# Prepared By Dr M R Choudhary K V SAC AHMEDABAD SOLUTION

#### **Concentration of Solutions:-**

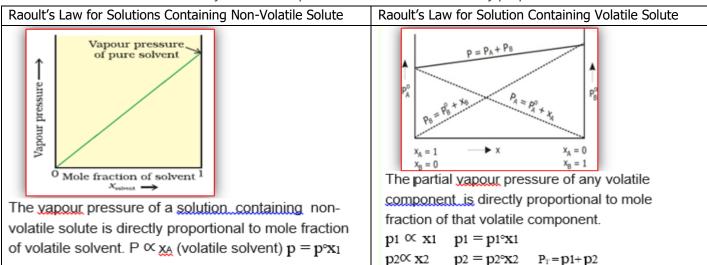
Molarity [M]:	No. of moles of solute present per liter of solution in called 'molarity of solution' It is		
	temperature dependent. M= No. of Moles of solute / Volume of solution in litre		
Molality [m]:	No. of moles of solute present per kg. of solvent is called molality. It is temperature		
	independent. m= No. of Moles of solute / Mass of Solvent in Kg		
Mole Fraction:	Ratio of moles of components to total no. of moles of all the components of solution		
	is called mole fraction (x) of the component.		

**Henry's law:** "The partial pressure of the gas in vapour phase p is proportional to the mole fraction of the gas x in the solution."  $P=K_H x$ 

**Applications of Henery Law**(1) In Packing of soda/ Soft drinks(2) In Deep see diving( He = 11.7 % ,  $N_2$  = 56.2 % and  $O_2$  =32.1% ) (3) Functions of lungs (4)At high altitudes pressure is low there for breathing problems lead to ANOXIA (unable to think and weak)

**Vapour Pressure:** The pressure exerted by vapours over the liquid surface at equilibrium is called *vapour pressure* of the liquid.

Raoult's Law: "The V.P. of any volatile component in the solution is directly proportional to its mole fraction".



#### Ideal and Non-Ideal Solutions:

iucai aliu Noll-Iucai Solutiolis.	
Ideal Solution	Non Ideal Solution
Follows Raoult's law at all temperature and concentrations. $P = P_A + P_B$	Does not follow Raoult's law at all temperature and pressure. $P \neq P_A + P_B$
Intermolecular forces in resulting solution are same as in pure components. A - B = A - A = B - B	Intermolecular forces in resulting solution are different from the inter molecular force of pure components. A $-B \neq A - A$ , $B - B$
No change in volume while mixing components. $\Delta \ V \ mix = 0$	Change in volume while mixing components. $\Delta$ V mix $\neq$ 0
No heat change take place while mixing the components. $\Delta$ H mix = 0	Heat changes take place while mixing the components. $\Delta$ H mix $\neq$ 0
Eg: n-hexane+ n-heptanes & benzene + toluene	Eg: Acetone + Water &Acetone + CHCl₃

#### Non Ideal Solution

<u> 11011 Ideal Solution</u>			
Showing Positive elevation from Raoult's Law	Showing Negative Deviation from Raoult's Law		
$P_T > P_A + P_B$ Resulting intermolecular force is weaker than pure components.	$P_T$ < $P_A$ + $P_B$ Resulting intermolecular force is stronger than pure components.		
$\Delta$ V mix = +ve	$\Delta$ V mix = -ve		
$\Delta$ H mix = +ve Endothermic mixing process	$\Delta$ H mix = -ve Exothermic process		
Acetone + Water , Alcohol + Water Carboxylic Acid + Water	Acetone + CHCl <sub>3</sub> , $H_3C$ $C=O^H$ $CCl$ $Cl$ $CH_3$		

Azeothrpes: (Constant Boiling Mixture):-Solution in which components are present in a fixed proportion, boils at a constant temperature irrespective of boiling point of pure components

Minimum Boiling Azeothrpes: Boils at a temperature lower than b.ps. of pure components. [95%

 Maximum Boiling Azeothrpes: Boils at a temperature higher than b.p.s. of pure components. [68%] HNO<sub>3</sub>]

**Colligative Properties:-** The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called *colligative properties* 

1-Relative Lowering of	2- Elevation of Boiling	3-Depression of Freezing	4- Osmotic Pressure
Vapour Pressure	<b>Point</b> : $\Delta T_b = K_b m$	Point	$\pi$ V = nRT
$\frac{p_{1}^{o} - p_{1}}{p_{1}^{o}} = \frac{\mathbf{w}_{2} \times M_{1}}{M_{2} \times \mathbf{w}_{1}}$	Wenitha X 1000	$\Delta T_f = K_f m$ $\Delta T_f = K_f \frac{W_{\text{solute }} \times 1000}{M_{\text{solute }} \times W_{\text{solvent}}}$	π = Osmotic pressure R =Gas constant Π =CRT (C= Molarity)

Osmosis:- The phenomenon of the passage of pure solven from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane.

Osmotic Pressure: Excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane.

Reverse Osmosis: If pressure greater than osmotic pressure is applied then, flow of solvent molecules is reversed, i.e. from a higher concentration solution to lower concentrated solution. This phenomenon is called "Reverse Osmosis". It is used in water purification and desalination of water.

Observed colligative property (actual) Van't Hoff Factor: Theoretica I colligative property (expected)

Q1. 18 g of glucose, C6H12O6, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar? Kb for water is 0.52 K kg mol-1.

Solution:- Number of kilograms of solvent = 1 kg Moles of glucose = 18 g/ 180 g mol-1 = 0.1 mol Thus molality of glucose solution = 0.1 mol kg-1 For water, change in boiling point

 $\Delta T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$ 

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15 + 0.052 = 373.202 K.

Q2. 45 g of ethylene glycol (C2HoO2) is mixed with 600 g of water. Calculate(a) the freezing point depression and(b) the freezing point of the solution.

Solution:- Molality = moles of ethylene glycol / mass of water in kilogram Moles of ethylene glycol = 45 / 62 g mol = 0.73 mol
Hence molality of ethylene glycol = 0.73/ 0.60 kg = 1.2 mol kg = 1.2 mol

Therefore freezing point depression,  $\Delta T_r = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$ 

Freezing point of the aqueous solution = 273.15 K - 2.2 K = 270.95 K

Q3, 200 cm3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57 × 10-3 bar. Calculate the molar mass of the protein.

Sol. = The various quantities known to us are as follows:  $\pi = 2.57 \times 10^{-3}$  bar,

 $V = 200 \text{ cm}^3 = 0.200 \text{ litre } T = 300 \text{ K}$ R = 0.083 L bar mol-1 K-1

Substituting these values in equation we get  $\pi = CRT$ 

$$M_2 = \frac{1.26 \text{ g} \times 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ bar} \times 0.200 \text{ L}} = 61.022 \text{ g mol}^{-1}$$

Q4. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, nonelectrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol-1). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

Given  $p_1^{\circ} = 0.850$  bar p = 0.845 bar:  $M_1 = 78$  g mol<sup>-1</sup>  $w_2 = 0.5$  g  $w_1 = 39$ g Substituting these values in

equation . 
$$\frac{P_1^0 - P_1}{P_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$
 $M_2 = 170 \text{ g mol}^{-1}$ 

Q5 If N2 gas is bubbled through water at 293 K, how many millimoles of N2 gas would dissolve in 1 litre of water. Assume that N2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N2 at 293 K is 76.48 kbar.

Solution :- According to Henry's law

$$x \text{ (Nitrogen)} = \frac{p(\text{nitrogen})}{K_H} = \frac{0.987 \text{bar}}{76,480 \text{ bar}} = 1.29 \times 10.5$$

As 1 litre of water contains 55.5 mol if n represents number of moles of N2 in sol,

n n mol = 55.5 = 1.29 × 10-5 x (Nitrogen) = n mol + 55.5 mol (n in denominator is neglected as it is <<55.5) Thus  $n=1.29\times10^{-5}\times55.5$  mol =  $7.16\times10^{-6}$  mol

- 7.16×10<sup>-4</sup> mol × 1000 mol 0.716 mmol mol

## **UNIT-3 ELECTROCHEMISTRY**

r			
SrNo	Те	rminology	
1.	<b>Conductance</b> : Reciprocal of the resistance $G = \frac{1}{R}$	Unit is $\Omega^{-1}$	
2	Specific Resistance/Resistivity: ρ= R A / I I/A :	G*(Cell Constant) Unit is ohm cm	
3	Specific Conductance or Conductivity : Conductivity	. K 1/P 1/101	
	of specific resistance and is denoted by $\kappa$ (Kappa) u		
4	Molar Conductivity: It is defined as the conducting po	ower of all the ions produced by ted by $\Lambda_{\rm m} = \frac{\kappa \times 1000}{{ m Molarity}}$	
	one gram mol of an electrolyte in a solution. It is deno	ted by ∧ <sub>m</sub> unit Scm²mol-1. Molarity	
5	Variation of molar conductivity with concentration	str.	
	For strong electrolytes λ decreases slightly with incre	316	
	due to increase in number of ions per unit volume. e	g KCI	
	For weak electrolytes it increases sharply with decrea	Weak electrolyte	
	as ionization of weak electrolytes increases on dilution	on e.g CH₃COOH	
6	Kohlrausch's Law: According to this law, molar cond	uctivity of an electrolyte, at infinite dilution can be expressed	
	as the sum of contributions from its individual ions e.g. $\wedge^{\circ} \operatorname{CaCl}_{2} = \lambda^{\circ} (\operatorname{Ca}^{2+}) + 2\lambda^{\circ} (\operatorname{Cl}^{-})$		
	Application of Kohlrausch's Law 1. For calculation of limiting molar conductivity $\lambda^{\circ} = \lambda^{c} \lambda_{m}$ $\alpha^{2}$		
	2. For calculation of degree of dissociation $\alpha = \frac{\Lambda}{\Lambda^{\circ}}$	3. For calculation of dissociation constant. $K_a = \frac{1}{(1-\alpha)}$	
7	Faraday – First law of electrolysis : The amount of	Faraday – Second Law: The amount of different substances	
	substance deposited during electrolysis is directly	librated by the same quantity of electricity passing through	
	proportional to quantity of electricity passed.	the electrolytic solution is proportional $\frac{w1}{w2} = \frac{E1}{E2}$	
	W=zit and W=EIt/96500	to their chemical equivalent weights w2 E2	
8	Nernst equation	<b>Equilibrium constant</b> $K_c$ At equilibrium $Q = K_c$ and $E_{cell} = 0$	
	$Ecell = E^{\circ}cell - \frac{0.059}{n} \log \frac{[product]}{[react.]}$	$E^{\circ}cell = \frac{0.059}{n} \log Kc$ $\Delta_{r}G^{\circ} = -nFE^{\circ}$	
		<i>n</i>	
9.	Electrochemical Cell and Gibbs energy of the		
	reaction	$\Delta_{r}G^{\circ} = -2.303RT \log K_{c}$	

#### Products of electrolysis

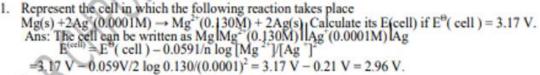
Electrochemical Cell

NaCl (molten)	Cathode : $Na^+(I) + e^- \rightarrow Na(s)$	Anode : $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$
NaCl (aq)	Cathode: $H_2O(I) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-$	Anode : Cl <sup>-</sup> → ½Cl <sub>2</sub> +e <sup>-</sup>
AgNO₃(aq)-Ag electrodes	Cathode : $Ag^+(aq) + e^- \rightarrow Ag(s)$	Anode: Ag(s) $\rightarrow$ Ag <sup>+</sup> (aq) + e <sup>-</sup>
AgNO₃(aq)- Pt electrodes	Cathode : $Ag^+(aq) + e^- \rightarrow Ag(s)$	Anode: $2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
CuCl(aq)- Pt electrodes	Cathode : Cu <sup>+</sup> (aq) + $e^- \rightarrow$ Cu(s)	Anode: $2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

