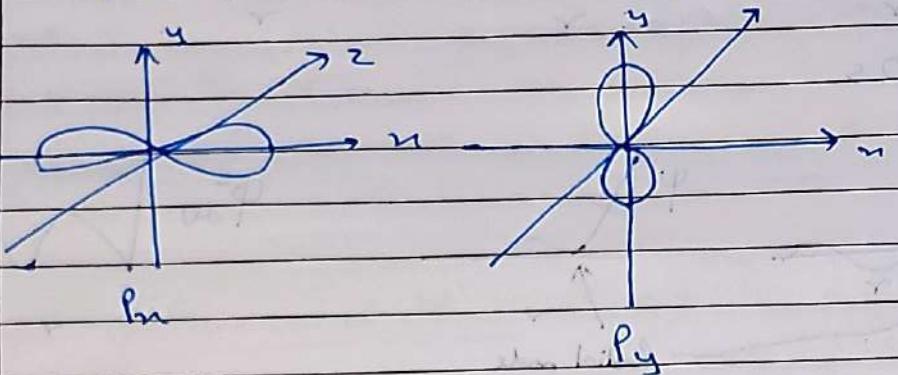
→ S-orbital is non-directional and is closest to the nucleus, having lowest energy.

→ s-orbital can have maximum $2 e^-$.



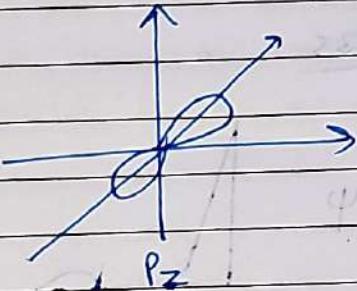
2) P-orbital:- Shape - dumbbell.

→ Dumbbell shape consists of two loops which are separated by a region of zero probability called node.

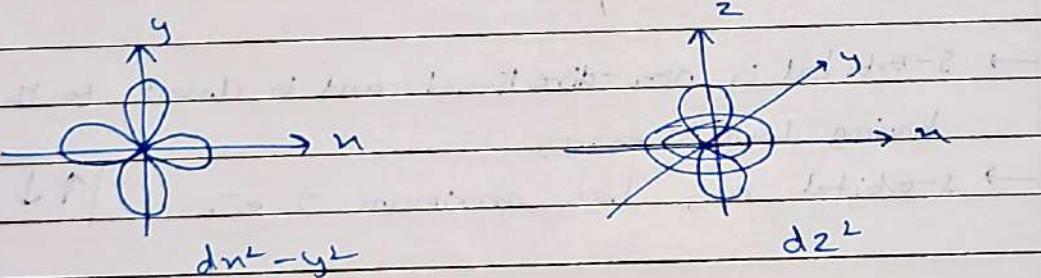
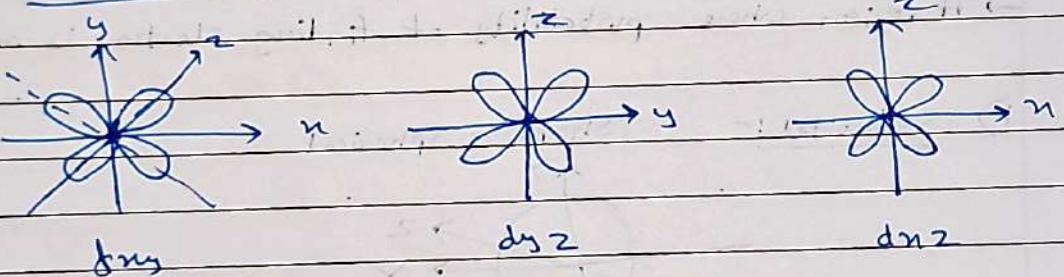


→ p-orbitals can accommodate maximum 6 electrons.

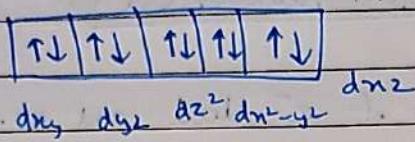
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
p_x	p_y	p_z



3) d-orbital:- Shape → double dumbbell.



→ It can accommodate 10 electrons



❖ Quantum numbers:

→ The set of four numbers required to define an electron completely in an atom. First 3 have been derived from Schrodinger wave equation.

(I) Principal quantum number (n):

→ It describes the size of the electron wave and the total energy of the electron.

→ It has integral values $1, 2, 3, 4, \dots$ etc and denoted by K, L, M, N, \dots etc

n	Subshell
1	S
2	S, P
3	S, P, D
4	S, P, D, F

→ no. of orbitals present in n^{th} shell = n^2

→ no. of maximum e^- which can be present in a principal energy shell is equal to $\underline{2n^2}$.

→ Angular momentum of any orbit = $\frac{n h}{2\pi}$

[I] Azimuthal quantum number (l):-

→ It describes shape of e^- cloud and no. of subshells.

→ Value ranges from 0 to $(n-1)$

Value of l	Subshell
0	s
1	p
2	d
3	f

→ no. of orbitals in a subshell = $(2l+1)$

→ maximum no. of e^- in particular subshell = $2(2l+1)$

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

for $s=0$

$$\rho = \frac{\sqrt{2} h}{2\pi}$$

$$d = \frac{\sqrt{3} h}{2\pi}$$

(II) Magnetic quantum number (m):-

→ It describes the orientations of the subshells.

→ It can have values from $+l, 0, -l$

(IV) Spin quantum number (s):-

→ It describes the spin of the e^- . It has values

$\pm \frac{1}{2}$ and $-\frac{1}{2}$. $+$ = clockwise $-$ = anticlockwise

\star Spin magnetic moment \pm it but M_s is spin magnetic moment

$$M_s = \frac{e\hbar}{2\pi m c} \sqrt{s(s+1)} \text{ or } M_s = \sqrt{n(n+1)} \text{ B.M.}$$

\star Maximum spin of atom $= \frac{1}{2} \times$ no. of unpaired electron

\star Value of spin angular momentum $= \frac{\hbar}{2\pi} (\sqrt{s(s+1)})$

\star Aufbau principle: (maximum)

→ orbital fills up from lowest energy orbital to highest energy orbital

→ energy of orbital is governed by $(n+l)$ rule.

s	sp	s'p'	1s	2s	2p	3s	3p			
sdp	sdp		4s	3d	4p	5s	4d	5p		
sfdp	sfdp		6s	4f	5d	6p	7s	5f	6d	7p

\star $n+l$ rule

$(n+l) \rightarrow \uparrow (n+l) \rightarrow \uparrow \text{energy}$

if $(n+l)$ is same at two orbitals

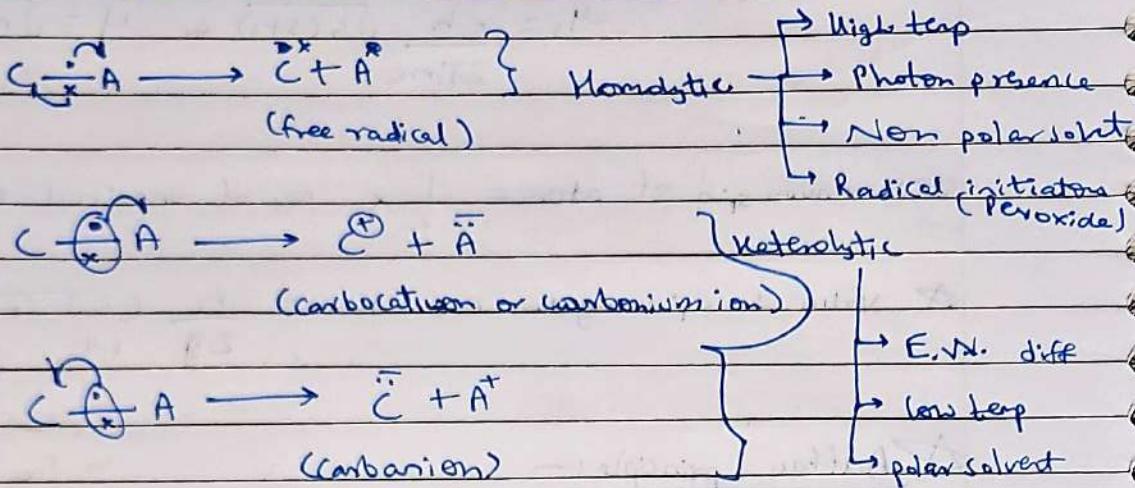
then $n \uparrow$ is $\uparrow \text{energy}$

\star Hund's rule:



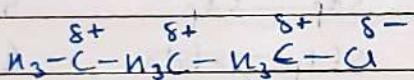
→ Pairing can be done only when all orbitals have atleast one electron with parallel spin.