**Electrolytic Cell** 

<ol> <li>It is device to convert chemical energy to electrical energy</li> <li>It is based upon redox reaction which is spontaneous.</li> </ol>		<ol> <li>It is device to convert electrical energy into chemical energy</li> <li>The redox reaction is non-spontaneous and takes place only when electrical energy is supplied.</li> </ol>			
SNO	Name of cell	Electrolyte	Chemical Reaction		Remark
1	Mercury Cell	Paste of	Anode:- zinc-mercury am	algam	Provide constant voltage and does
		кон &	$Zn(Hg) + 2OH^- \rightarrow ZnO($	$(s) + H_2O + 2e^-$	not corroded due to absence of
		Zn(OH) <sub>2</sub>	Cathode:- HgO and carbo	on _	ion in overall reaction.
			$HgO + H_2O + 2e^- \rightarrow Hg$	$(1) + 2OH^{-}$	Voltage 1.35V
			Overall reaction:- Zn(Hg)	+ HgO → ZnO + H <sub>2</sub>	
2	Dry Cell :	ZnCl <sub>2</sub> and	Anode :- Zinc rod	$Zn(s) \rightarrow Zn^{2+} + 2e^{-}$	Corroded due to the presence of
		NH <sub>4</sub> Cl	Cathode:-Carbon rod sur	rounded by MnO2	ion in overall reaction.
			$2MnO_2 + 2NH_4^+ + 2e^- \rightarrow N$	∕ln <sub>2</sub> O <sub>3</sub> +2NH <sub>3</sub>	ZnCl <sub>2</sub> is used to make a complex
			Overall Reaction:-		[Zn(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ] it saves the bursting
			$Zn + 2MnO_2 + 2NH_4^+ \rightarrow Zr$	n <sup>2+</sup> + Mn <sub>2</sub> O <sub>3</sub> + 2 NH <sub>3</sub>	of cell, Voltage 1.5V
3	Lead Storage	38% H <sub>2</sub> SO <sub>4</sub>	Anode:- Pb grid		Can be Recharged by reversing the
	(Secondary		$PbSO_4(s) + 2e^- \rightarrow Pl$	$b(s) + SO_4^{2-}(aq)$	electrodes Reactant become
	Batteries):		Cathode:-Pb grid filled with PbO <sub>2</sub>		products and products become
			=	$+2e^{-} \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	reactants
			Overall Cell Reaction:-	-1-1 - (1)	
			$Pb(s) + PbO_2(s) + 2H_2SO_4 -$	$\rightarrow 2PbSO_4(s) + 2H_2O(1)$	

4	Fuel Cell :	KOH solution	Anode :- $2H_2 + 4OH^-$ Cathode $O_2(g) + 2H_2O$ Overall Reaction:- $2H_2O$	$O(l) + 4e^- \rightarrow 4OH^-(aq)$	Eco friendly, Efficiency 60-70%
5.	Corrosion	H <sub>2</sub> CO <sub>3</sub>	Anode (oxidation) :- $Fa$ Cathode (Reduction) :- $O_2(g) + 4H^+(ag) + 4e^-$ Atmospheric Oxidation $2Fe^{2^+(aq)} + 2H_2O_{( )} + 1/2O_2$	$\rightarrow 2H_2O(l)$	Formula of rust Fe <sub>2</sub> O <sub>3.</sub> x H <sub>2</sub> O
	revention of Corrosion	By covering the surface with paint or by some chemicals (e.g. bisphenol). / Cover the metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical me electrode like Mg, Zn, etc.) which corrodes itself but saves the object.			
Observe the graph shown in figure between Am(molar conductivity) Vs C (Molar-concentration) and answer the questions based on graph.		(a)The curve 'Y' is for KCl or CH3 (b)What is intercept on $\Lambda$ m axis (c) Give mathematical equation $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$ (d) What is slope equal to? Ans: (e) What happens to molar condelectrolyte and why?	Slope = -A luctivity on dilution in case of weak reases sharply on dilution because		



- Calculate the equilibrium constant of the reaction:  $E^{\Theta}(\text{cell}) = 0.46 \text{ V}$  $Cu(s) + 2Ag^{\dagger}(aq) \rightarrow Cu^{2\dagger}(aq) + 2Ag(s)$ Ans:  $E^{\Theta}(\text{cell}) = 0.059 \text{ V/2 log } K_C = 0.46 \text{ V} \text{ or log } K_C = 0.46 \text{ V} \times 2/0.059 \text{ V} = 15.6$
- The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$  $\triangle G^{\Theta} = -nFE$  (cell) n in the above equation is 2, F = 96487 C mol<sup>-1</sup> and Therefore,  $\triangle G^{\Theta} = -2 \times 1.1 \text{V} \times 96487 \text{ C mol}^{-1}$ E(cell) = 1.1 V
- = -21.227 kJ mol-1 = -21227 J mol-1 Resistance of a conductivity cell filled with 0.1 mol L<sup>-1</sup> KCl solution is 100Ω. If the resistance of the same cell
  when filled with 0.02 mol L<sup>-1</sup> KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L<sup>-1</sup> KCl solution. The conductivity of 0.1 mol L<sup>-1</sup> KCl solution is 1.29 S/m.

Ans: The cell constant is given by the equation: Cell constant = G\* = conductivity × resistance

=  $1.29 \text{ S/m} \times 100\Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$ Conductivity of  $0.02 \text{ mol L}^{-1} \text{ KCl solution} = \text{cell constant} / \text{resistance}$ 

- = 1.29 cm<sup>-1</sup>/ 520  $\Omega$  = 0.248 × 10<sup>-2</sup> S cm<sup>-1</sup> and  $\Lambda$  m=  $\kappa$  × 1000 cm<sup>3</sup> L<sup>-1</sup>/molarity  $= 0.248 \times 10^{-2} \text{ S cm}^{-1} 1000 \text{ cm}^{3} \text{L}^{-1} / 0.02 \text{ mol L}^{-1}$
- Molar conductivities (Λ) at infinite dilution of NaCl, HCl and CH3COONa are 126.4, 425.9 and

91.0 S Cm mol-1 respectively. Find out the limiting molar conductivity Λ<sup>0</sup> for CH<sub>3</sub>COOH x= 516.9 - 126.4 = 390.5 Ans: 91 + 425.9 = 126.4 + xS Cm mol-1

- 6. The conductivity of  $0.001028 \text{ mol } L_s^{-1}$  acetic acid is  $4.95 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its dissociation constant if E°m for acetic acid is  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ .

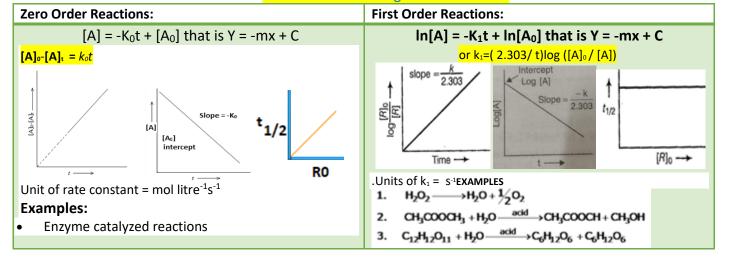
  Ans:  $\Lambda m = \kappa/c = 4.95 \times 10^{-5} \text{ S cm}^{-1}/0.001028 \text{ mol } L^{-1} \times 1000 \text{ cm}^{-1}/L = 48.15 \text{ cm}^2 \text{ mol}^{-1}$   $\alpha = \Lambda m/\Lambda^\circ m = 48.15 \text{ S cm}^2 \text{ mol}^{-1}/390.5 \text{ S cm}^2 \text{ mol}^{-1} = 0.1233$   $K = c\alpha^2/(1-\alpha) \ 0.001028 \text{ mol } L^{-1} \times (0.1233)^2/1 0.1233 = 1.78 \times 10^{-5} \text{ mol } L^{-1}$
- How much charge is required for the reduction of 1 mol of MnO<sub>4</sub> to Mn<sup>+2</sup>? Ans: 5× 96500 Colombes
- 8. A solution of Ni (NO<sub>3</sub>)<sub>2</sub> is electrolyzed between platinum electrode using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? [Ni= 58.7] Ans: O = it,  $5 \times 20 \times 60 = 6000C$

Reaction for the Ni, Ni<sup>+2</sup> + 2e<sup>-</sup>→ Ni, (2 mol × 96500C)  $58.7 \times 6000/2 \times 96500 = 1.8$ 

#### **CHAPTER-4 CHEMICAL KINETICS**

			CHAPTER-4	CH	EMICAL K	INETI	CS
RATE OF	The ch	ange in	concentration of eith	er reac	tant or produ	ct per un	it time.
<b>REACTION</b>	Example: $N_2 + 3H_2 - \rightarrow 2NH_3$						
	Rate of	reaction	$a = + \frac{1}{2} \frac{d(NH_3)}{dt} = - \frac{d}{dt}$	[N <sub>2</sub> ]	$\frac{1}{2} \frac{d[H_2]}{d[H_2]}$		
	raie o	reaction	2 dt	dt	3 dt		
<b>Unit of rate</b>	Mol L <sup>-1</sup>	time <sup>-1</sup>	or mol L <sup>-1</sup> S <sup>-1</sup>				
Rate Law	The ex	pressio	n of rate of reaction in	n term	of concentrat	ion of rea	ctant
	aA + bi	3 <del>→</del> Pro	duct Rate=K[A] <sup>x</sup> [B] <sup>y</sup>				
<b>Rate Constant</b>	Specifi	c Rate o	of reaction :-Rate of re	eaction	when concer	itration ai	re taken as unity Rate=K[A] <sup>x</sup> [B] <sup>y</sup>
			Rate=K				
Unit of rate constatnt	Unit	of <b>k</b> =	$\left[\frac{\text{mol}}{L}\right]^{1-n} \times \text{time}^{-1}$ For	r gaseo	us reaction u	nit of k n	nay be = $(atm)^{1-n} \times time^{-1}$
	N - Ord	ler of re	eaction				
Order of			werof concentration			•	sion
reaction			duct Rate=K[A] <sup>x</sup> [B] <sup>y</sup>			•	
			,Positive or Negative				
Mechanism of		-			•		and have exponant in rate law
Reaction	-		ual to their stochiome	etric co	efficient .Zerc	order re	action can not be an elementry
	reactio						
	Compl			x react	ion,the overa		is controlled by the slowest step
Difference			rder of Reaction		Molecularity		
between	1 1		of the exponents (powe		➤ 1.The no. atoms , ions or molecule that must collide with one another simultaneously so that		
Order of		ch the c ate law.	oncentration terms are	raised	chemical reaction take place		
Reaction and	-		ed Experimently by rate	law			t ,determined by slowest step
Molecularity			ero and negetive		➤ 3.Never be		
		ay be Fi			> 4.Neverbe		
<b>Pseudo first</b>	_		tion which seems to be	higher	order but actua	ally they ar	re of first order
order reaction			· ·			•	han one Example :- <u>Hydrolysis of</u>
			ic medium, Inversion o				
METHOD OF			_				Determine the order of the reaction
DETERMINING	with re						n. Also calculate rate constant.
ORDER OF		Exp.	Initial conc. (A)				ate (mol L <sup>-1</sup> s <sup>-1</sup> )
REACTION		1	0.10 M	1.00		2.1 x 10	
		2	0.20 M	1.00	M	8.4 x 10	
		3	0.20 M	2.00	M	8.4 x 10	) <sup>-3</sup>
	ANSWER:						
	Exp. Rate = $K[A]^x[B]^y$ Eq.(i)/(ii) Then(1/2) <sup>x</sup> = (1/4)						
	1 Rate = K $[0.10]^x [1.00]^y = 2.1 \times 10^{-3}$ (i) Therefore x = 2						
	2 Rate = K $[0.20]^{x} [1.00]^{y} = 8.4 \times 10^{-3}$ (ii) Eq.(ii)/(iii) Then(1/2) <sup>y</sup> = (1)						
	3 Rate = K $[0.20]^x [2.00]^y = 8.4 \times 10^{-3}$ (iii) Therefore y = 0						
	Rate law= $K[A]^2[B]^0$ $K = 2.1 \times 10^{-3} / [0.1]^2[1.00]^0$						

#### Differential and Integrated Rate Laws:



**Half Life:** Time required to consume the half of initial concentration of reactant is called half life period.

At t =  $t_{1/2}[A] = [A_0]/2$ 

 $K_0 t_{1/2} = [A]_0 - [A_0]/2$ 

 $t_{1/2} = [A]_0/2k$ 

Half life is directly proportion of the initial concentration of the reactant for a zero order reaction.