***Homolytic and Heterolytic bond cleavage :-**



***Inductive effect:-**

→ The inductive effect maybe defined as a permanent displacement of σ bond pair electrons due to a dipole (polar bond).



→ ~~+I effect~~: movement of e^- cloud from atom of lower electronegativity to atom of higher electronegativity.

~~+I~~ is shown by Lewis negative atoms

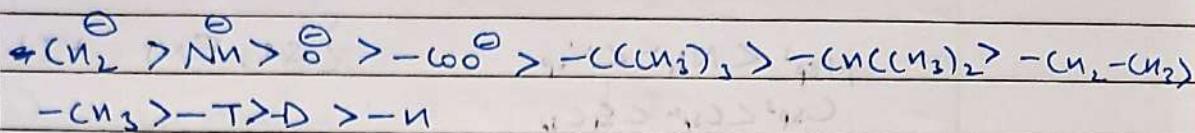
or

② -I effect: The group which withdraws electron cloud is known as -I group and its effect is called -I effect.

→ Various groups are listed in their decreasing -I strength as,

$$\begin{aligned} &-\text{NR}_3^+ > -\text{SR}_2^+ > -\text{NH}_3^+ > -\text{NO}_2 > -\text{SO}_2\text{R} > -\text{SO}_2\text{Ar} > -\text{COON} \\ &> -\text{F} > -\text{Cl} > -\text{Br} > -\text{I} > \text{OAr} > -\text{OR} > -\text{SR} > -\text{ON} > -\text{C(=O)R} \\ &> \text{Ar} > -\text{CH}=\text{CR}_2 \end{aligned}$$

(b) +I effect: The group which release e^- cloud is known as +I group and effect is +I effect.



→ The hydrogen atom is reference for +I and -I series. its inductive effect is assumed to be zero.

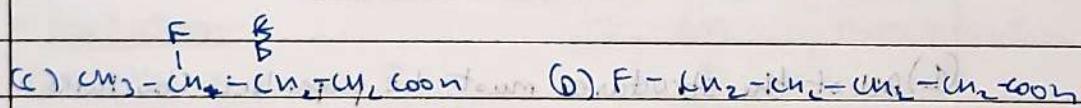
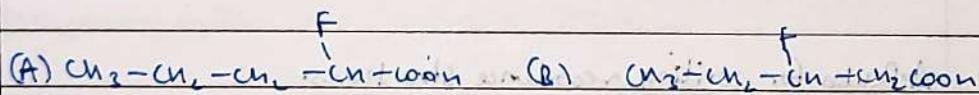
	+I	-I
Acidic nature	↓	↑
Basic nature	↑	↓
Carbocation	↑	↓
Carbanion	↓	↑
Free radical	↑	↓

*Factors affecting inductive effect:-

Distance > number > power.

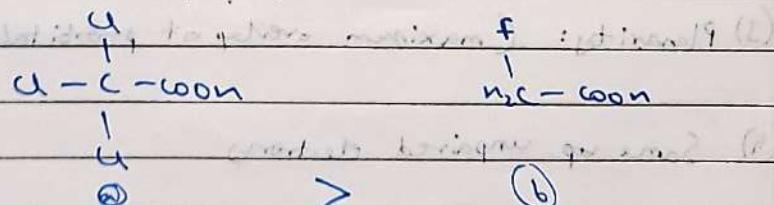
e.g:- 1)

Q Highest acidic nature?

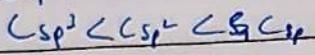
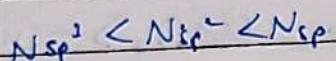
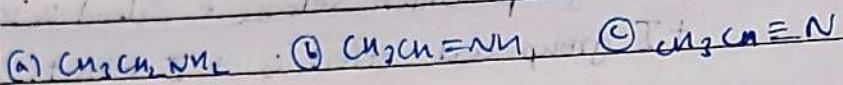


A > B > C > D

e.g 2)



∴ more O than F

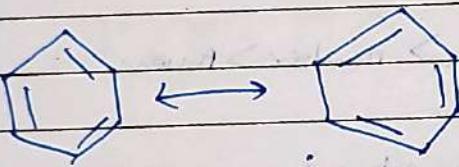
g) basic nature

$$\therefore (A) > (B) > (C)$$

{ S↑, E↑ + I↓ basicity }

Resonance

→ When two or more structures that differ in the distribution of electrons can be written for a molecule, no single Lewis structure is sufficient to describe its true electron distribution. The true structure is said to be a resonance hybrid of the various Lewis structures.

Rules for writing resonance structures

- (1) All of the structures must be proper Lewis structures.
- (2) Movement of electrons only.
- (3) Planarity: (maximum overlap of p-orbitals)
- (4) Same no. unpaired electrons

* How to compare stability of resonating structures:

Stability

- 1) Complete octet ↑
- 2) More covalent bonds ↑
- 3) Neutral structure ↑
- 4) Electronegativity (-ve charge on electropositive element) ↑
- 5) Benzenoid (structure with more benzene) ↑
- 6) Hyperconjugation

* Hyperconjugation:

→ It is delocalization of sigma electron also known as sigma-pi conjugation or no bond resonance.

Condition:-

→ Presence of δN with respect to double bond, triple bond carbon containing positive charge (in carbonyl ion) or unpaired electron.

* Hyperconjugation is a permanent effect.

* Application:-

- | | δN | Hyperconjugation |
|-------------------------------|------------|------------------|
| 1) Stability of Alkenes ↑ | ↑ | ↑ |
| 2) Stability of Carbocation ↑ | ↑ | ↑ |
| 3) Bond length ↑ | ↑ | ↑ |
| 4) Basic nature | | |
| 5) Acidic nature | | |

* Aromaticity:-

- Compound should be cyclic
- There must be cyclic delocalization of e^-
- Compound should follow Hückel rule

$$(4n+2) = \pi \quad \{n = 0, 1, 2, \dots\}$$

* Anti aromaticity:-

- Compound should be cyclic
- delocalisation of e^-
- No. of delocalized e^- should be haptic

Stability

Anti aromatic < Non aromatic < Aromatic

Hydrocarbons

Date: / /

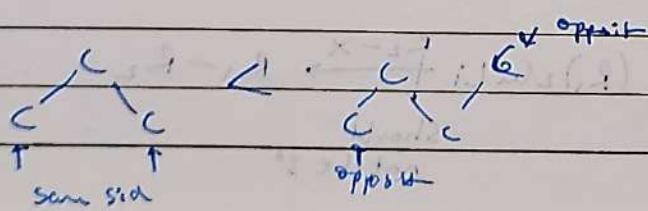
Physical properties :-

- (i) C₁ to C₄ gases; neopentane gas but n-pentane and isopentane are low B.P. Liquids.
- (ii) C₅ to C₁₈ are colorless liquids. above C₁₇ are waxy solids.
- (iii) Density ↑ with ↑ in molecular weight. but density becomes constant at 0.8 g/mol. ∴ all alkanes are lighter than water.
- (iv) Solubility: Alkanes being non-polar are insoluble in water but soluble in non-polar solvent like C₆H₆, CCl₄.
- Solubility ↓ molecular weight ↑
- Liquid alkanes are good non-polar solvents
- (v) B.P. & Molecular weight & Van der waals
- B.P. \propto $\frac{1}{\text{no. of chains}}$
- (vi) M.P. of alkanes do not show regular trend.

M.P. of odd < M.P. of even nos. C

no. (

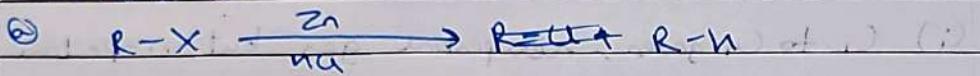
because C is in same side in odd and opposite in even



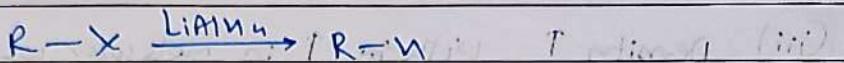
Preparation of alkenes :-

Z

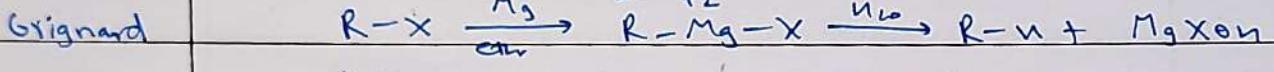
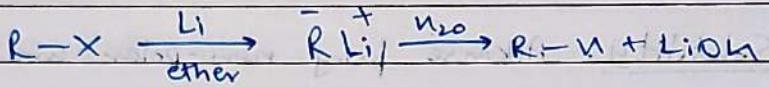
① from alkyl halide



③ reduction by LiAlD_4 , NaBH_4 , and Ph_2SnH

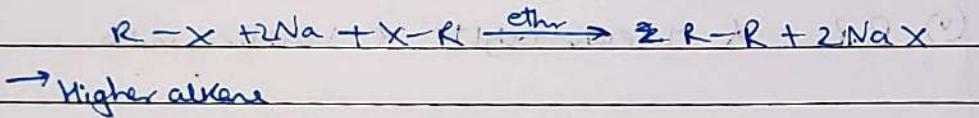


④ from organometallic compound

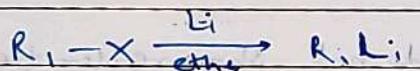


Wurtz

① Wurtz reaction



② Corey - House Synthesis



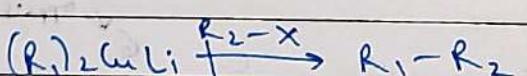
(dialkyl lithium cuprate)



Gillman's reagent

Sn⁺

mechanism

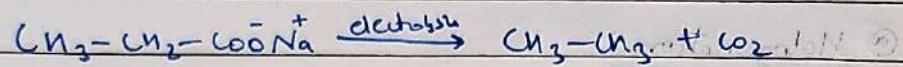


Should

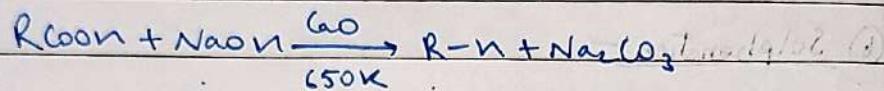
not be 3°

Date: / /

* Kolbe's electrolysis :-

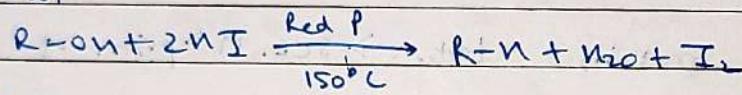


* Decarboxylation with Soda lime:-

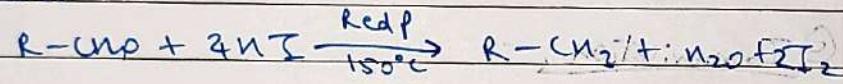


* Reduction:-

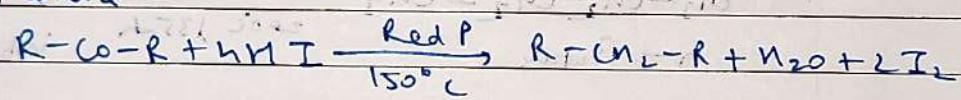
(a) Alkanes



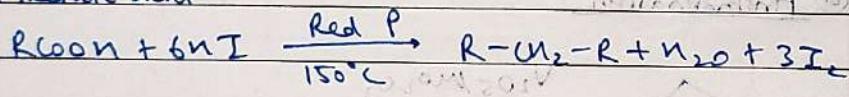
(b) Alkenes



(c) Alkanones

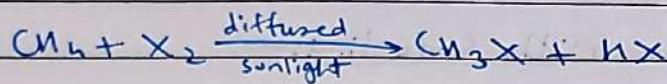


(d) Alkanic acid

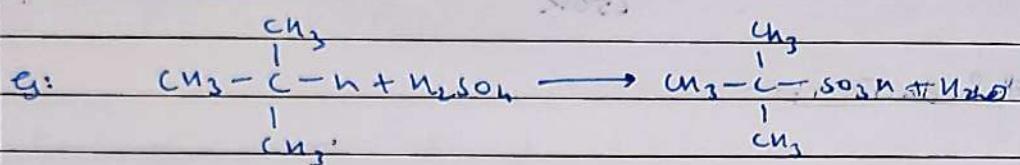


★ Chemical reaction:-

① Halogenation :-

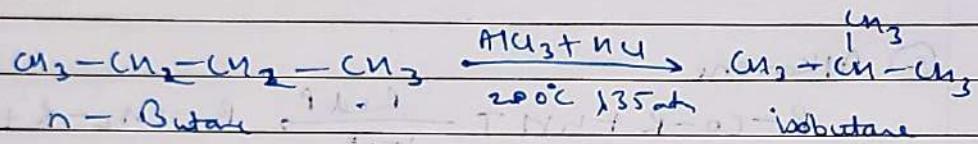


② Sulphonation:-

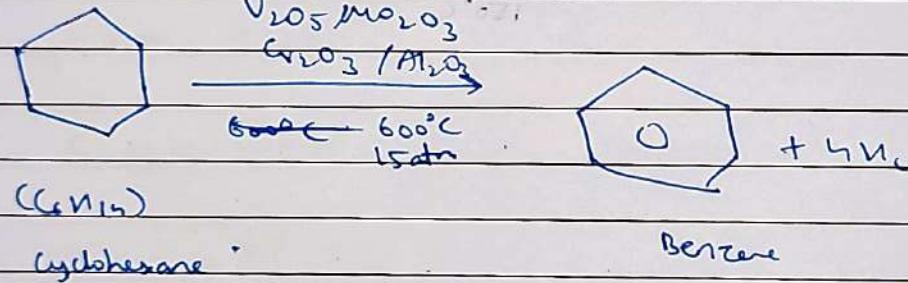


reactivity : tert. n > sec. n > prim. n.

③ Isomerisation:-



④ Aromatization

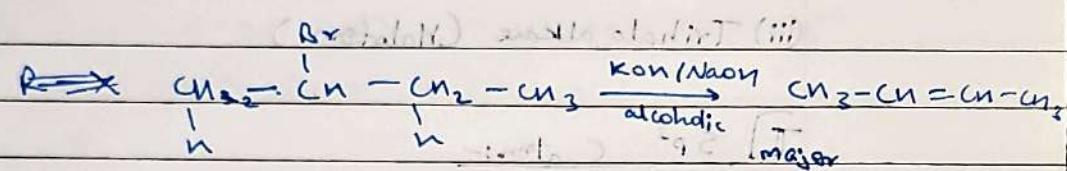


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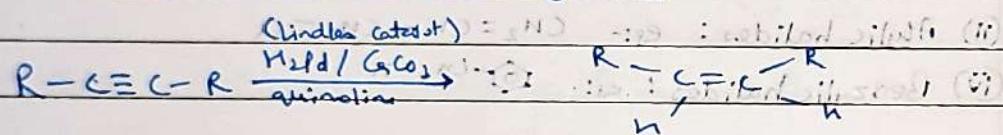
Preparation of alkene:-

① Dehydration of alcohols

② Dehydrohalogenation (-X) → good leaving group (i)



③ Partial reduction of alkynes :-



X-Na = NaX : stabilized Pb(IV) (iii)

X-Ca = CaX : stabilized Pb(II) (ii)

Lindlar catalyst for alkenes

(and catalyst) : Lindlar (i)

silver and zinc over zinc dust \rightarrow Pb^{2+} + Hg^{2+} + Ca^{2+}
 amalgam \rightarrow strong ring \rightarrow original
 Lindlar catalyst after removal of Pb^{2+} and Hg^{2+}
 Lindlar and silver amalgam together \rightarrow Lindlar
 catalyst without after removal of Pb^{2+} and Hg^{2+}

is - NaX

Halogen derivatives

Date: / /

* Classification:-

I] No. of halogen atoms:-

- (i) Monohalokane
- (ii) Dihalokane → (a) Geminal (b) Vicinal
- (iii) Trihalo alkane (Maloform)

II] sp^3 atom:-

- (i) Haloalkanes → (a) 1° (b) 2° (c) 3°
- (ii) Allylic halides: ex:- $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$
- (iv) Benzylic halides: ex:

III] sp^2 atom:-

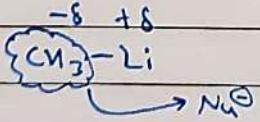
- (i) Vinylic halide: ex: $\text{CH}_2=\text{CH}-\text{X}$
- (ii) Aryl halide: ex:

* Nucleophile and Electrophile:-

(i) Nucleophile: (+ve charge loving)

⇒ HOMO

- = Highest occupied molecular orbital
- $\text{Nu}^- \rightarrow e^-$ rich species → -ve charge lone pair
 - e^- pair donate → HOMO
 - HOMO energy ↑ better the nucleophile
 - Neutral species having L.P. are nucleophile.
 - $>\text{C}=\text{C}<, -\text{C}\equiv\text{C}-$
 - σ bond with electropositive element



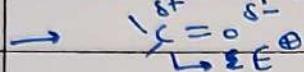
(ii) Electrophile:- (electron loving)

$\rightarrow e^-$ pair acceptor \Rightarrow LUMO. (lowest unoccupied molecular orbital)

\rightarrow LUMO energy \downarrow better the electrophile.