Half Life: Time required to consume the half of initial concentration of reactant is called half life period. At  $t = t_{1/2}[A] = [A_0]/2$   $k_1=(2.303/t_{1/2})\log([A]_0/[A_0/2])$   $t_{1/2}=0.693/k_1$ Half-life is independent of the initial concentration of the reactant for a first order reaction

The following data were obtained during the first order thermal decomposition of  $SO_2Cl_2$  at a constant volume.  $SO_2Cl_2$  (g)  $\rightarrow$   $SO_2(g) + Cl_2(g)$ . Calculate the rate constant.

Ex	p	Time/s <sup>-1</sup>	Total pressure/atm
1		0	0.5
2		100	0.6

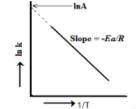
Ans: Given  $p_0 = 0.5$  atm  $P_t = 0.6$  atm t = 100 sec n = 2/1 = 2  $k_1 = (2.303/ t) log <math>(n-1)P_0 / nP_0 - P_t$  OR  $k_1 = (2.303/100) log (0.5) / 2(0.5) - 0.6 Or <math>K_1 = 2.231 \times 10^{-3}$  sec<sup>-1</sup>

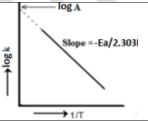
#### **Arrhenius Equation**

It shows the relationship between Activation energy and rate constant and effect of temp on rate constant.

$$\mathbf{k} = \mathbf{A} \mathbf{e}^{(-\mathbf{E}_a/RT)}$$

$$log(\frac{k_2}{k_1}) = \frac{Ea}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$





THRESHOLD ENERGY

The Minimum extra amt of energy which the reactants molecules must have sothat reactant molecule reacts and overcome the energy barriers and converts into products.

**ACTIVATION ENERGY** 

The Minimum extra amt of energy absorbed by the reactant molecule so that their energy becomes equal to threshold energy.

1. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Ans. For a first order reaction, the time required for 99% completion is

,,	1
$t_1 = \frac{2.303}{k} \log \frac{100}{100 - 99}$	For a first order reaction, the time required for 90% completion is
$=\frac{2.303}{k}\log 100$	$t_2 = \frac{2.303}{k} log \frac{100}{100 - 90} = \frac{2.303}{k} log 10$
$=2\times\frac{2.303}{k}$	$= \frac{2.303}{k}$ Therefore, $t_1 = 2t_2$

The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

$$\log \frac{k_{2}}{k_{1}} = \frac{E_{z}}{2.303R} \left( \frac{T_{2} - T_{1}}{T_{1}T_{2}} \right)$$

$$T_{1} = 293K$$
It is given that,  $k_{2} = 4k_{1}$ 

$$\log \frac{4k_{1}}{k_{2}} = \frac{E_{z}}{2.303 \times 8.314} \left( \frac{313 - 293}{293 \times 313} \right)$$

$$\log \frac{4k_{1}}{k_{2}} = \frac{E_{z}}{2.303 \times 8.314} \left( \frac{313 - 293}{293 \times 313} \right)$$

$$= 52.86k \text{Jmol}^{-1}$$

3. For a reaction,  $A + B \rightarrow$  'Product; the rate law is given by,  $r = K[A]^{1/2}[B]^2$ . What is the order of the reaction?

Ans. The order of the reaction  $=\frac{1}{2}+2$ 4. The conversion of malarity  $=\frac{1}{2}+2$ 

4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Ans:- Rate<sub>1</sub> = 
$$k.(a)_2 = ka_2$$

If the concentration of X is increased to three times, then  $[X] = 3a \, mol \, L^{-1}$ 

Now, the rate equation will be: Rate =  $k(3a)_2$ 

Hence, the rate of formation will increase by 9 times.