\rightarrow +ve charged \rightarrow $\text{Na}^+, \text{H}^+, \text{Br}^+, \text{Cl}^+, \text{I}^+, \text{NO}_3^-, \text{Mg}^{2+}$

\rightarrow Neutral species with vacant orbital.



\rightarrow σ bond with E.N. atom \Rightarrow $\text{H}-\text{I}^{\delta-}$

\rightarrow ~~XX~~ (X-X) are electrophile. ($\text{CH}_3, \text{I}_2, \text{Br}_2, \text{F}_2$)

Base



donate e^- pair to H^+

\rightarrow Steric hindrance doesn't matter.

Nucleophile



donate e^- pair to ^{the} atoms than H^+

\rightarrow Steric hindrance matters.

Solvent:

~~Not~~

Nu α : 1

steric
hindrance

$\mu =$ Dipole moment

~~Solvent~~:

Non polar ($\mu=0$)

e.g.: $\text{C}_6\text{H}_6, \text{CCl}_4, \text{CS}_2$

Polar ($\mu \neq 0$)

Polar aprotic solvent (PAs) Polar protic solvent (PPs)

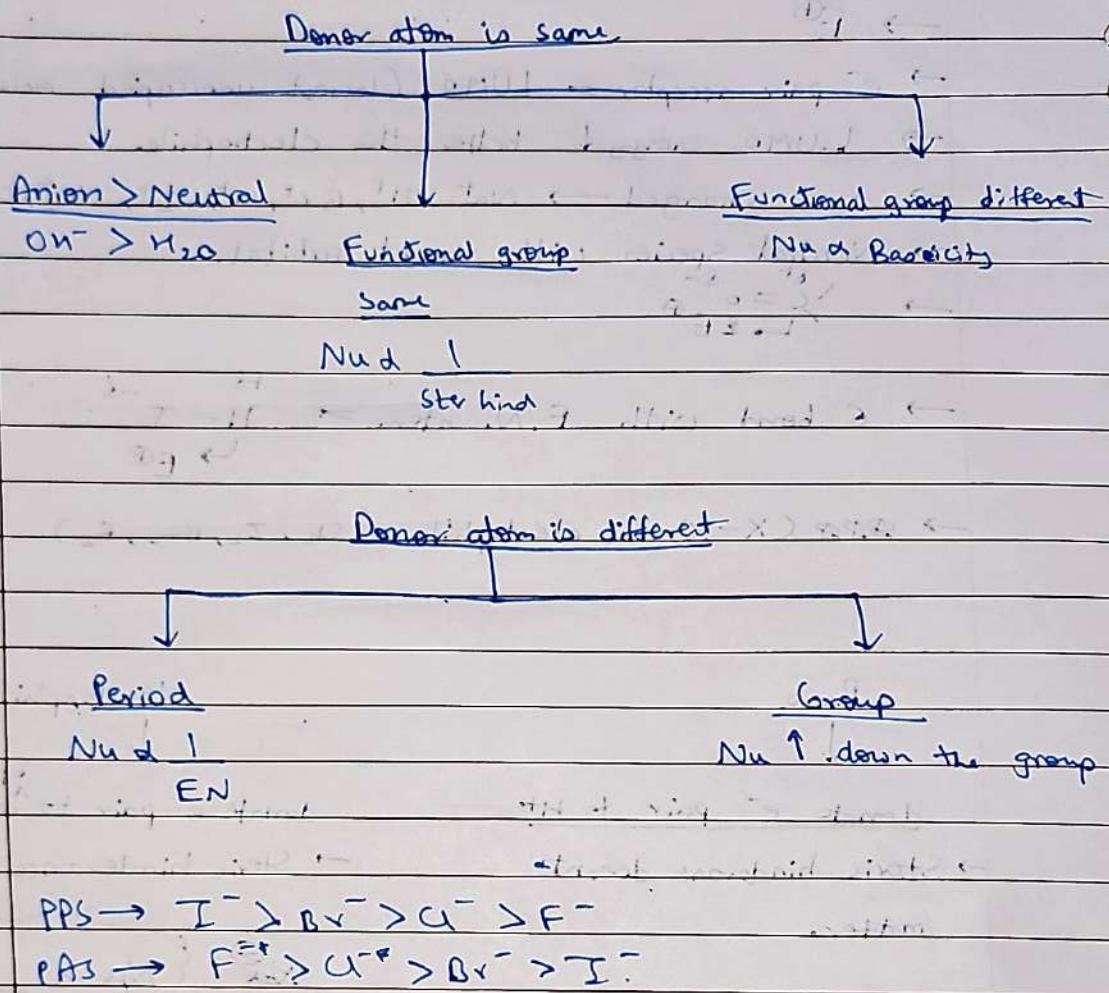
\rightarrow H is ^{not} connected to more EN atom.

e.g.: $\text{R}-\text{O}-\text{R}'$

\rightarrow H is connected to one EN atom.

e.g.: $\text{H}-\text{OH}$

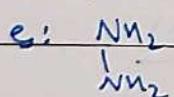
Factors affecting Nucleophilicity:



PAS → Solvation of cation

PPS → Solvation of both cation and anion

Nucleophile with lone pair on adjacent atom is better nucleophile



Leaving group ability:-

→ Leaving group leave ~~with~~ the ion so leaving group good when it stabilize anion.

* Preparation Methods :-

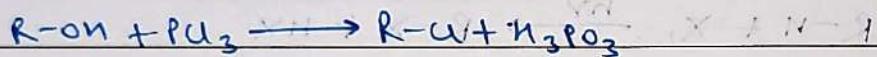
I] From alcohol

1) Alcohol with sodium halide and sulphuric acid :-

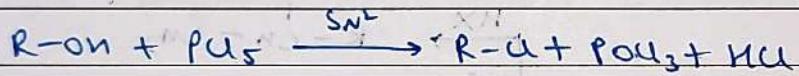


→ If $X = I$ we use $HgPO_4$

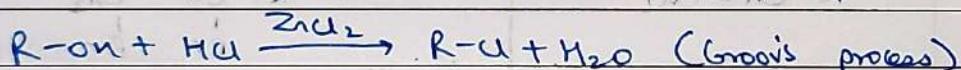
2) $PtCl_4$:-



3) PtS_2 :-



4) $Hg + ZnCl_2$:-



Reactivity: $3^\circ > 2^\circ > 1^\circ$ alcohol

Reactivity of HX : $HI > HBr > HCl > HF$

Lucas reagent \Rightarrow conc $HCl + \text{anhyd } ZnCl_2$

→ To distinguish b/w $1^\circ, 2^\circ, 3^\circ$ alcohol

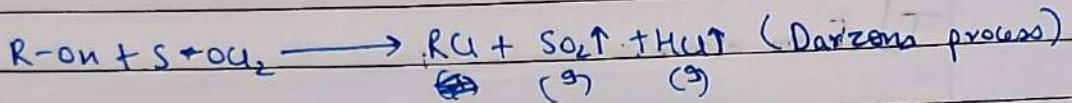
R-Cl turbidity.

$3^\circ R-OH \xrightarrow{L.R.}$ Immediate turbidity ($5-10s$)

$2^\circ R-OH \xrightarrow{L.R.}$ 5-10 min for turbidity

$1^\circ R-OH \xrightarrow{L.R.}$ No turbidity at room temperature.

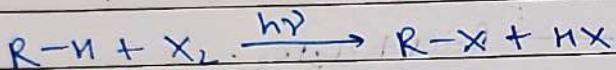
5) SO_2 :-



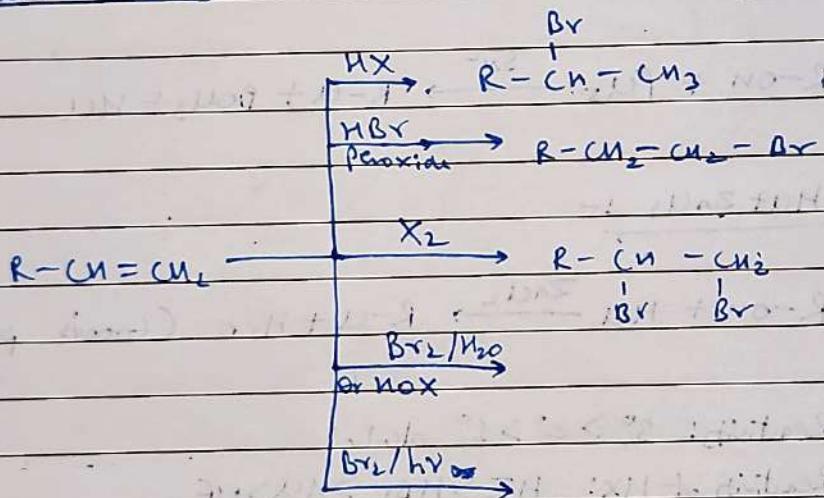
Best method to form RO because byproducts ~~explosive~~ are gaseous (SO_2 & H_2O).

II] From Hydrocarbons:-

(i) free radical halogenation:

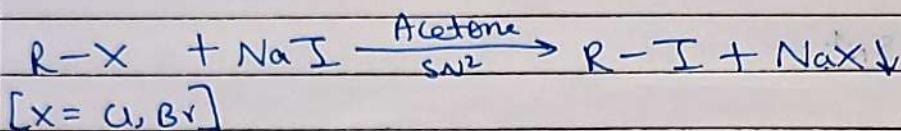
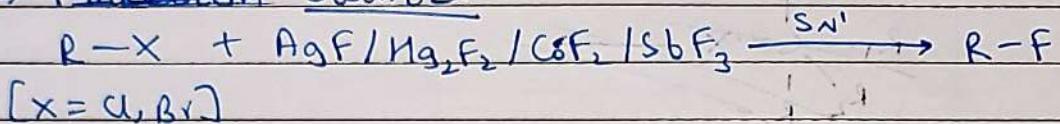
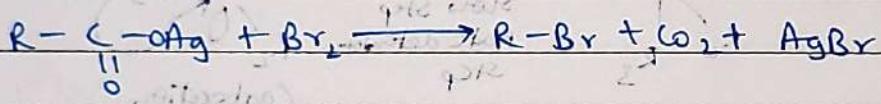


(ii) From alkenes:



~~III~~

: substitution and O.T.

1) Finkelstein reaction :-2) Finkelstein Swartz reaction :-3) Bardine Hunsdiecker reaction :-If $Br_2 \rightarrow I_2$ product is ester.★ Physical properties :-

→ Colourless.

→ Sweet smell.

→ Polar but insoluble in H_2O (No H-bonding).

→ Soluble in organic solvents.

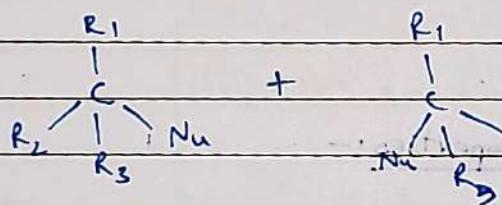
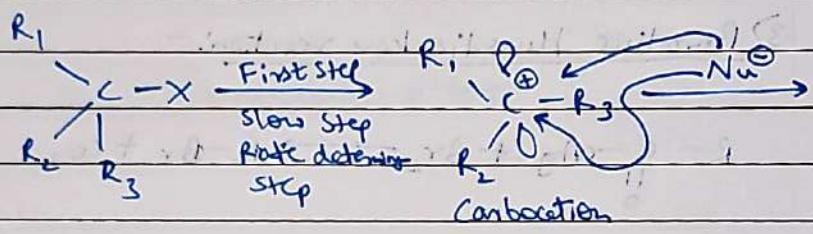
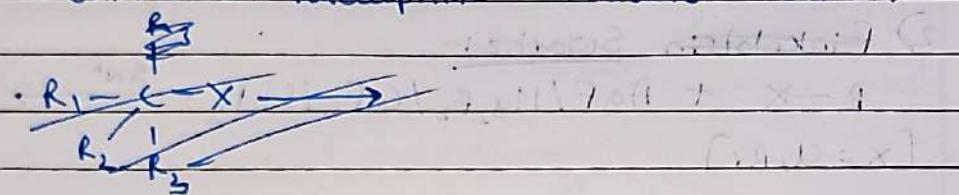
→ Polarity: $RF > RCl > RBr > RI$ \Rightarrow $C_2H_5Cl > C_2H_5F > C_2H_5Br$ → B.P.: $RF < RCl < RBr < RI$ → M.P. \rightarrow Symmetry

★ Chemical reactions :-

I] Nucleophilic substitution reaction:-

(i) S_N^1 :-

→ Unimolecular nucleophilic substitution reaction.



(± or d-d)

Racemic mixture

★ Characteristics :-

→ Unimolecular 2 step reaction

↳ Step 1: Leaving group leaves (Carbocation formation)

Step 2: In second step, Nu^- attacks.

→ First order reaction

→ Rate $\propto [R-X]^1$

→ Racemization occurs

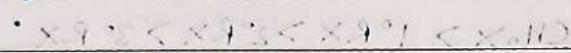
★ Factors affecting rate of S_N^2 :-

→ Carbon skeleton: more p-orbital atomic overlap → more stable



R or stability of C: → Rearrangement possible

→ Leaving group: higher Z, stronger with more electron density



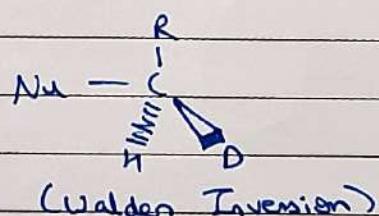
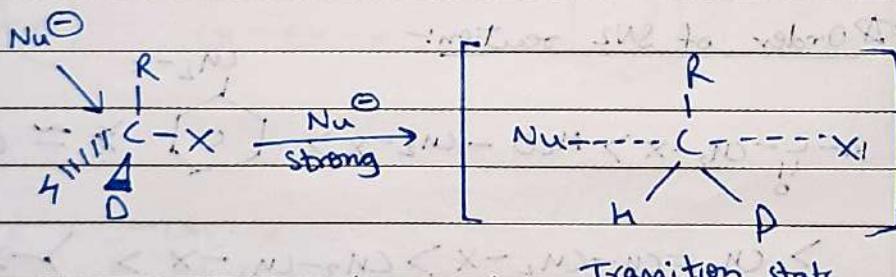
→ Nucleophile doesn't affect

→ Polar solvent (H_2O)

↓ Protic

(ii) S_N^2 :-

Bimolecular nucleophilic substitution reaction

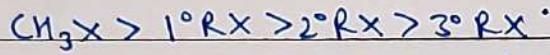


Characteristics:-

- Bimolecular single step reaction.
- Second order reaction.
- Rate $\propto [N\u2014^-][R-X]$
- Inversion of configuration takes place, if carbon is chiral

Factors affecting rate of reaction:-

→ Carbon skeleton



ROR, d + 1, steric hindrance

→ Leaving group



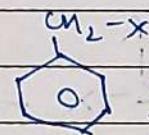
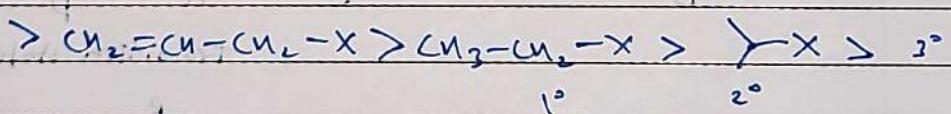
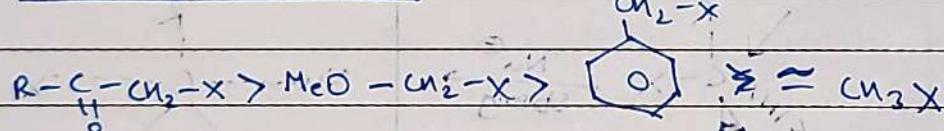
steric hindrance

→ Nucleophile

→ Polar aprotic solvent favours S_N^2 reaction.