# d and f- BLOCK ELEMENTS (By Dr M R CHOUDHARY 846913570)

2	1	d-block elements are called transition elements	incomplete d-orbitals in neutral or most stable oxidation state.
elements and why?	2	Zn. Hg. Cd. are not included as transition	as they have filled d-orbitals in neutral and most stable +2
Sei* has de configuration but it is transition metal   First series transition elements shows irregular trend of atomic radii   First series transition elements shows irregular trend of atomic radii of Zr to IIf are almost same.   Use to Lambenoid Contraction.   Use to Presence of Unpaired electrons form strong metal in Lambenoid Contraction.   Use to Presence of Unpaired electrons or partially filled dorbitals.   Use to Science of Unpaired Lambenoid Contraction.   Use to Science of Unpaired Lambenoid C		_	
First series transition elements shows irregular trend of atomic radii   Atomic radii of Zr to Ilf are almost same.   due to Lanthenoid Contraction.     First series transition elements shows irregular trend of IE   Transition metals have high enthalpy of atomization and melting point.     Zn, Cd. Hg are not very hard and have low M.P. and B.P.   due to presence of unpaired electrons from strong metallic bonding of atomization and melting point.     Due to presence of unpaired electrons from strong metallic bonding of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.   due to presence of unpaired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.   due to presence of unpaired electrons or partially filled doubtless than the of oxidation states and why?   due to presence of unpaired electrons or partially filled doubtless than the original properties of a contraction or partially filled doubtless than the original properties of the presence of unpaired electrons or partially filled doubtless than the original properties of the presence of unpaired electrons or partially filled doubtless than the properties of the presence of unpaired electrons or partially filled doubtless.   Mn shows highest number of oxidation state due presence of unpaired electrons or partially filled doubtless.   Mn shows highest number of oxidation state due presence of unpaired electrons or partially filled doubtless.   Mn shows highest number of oxidation state due presence of unpaired electrons or partially filled doubtless.   Mn shows highest number of unpaired electrons or partially filled doubtless.   Mn shows highest number of unpaired electrons or partially filled doubtless.   Mn shows highest number of unpaired electrons.   Mn shows highest	3		
trend of atomic radii of Zr to Hf are almost same.  First series transition elements shows irregular trend of IE  Transition metals have high enthalpy of atomization and melting point.  Another adii of Zr to Hf are almost same.  Transition metals have high enthalpy of atomization and melting point.  Another adii of Zr. Cd. Hg are not very hard and have low M.P. and B.P.  Due to presence of all paired electrons form strong metallic bonding  Due to presence of all paired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.  Due to presence of unpaired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.  Due to presence of unpaired electrons or partially filled dorbitals and why?  Due to presence of unpaired electrons or partially filled dorbitals on the state or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons or partially filled dorbitals or the presence of unpaired electrons form to partially filled dorbitals or the presence of unpaired electrons form to partial	4		
First series transition elements shows irregular trend of IE		_	
trend of IE orbitals after removal of one electron.  Transition metals have high enthalpy of atomization and melting point.  By Zn, Cd, Hg are not very hard and have low M.P. and B.P.  Due to presence of unpaired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.  Due to presence of all paired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.  Due to presence of unpaired electrons or partially filled dorbitals.  Which first series transition metal shows highest number of oxidation state due presence of highest number of oxidation state due presence of highest number of unpaired electrons.  Which first series transition metal do not show variable oxidation states and why?  Cri* is more stable in solution than Cu* due to stable half filled t <sub>2e</sub> ² configuration in +3 O.S  Cri* is more stable in solution than Cu* due to stable half filled t <sub>2e</sub> ² configuration.  Which first series transition metal shows +1 oxidation states and why?  Higher oxidation states of transition metals found in their oxides and fluorides of transition metals found in their oxides and fluorides of transition metals.  Which first series transition metals found in their oxides and fluorides of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals or one stable in first series transition metals in which group number and O.N. of transition metals or one stable in first series transition f	5	Atomic radii of Zr to Hf are almost same.	due to Lanthenoid Contraction.
Transition metals have high enthalpy of atomization and melting point.	6	_	
8         Zn, Cd, Hg are not very hard and have low M.P. and B.P.         Due to presence of all paired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.           9         d-block elements shows a large no. of oxidation state         due to presence of unpaired electrons or partially filled dorbitals.           10         Which first series transition metal shows highest number of oxidation states and why?         Mn shows highest number of oxidation state due presence of highest number of oxidation states and why?           12         Cr3* is more stable as compared to Cr2* diable oxidation states and why?         due to stable half filled tg2* configuration in +3 O.S           13         Cu2* is more stable in solution than Cu* due to high hydration enthalpy of Cu2* ion in solution.         Us shows +1 oxidation state in gaseous form due to stable full filled d30*0 configuration.           15         Higher oxidation states and movides and fluorides found in their oxides and fluorides of transition metals found in their oxides and fluorides of transition elements moving from left to right stransition elements moving from left to right to make a same-less negative but it shows irregular trend         as a number of unpaired electrons decreases.           18         Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-less negative but it shows irregular trend         moving from left to right E0 for M2*/M becomes less negative but it shows irregular trend         tit is due to low hydration enthalpy of Cu2* which cannot compensate Δ <sub>mab</sub> H0* HE1+ HE2.			
8       Zn, Cd, Hg are not very hard and have low M.P. and B.P.       Due to presence of all paired electrons they have least enthalpy of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.         9       d-block elements shows a large no. of oxidation state with low M.P. and B.P.       due to presence of unpaired electrons or partially filled dorbitals.         10       Which first series transition metal shows highest number of oxidation state due presence of highest number of oxidation state with number of oxidation states and humber of oxidation state in gaseous form due to stable full due to high hydration enthalpy of Cu² in thei	7	9 11	
g       d-block elements shows a large no. of oxidation state       of atomization, very weak metallic bond & are not very hard with low M.P. and B.P.         9       d-block elements shows a large no. of oxidation state on state       due to presence of unpaired electrons or partially filled dorbitals.         10       Which first series transition metal shows highest number of oxidation state due presence of highest number of oxidation state save flexible due to stable highlight filled tage configuration.         12       Present part oxidation states and why?       In oxidation state save and fluorides of transition metals in which group number and O.N. of trans			
delablock elements shows a large no. of oxidation state         with low M.P. and B.P.           10         Which first series transition metal shows highest number of oxidation state due presence of highest number of oxidation state due presence of highest number of unpaired electrons.           11         Which first series transition metal do not show variable oxidation states and why?         Sc. due to achieving noble gas configuration in +3 O.S           12         Cr³- is more stable as compared to Cr²- due to stable half filled t₂g² configuration.         due to stable half filled t₂g² configuration.           13         Cu²- is more stable as compared to Cr²- due to high hydration enthalpy of Cu²- ion in solution.         Cu shows +1 oxidation state in gaseous form due to stable full filled 3d¹0- configuration.           14         Which first series transition metal showl?         Cu shows +1 oxidation state in gaseous form due to stable full filled t₂g² configuration.           15         Higher oxidation states of transition metals found in their oxides and fluorides         because higher oxidation states stabilized by highly electronegative elements such as O and F           16         higher oxidation states are more common in oxides rather than fluorides of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals are same.         MnO <sub>4</sub> , Cr <sub>2</sub> O <sub>7</sub> ², VO <sub>3</sub> , CrO <sub>4</sub> ²           20         For Cr, E <sup>0</sup> Cr³-/Cu is +ve (+0.34 V)         it is due to low hydration ent	8		
9 d-block elements shows a large no. of oxidation states state         due to presence of unpaired electrons or partially filled dorbitals.           10 Which first series transition metal shows highest number of oxidation state due presence of nighest number of oxidation state due presence of highest number of oxidation state due presence of number of unpaired electrons.           11 Which first series transition metal do not show variable oxidation states and why?         due to stable half filled tag's configuration.           12 Which first series transition metal shows +1 oxidation states and why?         due to high hydration enthalpy of Cu²+ ion in solution.           14 Which first series transition metals found in their oxidation states of transition metals found in their oxidation states of transition metals.         because higher oxidation states stabilized by highly electronegative elements such as O and F           16 higher oxidation states are more common in oxides rather than fluorides of transition metals.         higher oxidation states and why?         as number of unpaired electrons decreases.           17 +2 O.S becomes more stable in first series transition metals in which group number and O.N. of transition metal are same.         the formation of dπ-pπ bond		and B.P.	
description         state         orbitals.           10         Which first series transition metal shows highest number of oxidation state due presence of highest number of unpaired electrons.           11         Which first series transition metal do not show variable oxidation states and why?         Sc, due to achieving noble gas configuration in +3 0.S           12         Cr³- is more stable as compared to Cr²- due to stable half filled t₂a² configuration.         due to stable half filled t₂a² configuration.           14         Which first series transition metal shows +1 doxidation states and why?         due to high hydration enthalpy of Cu²- ion in solution.           15         Higher oxidation states of transition metals found in their oxides and fluorides         Cu shows +1 oxidation state gaseous form due to stable full filled 3d¹o configuration.           16         higher oxidation states are more common in oxides rather than fluorides of transition metals.         due to formation of dπ-pπ bond between metal and oxygen.           17         +2 O.S becomes more stable in first series transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metals in which group number and O.N. of transition metal are same-less negative but it shows irregular trend         MnO₄, Cr₂O,²², VO₃, CrO₄²²           20         For copper E⁰ Cu²+/Cu is +ve (+0.34 V)         it is due to low hydration enthalpy of Cu²+ which cannot compensate Δ₂a, H³+ IE₂ - Eesa egative but it shows irregular trend         because Cr³+ is more stable due to half filled t₂a configuration.	9	d-block elements shows a large no of ovidation	
10         Which first series transition metal shows highest number of oxidation states and why?         Mn shows highest number of oxidation state due presence of highest number of oxidation states and why?           11         Which first series transition metal do not show variable oxidation states and why?         Sc, due to achieving noble gas configuration in +3 0.S           12         Cr²+ is more stable as compared to Cr²+ oxidation states and why?         due to stable half filled t₂₂ configuration.           13         Cu²+ is more stable in solution than Cu* oxidation states series transition metal shows +1 oxidation states and why?         due to high hydration enthalpy of Cu²+ ion in solution.           15         Higher oxidation states and why? oxidation states and why?         Cu shows +1 oxidation state in gaseous form due to stable full filled 3d¹0-configuration.           16         higher oxidation states are more common in oxides rather than fluorides of transition metals in which group number and 0.N. of transition metals in which group number and 0.N. of transition metal are same-less negative but it shows irregular trend         as number of unpaired electrons decreases.           19         Moving from left to right Eo for M²-/M becomes less negative but it shows irregular trend         trends due to irregular variation of IE₁ + IE₂.           20         For Cn, Eo Cr²-/Cu is +ve (+0.34 V)         it is due to low hydration enthalpy of Cu²- which cannot compensate Δ <sub>sub</sub> H0+ IE₁ + IE₂.           21         For Sh Mn, Eo Mn²-/Mp²- is +ve         because by conherting into Mn²- it achieves half filled		_	
number of oxidation states and why?         highest number of unpaired electrons.           11         Which first series transition metal do not show variable oxidation states and why?         Sc , due to achieving noble gas configuration in +3 O.S           12         Gr3 is more stable as compared to Gr2 due to stable half filled tz <sub>sc</sub> 3 configuration.         due to stable half filled tz <sub>sc</sub> 3 configuration.           13         Gu2* is more stable in solution than Cu* due to high hydration enthalpy of Cu2* ion in solution.         Cu3 hows +1 oxidation state in gaseous form due to stable full filled 3d¹0 configuration.           14         Which first series transition metal shows +1 oxidation states and why?         Cu shows +1 oxidation state in gaseous form due to stable full filled 3d¹0 configuration.           15         Higher oxidation states of transition metals.         because higher oxidation states stabilized by highly electronegative elements such as O and F           16         higher oxidation states are more common in oxides rather than fluorides of transition metals.         as number of unpaired electrons decreases.           17         +2 O.S becomes more stable in first series transition metals in which group number and O.N. of transition metal are same.         Immoderate transition metals function of dπ-pπ bond between metal and oxygen.           18         Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same.         Immoderate function of dπ-pπ bond between metal and oxygen.           19         Moving from left to	10		
Which first series transition metal do not show variable oxidation states and why?   due to stable half filled t <sub>28</sub> configuration in +3 0.S		_	_
12 Cr³+ is more stable as compared to Cr²+       due to stable half filled t₂g³ configuration.         13 Cu²+ is more stable as compared to Cr²+       due to high hydration enthalpy of Cu²+ ion in solution.         14 Which first series transition metal shows +1 oxidation states and why?       due to high hydration enthalpy of Cu²+ ion in solution.         15 Higher oxidation states of transition metals found in their oxides and fluorides       because higher oxidation states stabilized by highly electronegative elements such as 0 and F         16 higher oxidation states are more common in oxides rather than fluorides of transition metals.       due to formation of dπ-pπ bond between metal and oxygen.         17 +2 O.S becomes more stable in first series transition elements moving from left to right in which group number and O.N. of transition metals in which group number and O.N. of transition metal are same-       as number of unpaired electrons decreases.         19 Moving from left to right Eo for M²-/M becomes less negative but it shows irregular trend       trends due to irregular variation of IE₁ + IE₂.         20 For Cropper Eo Cu²-/Cu is +ve (+0.34 V)       it is due to low hydration enthalpy of Cu²- which cannot compensate A <sub>sub</sub> Ho+ IE₁ + IE₂.         21 For Mn , Eo Mn³-/Mn²- is +ve       because by converting into Mn²- it achieves half filled configuration.         22 For Cr , Eo Cr³-/Cr²- is -ve       because Cr²- is more stable due to half filled t₂g configuration.         24 (Sc³-, Ti⁴-) does not exhibit any colour       Due to absent of unpaired e- as d-d transition is not possible full filled d-orbitals (d¹0) a	11		-
13Cu²+ is more stable in solution than Cu¹due to high hydration enthalpy of Cu²+ ion in solution.14Which first series transition metal shows +1 oxidation states and why?Cu shows +1 oxidation state in gaseous form due to stable full filled 3d¹v configuration.15Higher oxidation states of transition metals found in their oxides and fluorides found in their oxides and fluorides are more common in oxides rather than fluorides of transition metals.because higher oxidation states stabilized by highly electronegative elements such as O and F16higher oxidation states are more common in oxides rather than fluorides of transition metals.due to formation of dπ-pπ bond between metal and oxygen.17+2 O.S becomes more stable in first series transition metals.as number of unpaired electrons decreases.18Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-MnO4*, Cr2O7²*, VO3*, CrO4²*19Moving from left to right E0 for M²*/M becomes less negative but it shows irregular trendtrends due to irregular variation of IE₁ + IE₂.20For copper E0 Cu²*/Cu is +ve (+0.34 V)it is due to low hydration enthalpy of Cu²* which cannot compensate Δ <sub>sub</sub> Hon+rIE₁ + IE₂.21For Mn , E0 Mn³*/Mn²* is +vebecause by converting into Mn²* it achieves half filled configuration.22For Cr , E0 Cr³*/Cr²* is -vebecause Cr³* is more stable due to half filled t₂s configuration.23Most of the compounds of transition metal are coloured in solid state as well as in their solutionTi is due to d-d transition24(Sc³*, Ti⁴*) does not exhibit any colourDue to absent of unpaired e as d-d transition is		variable oxidation states and why?	
14 Which first series transition metal shows +1 oxidation state in gaseous form due to stable full filled 3d <sup>10</sup> configuration.  15 Higher oxidation states of transition metals found in their oxides and fluorides  16 higher oxidation states are more common in oxides rather than fluorides of transition metals.  17 +2 O.S becomes more stable in first series transition elements moving from left to right  18 Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-  19 Moving from left to right E <sup>0</sup> for M <sup>2+</sup> /M becomes less negative but it shows irregular trend  20 For copper E <sup>0</sup> Cu <sup>2+</sup> /Cu is +ve (+0.34 V)  21 For Mn , E <sup>0</sup> Mn <sup>3+</sup> /Mn <sup>2+</sup> is +ve  22 For Cr , E <sup>0</sup> Cr <sup>3+</sup> /Cr <sup>2+</sup> is -ve  33 because by converting into Mn <sup>2+</sup> it achieves half filled configuration.  24 (Sc <sup>2+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour  25 (Zn <sup>2-</sup> , Cu <sup>1</sup> ) does not exhibit any colour  26 Transition metal form large number of coordination complexes  18 White oxidation states of transition metals because higher oxidation states stabilized by highly electronegative elements woidation states stabilized by highly electronegative elements oxidation states oxidation states stabilized by highly electronegative elements woidation states oxidation states stabilized by highly electronegative elements such as O and F  due to formation of dπ-pπ bond between metal and oxygen.  35 an number of unpaired electrons decreases.  36 an unpaired electrons decreases.  37 transition elements moving from left to right  48 due to formation of dπ-pπ bond between metal and oxygen.  49 MnO <sub>4</sub> , Cr <sub>2</sub> O <sub>7</sub> <sup>2</sup> , VO <sub>3</sub> , CrO <sub>4</sub> <sup>2-</sup> 40 it is due to irregular variation of IE <sub>1</sub> + IE <sub>2</sub> .  41 because by converting into Mn <sup>2+</sup> it achieves half filled configuration.  42 (Sc <sup>2+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour  41 because Cr <sup>3+</sup> is more stable due to half filled t <sub>2e</sub> configuration.  42 (Sc <sup>2+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour  43 because higher oxidation states stabilized by highly electronegative elements such as O and F	12	Cr³+ is more stable as compared to Cr²+	due to stable half filled $t_{2g}^3$ configuration.
Signature   Sig	13	Cu <sup>2+</sup> is more stable in solution than Cu <sup>+</sup>	due to high hydration enthalpy of Cu <sup>2+</sup> ion in solution.
Higher oxidation states of transition metals found in their oxides and fluorides   electronegative elements such as O and F	14	Which first series transition metal shows +1	Cu shows +1 oxidation state in gaseous form due to stable full
found in their oxides and fluorides lelectronegative elements such as O and F higher oxidation states are more common in oxides rather than fluorides of transition metals.  17		-	-
<ul> <li>higher oxidation states are more common in oxides rather than fluorides of transition metals.</li> <li>+2 O.S becomes more stable in first series transition elements moving from left to right</li> <li>Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-</li> <li>Moving from left to right E<sup>0</sup> for M<sup>2+</sup>/M becomes less negative but it shows irregular trend</li> <li>For copper E<sup>0</sup> Cu<sup>2+</sup>/Cu is +ve (+0.34 V)</li> <li>For Mn, E<sup>0</sup> Mn<sup>3+</sup>/Mn<sup>2+</sup> is +ve</li> <li>because by converting into Mn<sup>2+</sup> it achieves half filled configuration.</li> <li>For Cr, E<sup>0</sup> Cr<sup>3+</sup>/Cr<sup>2+</sup> is -ve</li> <li>Most of the compounds of transition metal are coloured in solid state as well as in their solution</li> <li>(Sc<sup>3+</sup>, Ti<sup>4+</sup>) does not exhibit any colour</li> <li>(Tansition metals or ions are paramagnetic in nature</li> <li>Transition metal form large number of coordination complexes</li> </ul>	15	9	
17+2 O.S becomes more stable in first series transition elements moving from left to rightas number of unpaired electrons decreases.18Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-MnO <sub>4</sub> , Cr <sub>2</sub> O <sub>7</sub> <sup>2</sup> , VO <sub>3</sub> , CrO <sub>4</sub> <sup>2</sup> -19Moving from left to right E <sup>0</sup> for M <sup>2+</sup> /M becomes less negative but it shows irregular trendtrends due to irregular variation of IE <sub>1</sub> + IE <sub>2</sub> .20For copper E <sup>0</sup> Cu <sup>2+</sup> /Cu is +ve (+0.34 V)it is due to low hydration enthalpy of Cu <sup>2+</sup> which cannot compensate Δ <sub>sub</sub> H <sup>0</sup> + IE <sub>1</sub> + IE <sub>2</sub> .21For Mn, E <sup>0</sup> Mn <sup>3+</sup> /Mn <sup>2+</sup> is +vebecause by converting into Mn <sup>2+</sup> it achieves half filled configuration.22For Cr, E <sup>0</sup> Cr <sup>3+</sup> /Cr <sup>2+</sup> is -vebecause Cr <sup>3+</sup> is more stable due to half filled t <sub>2g</sub> configuration.23Most of the compounds of transition metal are coloured in solid state as well as in their solutionIt is due to d-d transition24(Sc <sup>3+</sup> , Ti <sup>4+</sup> ) does not exhibit any colourDue to absent of unpaired e as d-d transition is not possible25(Zn <sup>2+</sup> , Cu <sup>+</sup> ) does not exhibit any colourfull filled d-orbitals (d <sup>10</sup> ) as d-d transition is not possible26Transition metals or ions are paramagnetic in natureDue to presence of unpaired electrons (d <sup>1-9</sup> )27Transition metal form large number of coordination complexesHigh charge by mass ratio, availability of vacant d-orbital & Variable oxidation state	1.5		-
17+2 O.S becomes more stable in first series transition elements moving from left to rightas number of unpaired electrons decreases.18Write oxoanions of first series transition metals in which group number and O.N. of transition metal are same-MnO <sub>4</sub> , Cr <sub>2</sub> O <sub>7</sub> <sup>2</sup> , VO <sub>3</sub> , CrO <sub>4</sub> <sup>2</sup> -19Moving from left to right E <sup>0</sup> for M <sup>2</sup> +/M becomes less negative but it shows irregular trendtrends due to irregular variation of IE <sub>1</sub> + IE <sub>2</sub> .20For copper E <sup>0</sup> Cu <sup>2</sup> +/Cu is +ve (+0.34 V)it is due to low hydration enthalpy of Cu <sup>2</sup> + which cannot compensate Δ <sub>sub</sub> H <sup>0</sup> + IE <sub>1</sub> + IE <sub>2</sub> .21For Mn, E <sup>0</sup> Mn <sup>3</sup> +/Mn <sup>2</sup> + is +vebecause by converting into Mn <sup>2</sup> * it achieves half filled configuration.22For Cr, E <sup>0</sup> Cr <sup>3</sup> +/Cr <sup>2</sup> + is -vebecause Cr <sup>3</sup> + is more stable due to half filled t <sub>2g</sub> configuration.23Most of the compounds of transition metal are coloured in solid state as well as in their solutionIt is <b>due to d-d transition</b> 24(Sc <sup>3</sup> +, Ti <sup>4</sup> +) does not exhibit any colourDue to absent of unpaired <b>e</b> as d-d transition is not possible25(Zn <sup>2</sup> +, Cu <sup>4</sup> ) does not exhibit any colourfull filled d-orbitals (d <sup>10</sup> ) as d-d transition is not possible26Transition metals or ions are paramagnetic in natureDue to presence of unpaired electrons (d <sup>1-9</sup> )27Transition metal form large number of coordination complexesHigh charge by mass ratio, availability of vacant d-orbital & Variable oxidation state	16	_	due to formation of $d\pi$ -p $\pi$ bond between metal and oxygen.
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in which group number and O.N. of transition metal are same-  19 Moving from left to right E <sup>0</sup> for M <sup>2+</sup> /M becomes less negative but it shows irregular trend  20 For copper E <sup>0</sup> Cu <sup>2+</sup> /Cu is +ve (+0.34 V) it is due to low hydration enthalpy of Cu <sup>2+</sup> which cannot compensate Δ <sub>sub</sub> H <sup>0</sup> + IE <sub>1</sub> + IE <sub>2</sub> .  21 For Mn , E <sup>0</sup> Mn <sup>3+</sup> /Mn <sup>2+</sup> is +ve because by converting into Mn <sup>2+</sup> it achieves half filled configuration.  22 For Cr , E <sup>0</sup> Cr <sup>3+</sup> /Cr <sup>2+</sup> is -ve because Cr <sup>3+</sup> is more stable due to half filled t <sub>2g</sub> configuration.  23 Most of the compounds of transition metal are coloured in solid state as well as in their solution  24 (Sc <sup>3+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour Due to absent of unpaired e as d-d transition is not possible  25 (Zn <sup>2+</sup> , Cu <sup>+</sup> ) does not exhibit any colour full filled d-orbitals (d <sup>10</sup> ) as d-d transition is not possible  26 Transition metals or ions are paramagnetic in nature  27 Transition metal form large number of coordination complexes  High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state	18		$MnO_{4}$ . $Cr_{2}O_{7}^{2}$ . $VO_{2}$ . $CrO_{4}^{2}$
metal are same-trends due to irregular variation of IE₁ + IE₂.19Moving from left to right E₀ for M²+/M becomes less negative but it shows irregular trendtrends due to irregular variation of IE₁ + IE₂.20For copper E₀ Cu²+/Cu is +ve (+0.34 V)it is due to low hydration enthalpy of Cu²+ which cannot compensate Δ <sub>sub</sub> H₀+ IE₁ + IE₂.21For Mn, E₀ Mn³+/Mn²+ is +vebecause by converting into Mn²+ it achieves half filled configuration.22For Cr, E₀ Cr³+/Cr²+ is -vebecause Cr³+ is more stable due to half filled t₂g configuration.23Most of the compounds of transition metal are coloured in solid state as well as in their solutionIt is <b>due to d-d transition</b> 24(Sc³+, Ti⁴+) does not exhibit any colourDue to absent of unpaired e⁻ as d-d transition is not possible25(Zn²+, Cu*) does not exhibit any colourfull filled d-orbitals (d¹₀) as d-d transition is not possible26Transition metals or ions are paramagnetic in natureDue to presence of unpaired electrons (d¹-9)27Transition metal form large number of coordination complexesHigh charge by mass ratio, availability of vacant d-orbital & Variable oxidation state			11104, 6120, , , 63, 61 64
Less negative but it shows irregular trendit is due to low hydration enthalpy of Cu²+ which cannot compensate Δ <sub>sub</sub> H₀+ IE₁ + IE₂.20 For Copper E₀ Cu²+/Cu is +ve (+0.34 V)it is due to low hydration enthalpy of Cu²+ which cannot compensate Δ <sub>sub</sub> H₀+ IE₁ + IE₂.21 For Mn, E₀ Mn³+/Mn²+ is +vebecause by converting into Mn²+ it achieves half filled configuration.22 For Cr, E₀ Cr³+/Cr²+ is -vebecause Cr³+ is more stable due to half filled t₂g configuration.23 Most of the compounds of transition metal are coloured in solid state as well as in their solutionIt is <b>due to d-d transition</b> 24 (Sc³+, Ti⁴+) does not exhibit any colourDue to absent of unpaired e⁻ as d-d transition is not possible25 (Zn²+, Cu⁺) does not exhibit any colourfull filled d-orbitals (d¹₀) as d-d transition is not possible26 Transition metals or ions are paramagnetic in natureDue to presence of unpaired electrons (d¹-๑)27 Transition metal form large number of coordination complexesHigh charge by mass ratio, availability of vacant d-orbital & Variable oxidation state			
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compensate Δ <sub>sub</sub> H <sup>0</sup> + IE <sub>1</sub> + IE <sub>2</sub> .  21 For Mn , E <sup>0</sup> Mn <sup>3+</sup> /Mn <sup>2+</sup> is +ve because by converting into Mn <sup>2+</sup> it achieves half filled configuration.  22 For Cr , E <sup>0</sup> Cr <sup>3+</sup> /Cr <sup>2+</sup> is -ve because Cr <sup>3+</sup> is more stable due to half filled t <sub>2g</sub> configuration.  23 Most of the compounds of transition metal are coloured in solid state as well as in their solution  24 (Sc <sup>3+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour Due to absent of unpaired e <sup>-</sup> as d-d transition is not possible  25 (Zn <sup>2+</sup> , Cu <sup>+</sup> ) does not exhibit any colour full filled d-orbitals (d <sup>10</sup> ) as d-d transition is not possible  26 Transition metals or ions are paramagnetic in nature  27 Transition metal form large number of coordination complexes  4 High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state		less negative but it shows irregular trend	
For Mn, E <sup>0</sup> Mn <sup>3+</sup> /Mn <sup>2+</sup> is +ve  because by converting into Mn <sup>2+</sup> it achieves half filled configuration.  For Cr, E <sup>0</sup> Cr <sup>3+</sup> /Cr <sup>2+</sup> is -ve  because Cr <sup>3+</sup> is more stable due to half filled t <sub>2g</sub> configuration.  It is <b>due to d-d transition</b> It is <b>due to d-d transition</b> Cloured in solid state as well as in their solution  Cloured in solid state as well as in their solution  Due to absent of unpaired <b>e</b> <sup>-</sup> as d-d transition is not possible  Cloured in solid state as well as in their solution  Transition metals or ions are paramagnetic in nature  Transition metal form large number of coordination complexes  Due to presence of unpaired electrons (d <sup>1-9</sup> )  High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state	20	For copper $E^0$ Cu <sup>2+</sup> /Cu is +ve (+0.34 V)	
configuration.  22 For Cr , E <sup>0</sup> Cr <sup>3+</sup> /Cr <sup>2+</sup> is –ve because Cr <sup>3+</sup> is more stable due to half filled t <sub>2g</sub> configuration.  23 Most of the compounds of transition metal are coloured in solid state as well as in their solution  24 (Sc <sup>3+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour Due to absent of unpaired e <sup>-</sup> as d-d transition is not possible  25 (Zn <sup>2+</sup> , Cu <sup>+</sup> ) does not exhibit any colour full filled d-orbitals (d <sup>10</sup> ) as d-d transition is not possible  26 Transition metals or ions are paramagnetic in nature  27 Transition metal form large number of coordination complexes  4 Variable oxidation state			<del>-</del>
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Most of the compounds of transition metal are coloured in solid state as well as in their solution  24 (Sc³+, Ti⁴+) does not exhibit any colour  25 (Zn²+, Cu⁺) does not exhibit any colour  26 Transition metals or ions are paramagnetic in nature  27 Transition metal form large number of coordination complexes  Due to absent of unpaired e as d-d transition is not possible  full filled d-orbitals (d¹0) as d-d transition is not possible  Due to presence of unpaired electrons (d¹-9)  High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state	20	F C F0 C 2: /C 2: 1	
coloured in solid state as well as in their solution  24 (Sc3+, Ti4+) does not exhibit any colour  25 (Zn2+, Cu+) does not exhibit any colour  26 Transition metals or ions are paramagnetic in nature  27 Transition metal form large number of coordination complexes  Due to absent of unpaired e- as d-d transition is not possible  full filled d-orbitals (d¹0) as d-d transition is not possible  Due to presence of unpaired electrons (d¹-9)  High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state		•	
24 (Sc <sup>3+</sup> , Ti <sup>4+</sup> ) does not exhibit any colour  Due to absent of unpaired <b>e</b> <sup>-</sup> as d-d transition is not possible  (Zn <sup>2+</sup> , Cu <sup>+</sup> ) does not exhibit any colour  full filled d-orbitals (d <sup>10</sup> ) as d-d transition is not possible  Transition metals or ions are paramagnetic in nature  Due to presence of unpaired electrons (d <sup>1-9</sup> )  High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state	23	-	it is que to a-a transition
25 (Zn²+, Cu+) does not exhibit any colour full filled d-orbitals (d¹0) as d-d transition is not possible  26 Transition metals or ions are paramagnetic in nature  27 Transition metal form large number of coordination complexes  4 Variable oxidation state	24		Due to abcent of unnaired a: as d d transition is not nessible
Transition metals or ions are paramagnetic in nature  Due to presence of unpaired electrons (d¹-9)  High charge by mass ratio, availability of vacant d-orbital & Variable oxidation state			
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Transition metal form large number of coordination complexes of Variable oxidation state			2 de la presence or anpanea electrons (a )
coordination complexes Variable oxidation state	27		High charge by mass ratio, availability of vacant d-orbital &
		0	
28 What are Interstitial compounds? Compounds in which small elements like H, B, C, N trapped in	28	7	Compounds in which small elements like H, B, C, N trapped in
the interstitial space of metal lattice.			the interstitial space of metal lattice.
29 Transition metals form Interstitial compounds. due to availability of interstitial space in metal lattice.	29	Transition metals form Interstitial compounds.	due to availability of interstitial space in metal lattice.