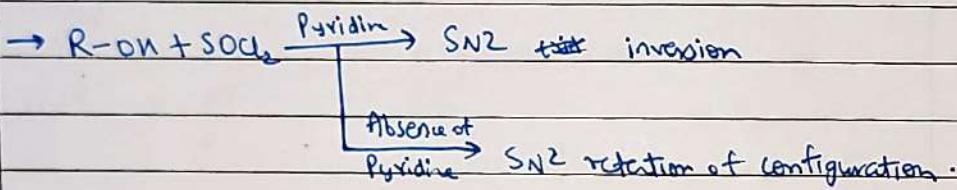
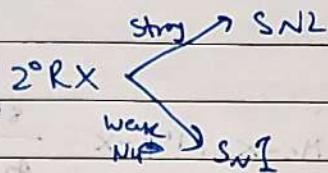
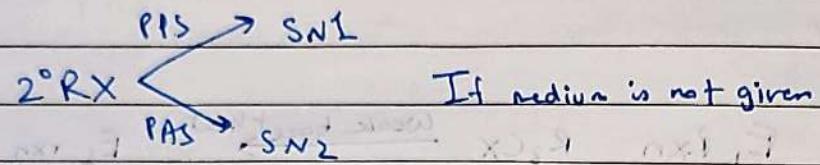
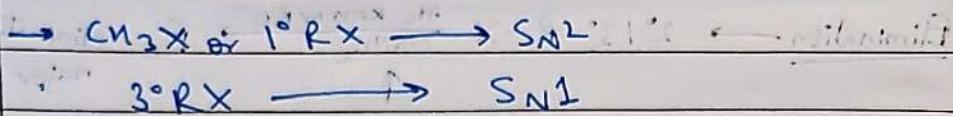
(Mostly : Aromatic nucleophile gives S_N^2 reaction)

Order of S_N^2 reaction:-

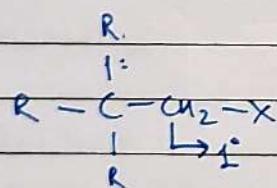
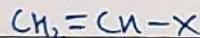


Date: / /

★ Identification of S_N1 and S_N2 :-

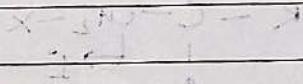
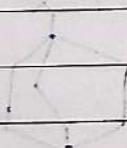
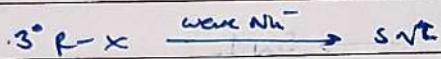
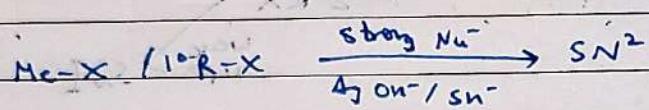
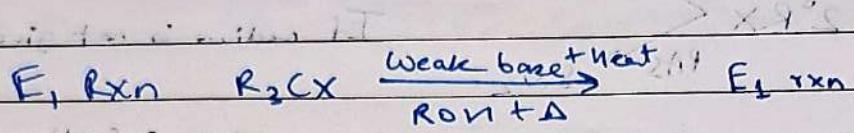
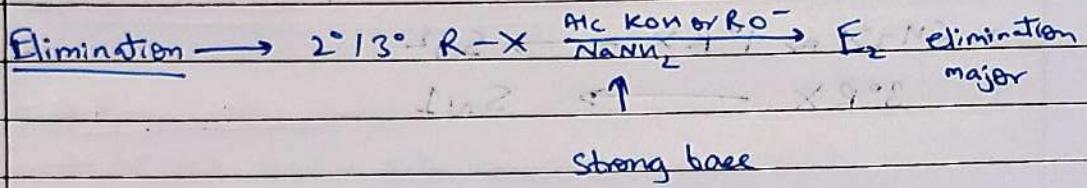


★ Following compounds do not give S_N1 and S_N2 reaction,



Date: / /

Substitution v/s Elimination



~~★ Nucleophilic substitution reactions :-~~

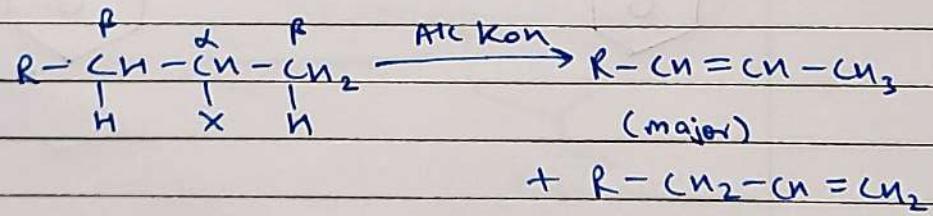
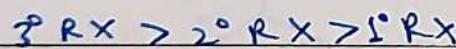
- 1) $R-X \xrightarrow{NaONaOH} RON$ (alcohol)
- 2) $R-X \xrightarrow{H_2O} RON$ (alcohol)
- 3) $R-X \xrightarrow{NaOR'} ROR'$ (ether)
- 4) $R-X \xrightarrow{NH_3} RNN_2$ (1° amine)
- 5) $R-X \xrightarrow{R'NH_2} R'NHR$ (2° amine)
- 6) $R-X \xrightarrow{RR''NH} R'R''NR$ (3° amine)
- 7) $R-X \xrightarrow{KCN} RCN$ (Nitrile)
- 8) $R-X \xrightarrow{AgCN} RNC$ (isonitrile)
- 9) $R-X \xrightarrow{KNOL} R-ONO$ (Alkyl nitrite)
- 10) $R-X \xrightarrow{AgNO_2} R-NO_2$ (Nitroalkane)
- 11) $R-X \xrightarrow{R'COOPr} RCOOR'$ (Ester)
- 12) $R-X \xrightarrow{LiAlD_4} RH$ (Hydrocarbon)
- 13) $R-X \xrightarrow{R-M^+} RR'$

~~★ Neighbouring group~~

~~★ Elimination reaction (Dehydrohalogenation) :-~~

→ Molecule having β -hydrogen atom undergoes β -elimination when heated with alcoholic solution of KOH or $NaNN_2/KNN_2$.

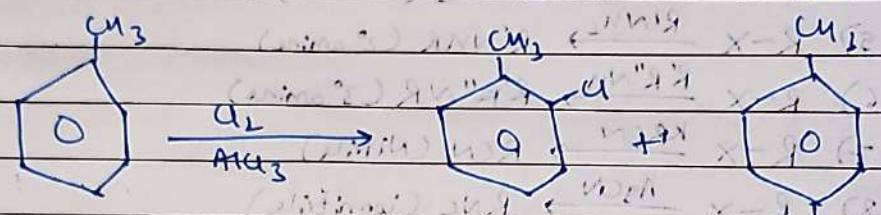
→ Reactivity:



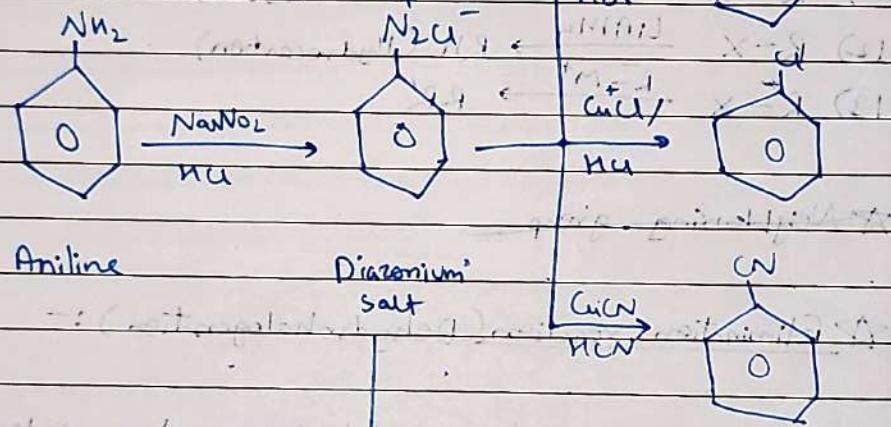
★ Halocarbenes / Aryl halides :- (using Michaelis-Kellogg method)

★ Preparation :-

A) Electrophilic substitution:-



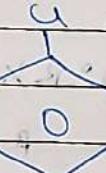
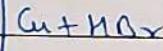
B) Sandmeyer's reaction:-

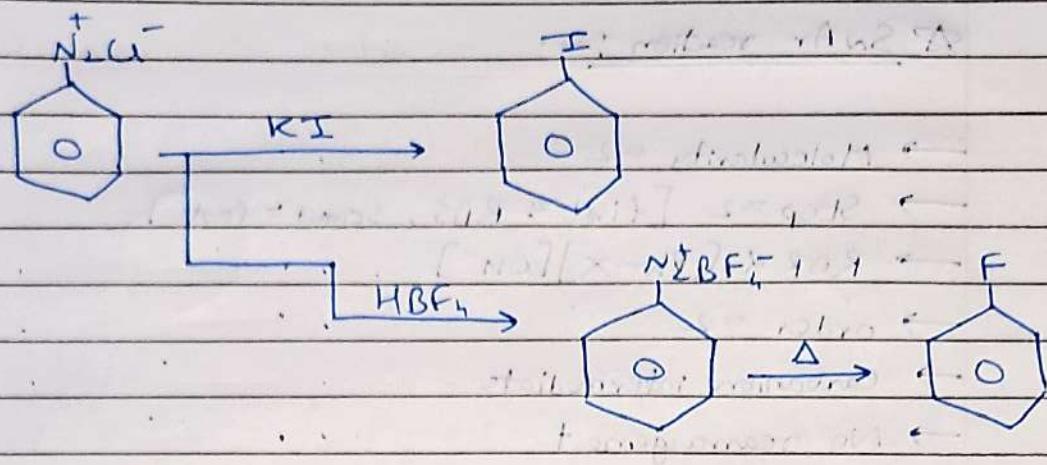


Aniline

Diazonium
salt

Gatterman reaction





* Chemical properties of Haloarenes :-

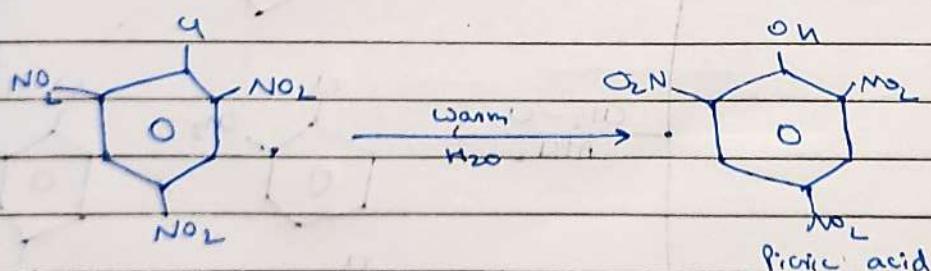
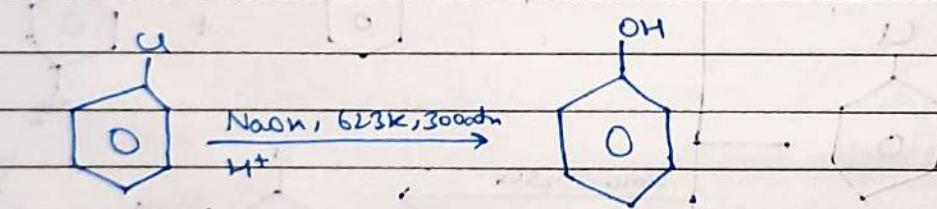
→ Aryl halides are extremely less reactive towards nucleophilic substitution reactions because:-

(i) Resonance effect:

(ii) Difference in hybridization carbon atom in C-X bond.

(iii) Instability of phenyl cation.

* Dows process:-



★ S_NAr reaction :-

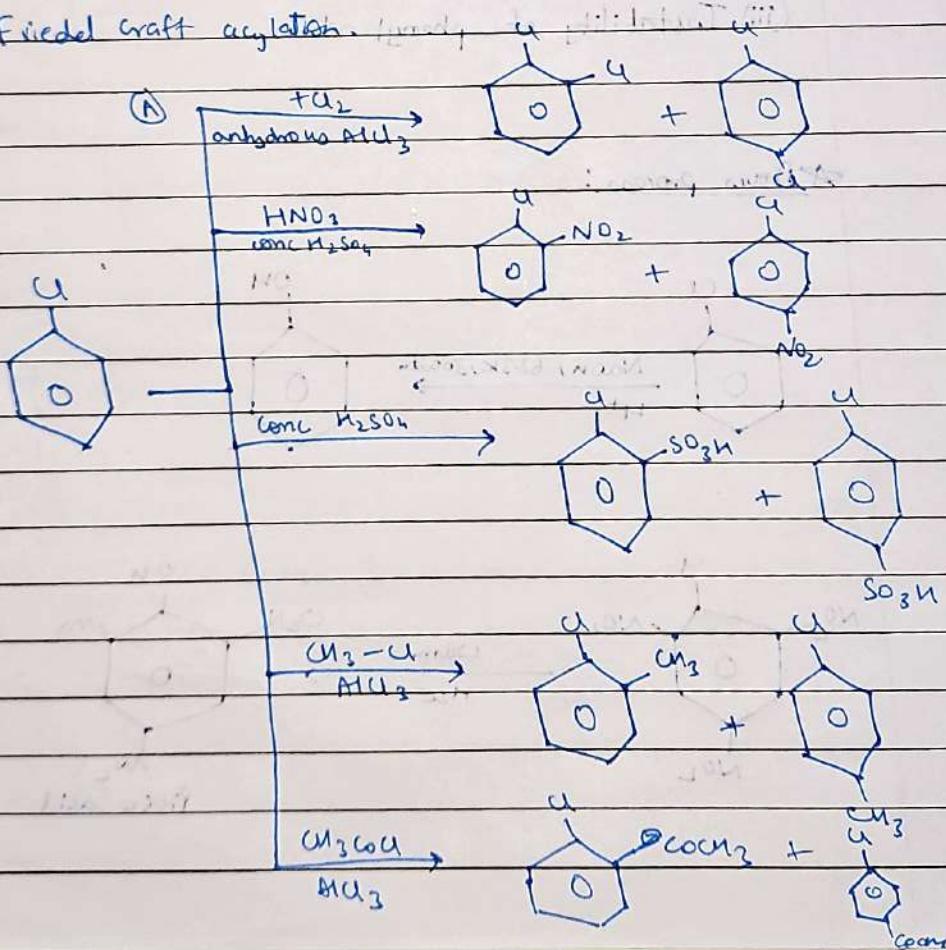
- Molecularity = 2
- Step = 2 [first = RDS, second = fast]
- ROR + (Ph-X)[On⁻]
- order = 2
- Carbanion intermediate
- No rearrangement

★ Electrophilic aromatic substitution :-

(a) Halogenation (b) Nitration (c) Sulphonation

(d) Friedel-Crafts alkylation

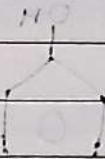
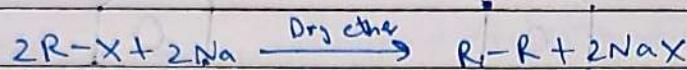
(e) Friedel-Crafts acylation



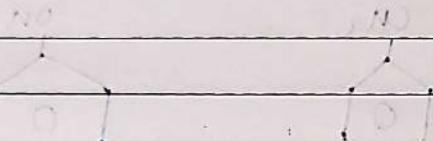
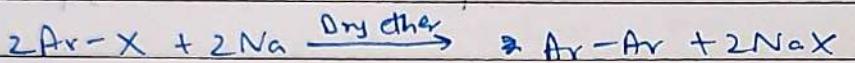
Date: / /