30 Why interstitial compounds are found to be more	These compounds have high M.P as compared to pure metals.
useful than pure metal?	These are very hard and are Chemically inert.
31 Transition metals and their compounds are	Due to large surface area, variable oxidation state & Availability
widely used as catalyst	of vacant d-orbitals
32 transition metals form alloy.	Due to comparable metallic radii
33 Why oxides of Higher oxidation states of	Higher oxidation states are more polarizing in nature . hence
transition metals are acidic in nature whereas	are acidic in nature whereas lower O.S. are less polarizing
lower O.S. are basic in nature?	hence are basic in nature.
34 Actinoids shows greater number of oxidation	Due to comparable energy of 5f, 6d, and 7s orbitals.
states then lanthanoids	
35 It is difficult to study chemistry of actinoids.	Due to radio active nature and small half life
36 Ce(IV) is a good oxidizing agent in aq. sol <sup>n</sup>	because in aq. solution its $E_{Ce^{4+}/Ce^{3+}}$ is +1.74 V
37 Actinoid contraction is greater from element to	because of poor shielding by 5f orbitals due to its superficial
element as compared to lanthanoids.	position.
Potassium Dichromate [K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ]	Potassium Permanganate [KMnO <sub>4</sub> ]
Preparation:	Preparation: from pyrolucite ore [MnO <sub>2</sub> ]
It is prepared from chromite ore: FeCr <sub>2</sub> O <sub>4</sub> / FeO Cr <sub>2</sub> O <sub>3</sub>	<u>Step 1</u> :
<u>Step 1</u> :	$2MnO_2$ (Black)+ $4KOH+O_2 \longrightarrow 2K_2MnO_4$ (Green)+ $2H_2O$
$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$	<u>Step 2</u> :
Step 2: $2Na_2CrO_4$ (Yellow)+ $H_2SO_4$ $\longrightarrow$	$3MnO_4^{2-}$ (Green)+ $4H^+ \rightarrow 2MnO_4^-$ (Purple)+ $MnO_2$ + $2H_2O$
$Na_2Cr_2O_7(Orange) + Na_2SO_4 + H_2O$	Oxidizing Character: (Oxidation in acidic medium)
Step 3: $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
Orange Orange	Eq. mass of $KMnO_4 = 158/5 = 31.6$
Effect of pH:	$MnO_4$ :+5Fe <sup>2+</sup> +8H+ $\longrightarrow$ $Mn^{2+}$ +5Fe <sup>3+</sup> + 4H <sub>2</sub> O
$Cr_2O_7^{2-}$ (Orange) + 20H <sup>-</sup> $\longrightarrow$ 2CrO <sub>4</sub> <sup>2-</sup> (Yellow) + H <sub>2</sub> O	$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$
$2CrO_4^{2-}$ (Yellow) + $2H^+ \longrightarrow Cr_2O_7^{2-}$ (Orange) + $H_2O$	$2MnO_{4}^{-} + 5C_{2}O_{4}^{2} + 16H^{+} \longrightarrow 2Mn^{2} + 10CO_{2} + 8H_{2}O$
Oxidizing Character: Dichromate ion acts as strong	$2MnO_{4}^{-}+5SO_{3}^{2-}+6H^{+} \longrightarrow 2Mn^{2+}+5SO_{4}^{2-}+3H_{2}O$
oxidizing agent in acidic medium.	$2MnO_4$ + $5NO_2$ + $6H^+ \longrightarrow 2Mn^{2+} + 5NO_3$ + $3H_2O$
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	$2MnO_{4} + 5S^{2} + 16H^{+} \longrightarrow 2Mn^{2+} + 5S + 8H_{2}O$
$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$	$2MnO_{4} + 3H_{2}O + I - \longrightarrow 2MnO_{2} + IO_{3} + 2OH$
$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} 7H_2O + 6Fe^{3+}$	$8MnO_{4}^{-} + 3S_{2}O_{3}^{2-} + H_{2}O \longrightarrow 8MnO_{2} + 6SO_{4}^{2-} + 2OH^{-}$
$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} 7H_2O + 3Sn^{4+}$	$2MnO_{4^{-}} + 3 Mn^{2+} + 2 H_{2}O \longrightarrow 5MnO_{2} + 4H^{+}$
$Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$	
<u>f-Block Elements</u>	Consequences: 1. Resemblance in the properties of second and
General configuration $(n-2)$ f <sup>1-14</sup> $(n-1)$ d <sup>0-1</sup> ns <sup>2</sup>	third transition series from Zr & Hf) atomic size of 2 <sup>nd</sup> and 3 <sup>rd</sup>
$    _{57}$ La [Xe] $5d^1 6s^2$ $  _{89}$ Ac [Rn] $6d^1 7s^2$ -	transition series become same.
$   _{58}$ Ce [Xe] $4f^1 5d^1 6s^2  _{91}$ Pa [Rn] $5f^2 6d^1 7s^2  _{91}$	2. Similarity in the properties of Lanthanoids:- The decrease in
$     _{63}$ Eu [Xe] $4f^7 5d^0 6s^2  _{92}$ U [Rn] $5f^3 6d^1 7s^2$	atomic radii from Lanthenoid to Lanthenoid is very less hence
$    _{64}Gd  [Xe] 4f^7 5d^1 6s^2   _{94}Pu  [Rn] 5f^6 6d^0 7s^2  $	it is very difficult to separate these elements in pure state.
	3. Basic strength of hydroxides of Lanthanoids decreases from
<b>Lanthanoid Contraction</b> - Regular decrease in atomic	Lanthenium (La) to Lutesium (Lu).
or ionic radii of Lanthenoid with increase in atomic	Misch Metal – It is alloy of Lanthanoids(95%) with iron
number is called Lanthenoid contraction.	(5%)and Trace of S, C, Al ,Ca Lanthenoid – 95% Metal + Trace
<u>Cause</u> : It is due to imperfect shielding of one 4f orbital	of S, C, Al, Ca + Iron – 5%
by another 4f orbital due to which ENC regularly	<b>Uses-</b> making bullet shells and flinter of lighters.
increases with increase in atomic number.	
Lanthanoids	Actinoids
Last electron enters in 4f orbital	Last electron enters in 5f orbital
Are natural elements and non radioactive in nature	Are radioactive in nature and after Np they are synthetic
	elements
Shows less number of oxidation states [+2,+3,+4]	Shows greater number of oxidation states [+3,+4,+5,+6,+7]
Element to element lanthanoid contraction is less	Element to element actinoid contraction is more