★ Reactions with metals :-

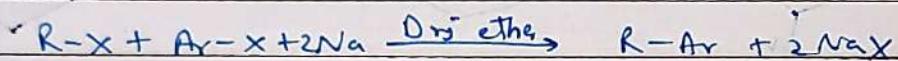
1) Wurtz:-



2) Fittig:-



3) Wurtz Fittig:-



4) Grignard reagent:-



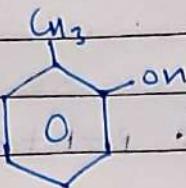
Alcohol, Phenol and Ether

Date: / /

* Imp. compounds:-

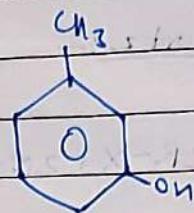


Phenol



Phenol

O-Cresol



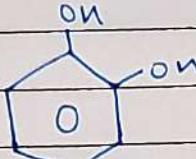
m-Cresol

3-Methyl phenol



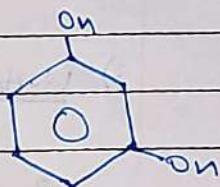
p-Cresol

4-Methylphenol



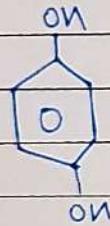
Catechol

Benzene-1,2-diol



Resorcinol

Benzene-1,3-diol

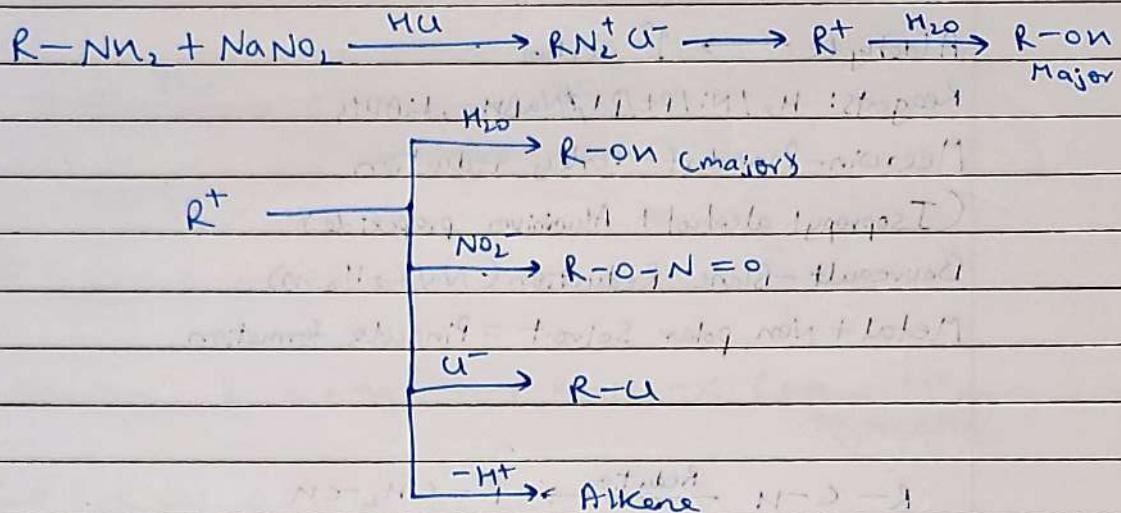


Hydroquinone or quinol

Benzene-1,4-diol

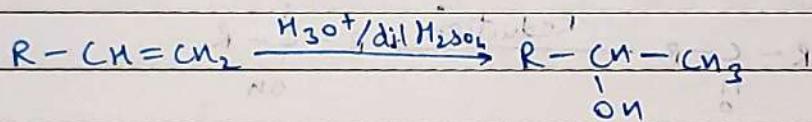
★ Preparation of Alcohols:-

1) From primary aliphatic Amines

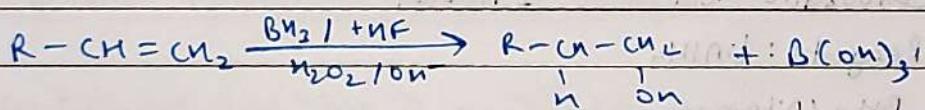


2) From Alkenes:-

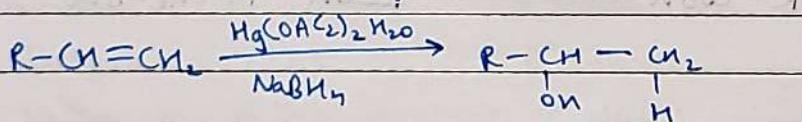
(i) By acid catalysed hydration



(ii) By hydroboration-oxidation:-



(iii) By oxymercuration-demercuration



3) From Carbonyl compounds:

→ By reduction of Aldehydes and Ketones:

Aldehyde \longrightarrow 1° alcohol

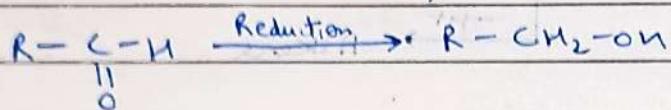
Reagents: $H_2/Ni/Pt/Pd, NaBH_4, LiAlH_4$

Meerwin-Ponndorf-Verley reduction

(Isopropyl alcohol + Aluminium propoxide)

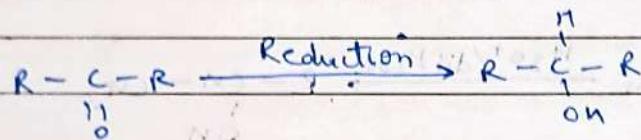
Bouveault-Blanc Reduction (Na/C_2H_5ONa)

Metal + Non polar Solvent = Pinacole formation



Ketone \longrightarrow 2° Alcohol

Reagents: $H_2/Ni/Pt/Pd, NaBH_4, LiAlH_4$

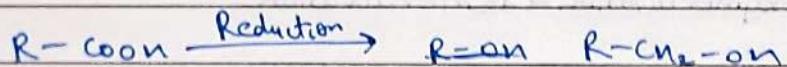


Carboxylic acid \longrightarrow 1° Alcohol

Reagents: $LiAlH_4$

$BrMgI$ / Diborane

(only for acid and amides)

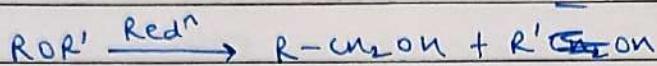


Ester \longrightarrow $^1\text{ Alcohol} + \text{Alcohol}$

Reagent: LiAlD_4

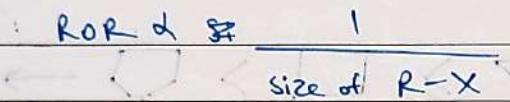
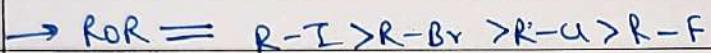
DIBAL - H

Boucquet-Blanc Reduction ($\text{Na}/\text{C}_2\text{H}_5\text{OH}$)



* Grignard reagent :-

Formation: $\text{R-X} + \text{Mg} \longrightarrow \text{R-Mg-X}$ (Ether (3° amine is used as solvent))

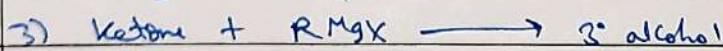
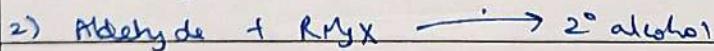
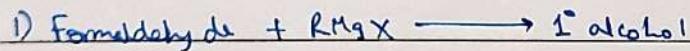


$\rightarrow \text{R-X}$ and Mg should be in 1:1 ratio or else further Alkene and alkene will form.

* Chemical reactions of Grignard reagent :-

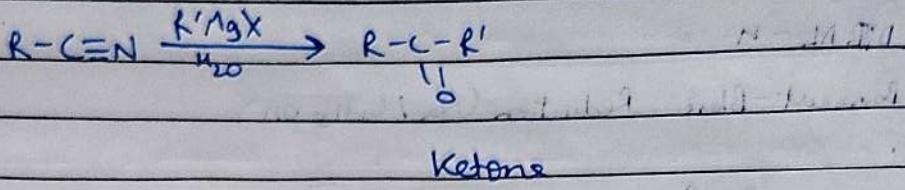
Reactivity \rightarrow Acid + base $>$ Nu⁻ + R-X

Reactivity \rightarrow R-Na $>$ R-MgX $>$ R-Cu



Date: / /

* Reaction with Nitrile:-

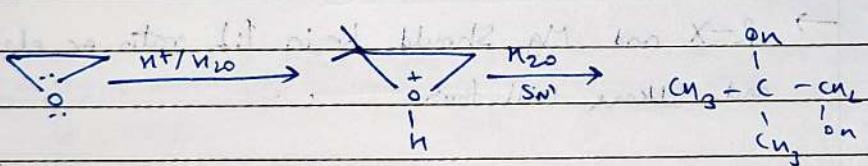


→ When H_2O is added in the middle of reaction then remaining $R-MgX$ react with water. Add base $> NH^-$ than



* Reaction with epoxide :-

Reactivity $\text{O} > \text{C}_2 > \text{C}_3 \rightarrow \text{Solvent}$



★ Physical properties :-

1) B.P. = B.I. & M.W.

B.P. \propto 1

Branching

B.P. \propto no. of OH groups

→ For comparable masses, Boiling point of alcohols and phenols are higher than hydrocarbons, ethers, haloalkanes and halohydrines.

Solubility \propto 1

size of alkyl group

Chemical reactions

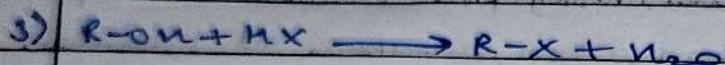
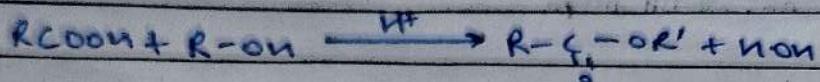
Cleavage of O-H bond

Cleavage of C-O bond

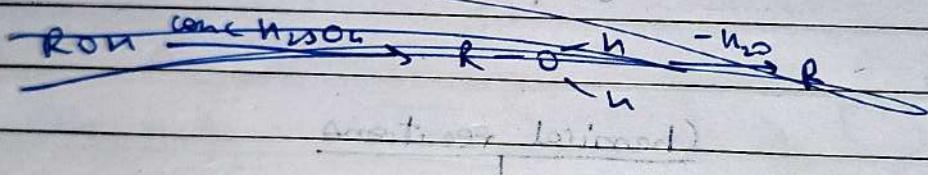
1) Acidity of alcohols and phenols

1) Reactivity of alcohols:-

A. Reaction with metals.

2) Esterification:-

Lucas reagent

4) Dehydration

loss

heat

leads to $\text{C}_6\text{H}_5\text{CO}_2$

strongly