#### **Coordination Compounds**

**<u>Ligand</u>**: Provide pair of electron for formation of coordinate bond to central metal atom is called ligand. (Lewis Base)

Types of ligands:-

- (a) Monodentate :- One donar atom
- (b) Bidentate :- Two donar atom
- (c) Ambidentate:- Two donar atom but at a time form only one bond Eg: SCN- and NCS-

F--Fluorido, Cl--Chlorido, Br--Bromido

I- - Iodido, H- -Hydrido, OH- - Hydroxido

CN--Cyanido, SCN-- Thiocyanato

NCS- - Isothiocyanato, CH<sub>3</sub>COO- -Acetato

 $SO_4^{2-}$  - Sulphato,  $CO_3^{2-}$  - Carbonato

 $(COO^{-})_2$  or  $C_2O_4^{2-}$  - Oxalato (ox),  $NO_3^{-}$  - Nitrato

 $NO_2$  - Nitrito(N),  $PO_4$ <sup>3</sup> - Phosphato

Neutral ligands- H<sub>2</sub>O- Aqua, NH<sub>3</sub> - Ammine

R NH<sub>2</sub> -Alkanamine, CO -Carbonyl,

H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> - ethane-1,2-diamine

Ethylenediaminetetraacetate ion (EDTA4-)

Ligand which has two different donor atoms and either of the two ligetes in the complex is called **ambidentate ligand**. Examples NO<sub>2</sub> - and SCN-

<u>Coordination Number:</u> Number of coordinate bonds formed by ligands with central metal atom in the complex is called coordination number of complex.

#### 5) Homoleptic and Hetroleptic Complexes:

A complex with same type of ligands surrounding central metal atom is called homoleptic complex. E.g.- $[Cu(NH_3)_4]^{2+}$ ,  $[Pt(NH_3)_4]^{2+}$ 

A complex with different types of ligands surrounding central metal atom is called hetroleptic complex. E.g.  $[Pt(NH_3)_2 Cl_2]$ 

**6. Coordination Polyhedron:** Spatial arrangement of ligands around central metal atom or ion is called coordination polyhedron.

#### **Writing Formula of Coordination Complex:**

- 1. Cation is written first followed by anion.
- 2. In coordination sphere central metal atom is written first followed by ligands.
- 3. If more than one type of ligands are present then alphabet is followed.  $Na_2[Fe(H_2O)_4 (NO) Br]$

#### Nomenclature of Coordination Compounds:

(1)  $Na_2$  [Fe (H<sub>2</sub>O) Br<sub>4</sub> (NO)]

Sodium tetrabromidonitrosylferrate (II)

(2) [Fe  $(H_2O)_4$  Br (NO)]  $SO_4$ 

Tetraquabromidonitrosyliron (III) sulphate

- (3)  $K_4$  [Fe (CN)<sub>6</sub>]
  - Potassium hexacyanoferrate (II)
- (4)  $[Cr (NH_3)_3 (H_2O)_3] Cl_3$

Triamminetriaquachromium (III) Chloride

- (5) [Pt (NH<sub>3</sub>)<sub>2</sub> Cl (NO<sub>2</sub>)] Diamminechloridonitritoplatinum (II)
- (6) [Ni (CO)<sub>4</sub>] Tetracarbonyl Nickel (O)
- (7)  $CO (NH_3)_5 CO_3 Cl$

Pentamminecarbonato cobalt (III) chloride

(8)  $K_3 [Cr (C_2O_4)_3]$ 

Potassium trioxalate chromate (III)

(9)  $Hg [Co (SCN)_4]$ 

Mercury tetrathiocyanato cobaltate (III)

#### **Isomerism in Coordination Compounds**

- (a) Structural isomerism
- (i) Linkage isomerism- ambidentate ligand. M–SCN, M–NCS & (–NO<sub>2</sub> ), (–ONO)
- (ii) Coordination isomerism-Both complex  $[Co(NH_3)_6][Cr(CN)_6] \& [Cr(NH_3)_6][Co(CN)_6]$
- (iii) Ionisation isomerism-

 $[Co(NH_3)_5(SO_4)]Br \& [Co(NH_3)_5Br]SO_4.$ 

(iv) Solvate isomerism- exchange of  $H_2O$  as ligand and counter anion  $[Cr(H_2O)_6]Cl_3\&[Cr(H_2O)_5Cl]Cl_2.H_2O$ 

- (b) Stereoisomerism
- (i) Geometrical isomerism-

Square planner complexes with formula  $MA_2B_2$ - two geometrical isomers, MABCD- Three isomers

Octahedral complexes-  $MA_4B_2$ ,  $M(aa)_2\,A_2$  – Cis & trans

MA<sub>3</sub>B<sub>3</sub>- Fac & mer isomers

**(ii) Optical isomerism-** Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers.

 $[PtCl_2 (en)_2]^{2+}$ 

#### **Bonding in coordination compounds-**

#### (I) Werner's Coordination Theory-

Primary valence is ionizable and refers charge present on complex ion.

Secondary valence is non-ionizable and refers coordination number of complex.

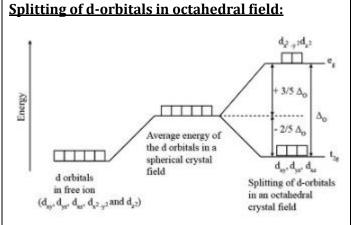
The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

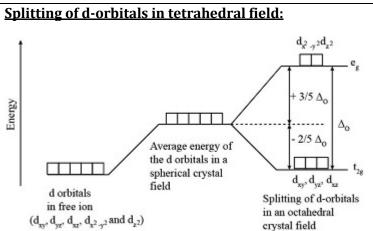
#### 2) Valence Bond Theory or VBT

Complex	Oxidation	Hybridi	Geometry	Magnetic nature	unpaired	Outer sphere /
	state of CMA	-zation			electrons	Inner sphere
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	+3	d <sup>2</sup> sp <sup>3</sup>	Octahedral	Diamagnetic	0	Inner sphere

[CoF <sub>6</sub> ] <sup>3-</sup>	+3	sp³ d²	Octahedral	Paramagnetic	0	Outer sphere
$[Co(C_2O_4)_3]^{3-}$	+3	d <sup>2</sup> sp <sup>3</sup>	Octahedral	Diamagnetic	0	Inner sphere
[Mn(CN) <sub>6</sub> ] <sup>4-</sup>	+2	d <sup>2</sup> sp <sup>3</sup>	Octahedral	Paramagnetic	1	Inner sphere
[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	+3	d <sup>2</sup> sp <sup>3</sup>	Octahedral	Paramagnetic	1	Inner sphere
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	+3	sp³ d²	Octahedral	Paramagnetic	5	Outer sphere
[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	+2	sp³ d²	Octahedral	Paramagnetic	2	Outer sphere
[NiCl <sub>4</sub> ] <sup>2-</sup>	+2	sp <sup>3</sup>	Tetrahedral	Paramagnetic	2	
[Ni(CO) <sub>4</sub> ]	0	sp <sup>3</sup>	Tetrahedral	Diamagnetic	0	
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	+2	dsp <sup>2</sup>	Square planner	Diamagnetic	0	

#### 3) Crystal Field Theory [CFT]

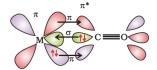




**Metal Carbonyls:** Homoleptic complex of transition metal with carbonyl ligand are called metal carbonyls. E.g.  $[Ni(CO)_4]$ ,  $[Fe(CO)_5]$ ,  $[Cr(CO)_6]$ ,  $[CO_2(CO)_8]$ ,  $[CO_3(CO)_{12}]$ ,  $[Mn_2(CO)_{10}]$ 

The metal-carbon bond in metal carbonyls possess both  $\sigma$  and  $\pi$  character. The M–C  $\sigma$  bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C  $\pi$  bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding  $\pi^*$  orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

dπ-pπ Back Bond



#### **Application of Coordination Complexes:**

a) Biological System: Chlorophyll – complex of Mg Haemoglobin – complex of Fe, Vit. B-12 – complex of Co b) Metallurgy:

Extraction of Au, Ag, by cyanide process.

Refining of Ni by Mond's process

Refining of Zr by Van Arkel process.

- c) Quantitative Analysis: Estimation of hardness of water Ca<sup>2+</sup> and Mg<sup>2+</sup> are estimated by complexomatric titration using EDTA.
- d) Qualitative Analysis: Cu<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, NO-<sub>3</sub>, etc ions are confirmed by reactions involving complex formation.
- e) Industrial Catalyst: [(Ph<sub>3</sub>P)<sub>3</sub>RhCl], a Wilkinson catalyst, is used for the hydrogenation of alkenes
- f) Black & White Photography:

In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion,  $[Ag(S_2O_3)_2]^{3-}$ 

g) As medicines: Cisplatin [Cancer Treatment], EDTA [Used to remove heavy metal poison using chelate therapy.

# NAME REACTION HALOALKANES AND HALOARENES

A. <u>HALOALK</u>	ANES AND HALOARENES
<u>Wurtz reaction</u> : Alkyl halides react with sodium in dry ether to give hydrocarbons(Alkanes) containing double the number of carbon atoms present in the halide.	$2R - X + 2Na \xrightarrow{Dry ether} \rightarrow R - R + 2NaX$ $2CH_3 - Br + 2Na \xrightarrow{Dryether} CH_3 - CH_3 + 2Na Br$
Fittig reaction: Aryl halides(Haloarenes) when treated	$2Ar - X + 2Na^{Drydner} \rightarrow Ar - Ar + 2NaX$
with sodium in dry ether gives in which two aryl groups	<u>-</u>
are joined together.	2 X + Na Ether + 2NaX
Wurtz-Fittig reaction : A mixture of an alkyl halide	$Ar - X + Na + R - X \xrightarrow{Drycher} Ar - R + 2NaX$
(Haloalkanes) and aryl halide(Haloarenes.) gives	X Ribert R
alkylarene when treated with sodium in dry ether.	+ Na + RX Ether + NaX
Finkelstein reaction: Alkyl chlorides/ bromides reacts	$R - CI + NaI \xrightarrow{a cetone} R - I + NaCI$
with NaI in dry acetone to give Alkyl iodides.	$R - Br + Nal \xrightarrow{acetone} R - I + NaBr$
Swarts reaction Heating of alkyl chloride/bromide in the	$R-X$ $AgF,Hg,F_2,CoF_2orSbF_3 \rightarrow R-F$
presence of a metallic fluoride such as AgF,Hg <sub>2</sub> F <sub>2</sub> , CoF <sub>2</sub> or	$CH_3 -Br + AgF \longrightarrow CH_3 -F + AgBr$
SbF <sub>3</sub> to give alkyl fluorides	c.13 51 17 g. 7 c.13 1 17 gs.
12. ALCOHOLS,P	HENOLS AND ETHERS
<b>Hydroboration –oxidation reaction</b> : The alcohol obtained through anti- Markownikov 's addition of $H_2O$	$CH_3\text{-CH=CH}_2(\underline{i})\underline{B_2}\underline{H_6}(\underline{i}\underline{i})\underline{H2O2}/\underline{O}\underline{H^-} \longrightarrow CH_3\text{-CH}_2\text{-}CH_2\text{-}OH$
Reimer-Tiemann reaction-	он он
Phenol reacts with chloroform and NaOH to give	CHCl <sub>3</sub> + aq NaOH
salicylaldehyde	Salicylaldehyde
Kolbe's reaction:-	OH ONa OH
Phenol reacts with NaOH followed by CO <sub>2</sub> in acidic	NaOH (1) CO,
mediumto give salicylaldehyde	(Salicylic acid)
Williamson's synthesis: In this method an primary	CH₃Cl + CH₃ ONa → CH₃OCH₃ + NaCl
alkyl halide reacts with a sodium alkoxide to form	$R-X + R'-\ddot{Q} Na \longrightarrow R-\ddot{Q}-R' + Na X$
symmetrical or unsymmetrical ethers.	" "
12. ALDEHYDES, KETO	NES AND CARBOXYLIC ACID
Aldol Condensation : Aldehydes and ketones having at least one $\alpha$ – hydrogen undergo a condensation reaction in the presence of dilute alkali (NaOH ,KOH etc.) as catalyst to form $\beta$ - hydroxyaldehyde (aldol) or $\beta$ – hydroxyketone (ketol) respectively	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
Cross Aldol Condensation: When aldol condensation is ca	arried out between two different aldehydesand / or ketones, it
is called <b>cross aldol condensation</b> . If both of them contain	n $\alpha$ -hydrogen atoms, it gives a mixture of four products.
CH <sub>3</sub> CHO  1. NaOH  CH <sub>3</sub> -CH=CH-CHO	CH <sub>3</sub> CH <sub>2</sub> -CH=CHCHO
CH <sub>3</sub> -CH <sub>2</sub> CHO CH <sub>3</sub> -CH=C-CHO	CH <sub>3</sub> CH <sub>2</sub> -CH=C-CHO
CH,	CH <sub>3</sub>
Cannizzaro Reaction: Aldehydes, which do not have an $\alpha$ -hydrogen atom, undergo self oxidation and reduction reaction on treatment with concentrated alkali.In this reaction one molecule of the aldehydeis reduced to alcohol and another is oxidized to carboxylic acid salt.	H C=O + H C=O + Conc. KOH  H C=O + Conc. KOH  H CON H CON Methanol Potassium formate  CH2OH + CONC. NaOH  Benzaldehyde  Benzyl alcohol Sodium benzoate
Clemmensen Reaction: The carbonyl group of	CH <sub>3</sub> CHO $Z_n$ –Hg, Conc. HCl $\rightarrow$ CH <sub>3</sub> CH <sub>3</sub>
aldehydes and Ketones are reduced to CH₂ group on	7 II II Cl
treatment with zinc amalgam(Zn/Hg) and concentrated	$CH_3CO CH_3 \xrightarrow{Z n - H g, H Ct} \rightarrow CH_3CH_2CH_3$

hydrochloric acid.(Conc.HCl)

Wolf Kishner Reaction:- reaction used to convert carbonyl group (-CO-) into methylene groups through reaction with hydrazine and KOH- ethylene glycol	$CH_3 - C = O + NH_2NH_2 \frac{KOH_3}{Glycol} CH_3 - CH_3 + N_2 + H_2O$			
Rosenmund Reaction: Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on BaSO <sub>4</sub>	$\begin{array}{c} O \\ II \\ CI \\ \hline Pd - BaSO_4 \end{array} \longrightarrow \begin{array}{c} CHO \\ \\ Benzoyl \ chloride \end{array}$			
Etard Reaction- oxidation of toluene with chromyl chloride (CrO <sub>2</sub> Cl <sub>2</sub> ) in CCl <sub>4</sub> to give aromatic aldehyde	$CH_3 + CrO_3Cl_3 \xrightarrow{CS_3} CH(OCrOHCl_3)_3 \xrightarrow{H_9O'} CHO$ Toluene Chromium complex Benzaldehyde			
Stephen Reaction: Alkyl nitriles on reduction with SnCl <sub>2</sub> and Conc. HCl, give corresponding aldehydes.	$RCN \xrightarrow{SnCl_3 + HCl} RCHO$			
Gatterman-Koch reaction: benzene is treated with carbon monoxide in the acidic medium in presence of anhydrous aluminium chloride to give benzaldehyde	CO, HCl Anhyd. AlCl <sub>s</sub> /CuCl Benzene Benzaldehyde			
<b>Ozonolysis</b> of alkenes involves the addition of ozone molecule to alkene to form ozonide, and thencleavage of the ozonide by Zn-H <sub>2</sub> O to Aldehyde and/or Ketones.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$			
<b>Decarboxylation</b> : Sodium salts of acids when heated with soda lime, alkanes are formed.	$R$ —COONa + NaOH $\xrightarrow{\text{CaO}}$ $\xrightarrow{\text{CaO}}$ $\xrightarrow{\text{Alkane}}$ $R$ —H + Na <sub>2</sub> CO <sub>3</sub>			
Hell Volhard Zelinsky: (HVZ) Carboxylic acids having an $\alpha$ -hydrogen are halogenated at the $\alpha$ -position on treatment with halogenin the presence of small amount of red phosphorus to give $\alpha$ - halocarboxylic acids	$RCH_{2}\text{-COOH} \xrightarrow{\text{i } X_{2}/\text{ Red phosphorus}} R-CH-COOH$ $X = C1 ,Br \qquad \qquad R-CH-COOH$ $X = C1 ,Br \qquad \qquad X = \alpha - \text{halocarboxylic acids}$			
	AMINES			
Hoffmann bromamide degradation reaction: primary amides are treated with bromine in thepresence of an alkali, a primary amine containing one carbon less than the amide is formed.	RCONH <sub>2</sub> + 4NaOH + Br <sub>2</sub> $\rightarrow$ RNH <sub>2</sub> + 2 NaBr + Na <sub>2</sub> CO <sub>3</sub> + 2H <sub>2</sub> O CH <sub>3</sub> -CO-NH <sub>2</sub> + Br <sub>2</sub> + 4 KOH $\rightarrow$ CH <sub>3</sub> NH <sub>2</sub> + K <sub>2</sub> CO <sub>3</sub> + 2KBr + 2H <sub>2</sub> O			
Gabriel phthalimide synthesis: Phthalimide on treatment with KOH which on heating with alkyl halidefollowed by alkaline hydrolysis produces the corresponding primary amine.				
$ \begin{array}{c c}  & O \\  & C \\  & C \\  & O \\$	N - R NaOH(aq) C ONa <sup>+</sup> + R - NH <sub>2</sub> (1°amine)			
Carbylamine reaction(Isocyanide test): Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> + CHCl <sub>3</sub> + 3KOH $\longrightarrow$ CH <sub>3</sub> CH <sub>2</sub> NC + 3KCl + 3H <sub>2</sub> O  Ethyl Amine alcoholic Ethyl isocyanide  Isocyanides or carbylamines which are foul smelling			
Diazotization reaction- Aromatic amine reacts with nitrous acid and Conc HCI to form diazonium salt	$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2Cl + NaCl + 2H_2O$			
Sandmeyers reaction: The Cl–, Br– and CN– nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion [CuCl]	$ArN_{2}^{+}X \xrightarrow{CuCl/HCl} ArCl + N_{2}$ $CuBr/HBr \rightarrow ArBr + N_{2}$ $CuCN /KCN \rightarrow ArCN + N_{2}$			
<b>Gatterman reaction:</b> The Cl–, Br– and CN– nucleophiles can easily be introduced in the benzene ring in the presence of copper powder	$ \begin{array}{c} \stackrel{+}{\text{ArN}_2X} \xrightarrow{\text{Cu/HCl}} \text{ArCl} + \text{N}_2 + \text{CuX} \\ \stackrel{+}{\text{Cu/HBr}} \text{ArBr} + \text{N}_2 + \text{CuX} \end{array} $			
Coupling reaction:	$H \rightarrow N = N - OH + CI + H_2O$			
	p-Hydroxyazobenzene (orange dye)			

## **DISTINGUISH TEST**

		וועסטוטוו ובטו	
S.No	Test	Reagent	Inference
1.	<b>Lucas test</b> : To distinguishbetween Primary (1 <sup>0</sup> ), Secondary (2 <sup>0</sup> ), & Tertiary (3 <sup>0</sup> ) Alcohols)	ZnCl <sub>2</sub> /HCl	$(3^0)$ Alcohols gives Turbidity (immediately), $2^0$ Turbidity after some time (5-10 min) $1^0$ does not give Turbidity at room temp.
2.	Iodoform test (Alcohols containing CH3-CH(OH)-linkage) and CH3CO- in Ald/Ketone	I <sub>2</sub> / NaOH	Yellow Ppt of CHI <sub>3</sub> is formed
3.	Neutral ferric chloridetest (Phenol)	Neutral FeCl <sub>3</sub>	Phenols give Violet colouration
4.	Tollens test [Aliphatic Aldehydes(e.g.Ethanal,Pro panal etc) & Aromatic Aldehydes (Benzaldehyde)	Ammonical AgNO <sub>3</sub>	Bright silver mirror [Ag] is produced due to the formation of silver metal. (HCOOH is gives this test)
5.	Fehling's test [OnlyAliphatic Aldehydes]  **Aromatic aldehyde do not give this test	Fehling solution A (aqueous CuSO <sub>4</sub> & Fehlingsolution B alkalinesodium potassium tartarate)	Reddish brown precipitate of [Cu2O] is obtained. (alkalinesodium potassium tartarate is also known as Rochelle salt)
6.	<b>Sodium bicarbonate test</b> (Aliphatic & AromaticCarboxylic acids)	NaHCO3 Sodium Hydrogencarbonate	Effervescence due to evolution of CO2 gas.
7.	Isocyanide test Primary Aliphatic & Aromatic amines.	Chloroform(CHCl₃) + Alcoholic KOH	Unpleasent odur (foul smelling) of isocyanides or carbylamines.
8.	Heinsberg test(To distinguish between (1°), (2°), & (3°) Amines.	Benzenesulphonyl chloride C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> Cl	Product of 1° Amines soluble in alkali. Product of 2° Amines are insoluble in alkali 3° amines do not react.
9.	Azo dye test(Aniline)	(NaNO <sub>2</sub> + HCl) [Nitrous acid] followed by β -napthol	Reaction with $NaNO_2$ + HCl at 273-278 K gives BDC which forms a brilliant orange Azo dye with $\beta$ -napthol in sodium hydroxide

### **REASONING TYPE OF QUESTIONS**

	10. HALOALKANES AND HALOARENES				
	QUESTION- <b>REASON</b> ING	ANSWER- <b>REASON</b>			
1	Benzyl chloride is highly reactive towards the SN1	Due to the stability of benzyl carbocation due to			
	reaction.	resonance			
2	2-bromobutane is optically active but 1-	Because 2-Bromobutane has a chiral centre so mirror			
	bromobutane is optically inactive	image are nonsuperimposable			
3	Electrophilic substitution reactions in haloarenes	Due to – I effect of halogen predominant over +R			
	occur slowly.	effect			
4	Which would undergo SN <sub>1</sub> reaction faster	because 3° carbocation is more stable than			
	CH <sub>3</sub>	1°carbocation			
	CH <sub>3</sub> - CH <sub>2</sub> - Br and CH <sub>3</sub> - C - CH <sub>8</sub>				
5	Why haloarenes are less reactive than haloalkanes	In haloarenes C—X bond acquires a partial double			
	towards nucleophilic substitution reactions	bond character due to resonance			
6	Which compound in each of the following pairs will	(i) iodine is a better leaving group because of its larger			
	react faster in SN₂ reaction? Why?	size. (ii) three bulky methyl group hinder the			
	(i) CH <sub>3</sub> Br or CH <sub>3</sub> I (ii) (CH <sub>3</sub> ) <sub>3</sub> C-Cl or CH <sub>3</sub> -Cl	approaching nucleophile			
7	Which one of the following reacts faster in an SN1	Compound (I) reacts faster in SN <sub>1</sub> reaction as it is a 2°			
	reaction and why? Or Or CI	alkyl halide			
8	A solution of KOH hydrolyses CH <sub>3</sub> CH(CI)CH <sub>2</sub> CH <sub>3</sub> and	CH <sub>3</sub> CH <sub>2</sub> C/CHCH <sub>3</sub> more easily hydrolysed as it forms 2 <sup>0</sup>			
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CI. Which one of these is more easily	carbocation which is more stable than 10 carbocation			
	hydrolysed and why?				
9	State one use each of DDT and iodoform	DDT: It is used as insecticide lodoform: lodoform is			
		used as an antiseptic.			
10	What is known as a racemic mixture? Give an	An equi-molar mixture of d- and I- isomers(50:50 d+I)			
	example.	For example, butan-2-ol. A racemic mixture is optically			
		inactive due to external compensation			

11	Although chlorine is an electron withdrawing	Through resonance effect, chlorine tends to stabilize
	group, yet it is ortho-, para-directing in	the carbocation and the effect is onlyapplicable at
	electrophilic aromatic substitution reactions.	ortho and para-positions.
	Explain why it is so?	
12	Grignard's reagents should be prepared under	This is because Grignard reagent forms alkanes by
	anhydrous conditions, why?	reacting with moisture.
13	the dipole moment of Chlorobenzene is lower than	due to resonance ,Chlorobenzene shorter C—Cl
	that of Cyclohexyl chloride	bond(sp²)than cyclohexyl chloride C—Cl bond(sp³)
14	Chloroform is stored in closed dark brown bottles	chloroform is slowly oxidised by air in the presence of
		light to form poisonous gas phosgene.COCl <sub>2</sub>

11. ALCOHOL, PHENOL AND ETHER

1	p-nitro phenol is more acidic than p-methyl phenol	Due to -I/-R effect of -NO <sub>2</sub> group & +I /+R effect of CH3
2	p-nitrophenol is more acidic than o-nitrophenol <b>OR</b>	p-nitro phenol has intermolecular H-bond while o-nitro
	O-nitrophenol is steam volatile ,not p-nitrophenol	phenol has intramolecular H-bond.
3	Phenol is more acidic than ethanol.	phenoxide ion stabilised by resonance)
4	Boiling point of ethanol is higher in comparison to	Because of hydrogen bonding in ethanol
	methoxymethane.	
5	The C – O – H bond angle in alcohols is slightly less	Due to lone pair- lone pair repulsion on oxygen
	than the tetrahedral angle (109°28').	
6	Although phenoxide ion has more number of	carboxylate ion stabilized through equivalent resonance
	resonating structures than carboxylate ion,	whereas phenoxide ion through non equivalent
	carboxylic acid is a stronger acid than phenol.	resonance

#### 12. ALDEHYDES KETONES AND CARBOXYLIC ACIDS

1	Increasing order reactivity towards nucleophilic	$C_6H_5 CO C_6H_5 < CH_3COCH_3 < CH_3CHO$
	addition <b>OR</b> (reactivity towards HCN)	Butanone < Propanol < Ethanal
	C <sub>6</sub> H <sub>5</sub> CHO < CH <sub>3</sub> CHO < HCHO	Methyl tert-butyl ketone < Acetone < Acetaldehyde
2	Acidic Character =(1/ pKa)	CI - CH <sub>2</sub> - COOH < CI <sub>2</sub> CH - COOH < CCI <sub>3</sub> - COOH
	(CH <sub>3</sub> ) <sub>2</sub> CHCOOH < CH <sub>3</sub> CH(Br) CH <sub>2</sub> COOH <	CH3COOH < Cl-CH <sub>2</sub> -COOH < F-CH <sub>2</sub> -COOH
	CH₃CH₂CH(Br)COOH	4-Methoxy benzoic acid <benzoic 4-nitrobenzoic<="" <="" acid="" th=""></benzoic>
		acid < 3, 4-Dinitrobenzoic acid.
3	Aldehydes are more reactive than ketones towards	due to steric hinderence of 2-alkyl group in ketone
	nucleophilic addition	and more +I effect of 2-alkyl group in ketone
4	Cyclohexanone forms cyanohydrin in good yield but	due to steric hindrance in 2, 4, 6-trimethyl
	2, 4, 6-trimethylcyclohexanone does not.	
5	Carboxylic acids are higher BP than alcohols	due to more intermolecular hydrogen bonding

#### 13. AMINES AND DIAZONIUM SALT

1	increasing order of basic strength, aqueous solutions	$C_6H_5-NH_2 < CH_3-CH_2-NH_2 < (C_2H_5)_3N < C_2H_5-NH-C_2H_5$
		$NH_3 < (CH_3)_3N < CH_3 - NH_2 < (CH_{3)2}NH$ .
2	increasing order of basic strength, gas phase	$C_6H_5-NH_2 < CH_3-CH_2-NH_2 < C_2H_5-NH-C_2H_5 < (C_2H_5)_3N$
3	In increasing order of solubility in water	$(CH_3)_3N < CH_3 NHCH_3 < CH_3NH_2$
4	p-methylaniline is more basic than p-nitroaniline	—CH₃ group +I – effect ,–NO₂ group shows –I Effect (
5	Acetylation of – NH <sub>2</sub> group is done in aniline before preparing its ortho and para compounds.	To reduce activating effect of −NH <sub>2</sub> group.
6	pKb for aniline is more than that for methylamine	In aniline due to resonance
7	Aniline does not undergo Friedel-Crafts reaction	Aniline Lewis base, reacts lewis acid AlCl <sub>3</sub> to form salt.
8	Why do amines behave as nucleophiles?	Due to the presence of a lone pair
9	Aniline, p-nitroaniline and p-toluidine	<i>p</i> -Toluidine > Aniline > tr-nitroaniline
10	Aromatic primary amines cannot be prepared by	aryl halides do not undergo nuleophilic substitution
	Gabriel phthalimide synthesis.	easily due to presence of partial double character
11	Although amino group is o- and p- directing in	In presence of conc HNO <sub>3</sub> ,aniline gets protonated to
	electrophilic substitution rea <sup>n</sup> , aniline on nitration	form the anilinium ion which is meta directing
	gives a substantial amount of m-nitroaniline.	

#### **MECHANISM**

#### 1. SN1 mechanism

- It is Two step reactions.
- Step I: In the first step slow dissociation of alkyl halide takes place by reversible reaction forming a carbocation.

$$(CH_3)_3CBr$$
 $\xrightarrow{\text{step I}}$ 
 $H_1C$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

• **Step II**: The carbocation at once combines with the nucleophile to form final product (racemic mixture)

#### 2. SN2 mechanism

• It is One step reaction

#### 3. Mechanism for the Hydration of alkenes to alcohol

**Mechanism**- The mechanism of the reaction involves the following three steps:

The meenanism of the reaction involves the following times steps.				
<b>Step 1</b> : Protonation of alkene to form carbocation by electrophilic attack of H3O <sup>+</sup> .	$\begin{array}{cccccccccccccccccccccccccccccccccccc$			
Step 2: Nucleophilic attack of water on carbocation	$-\overset{{}}{}_{}-\overset{}{}\overset{}{}$			
Step 3: Deprotonation to form an alcohol	$-\overset{\cdot}{C} - \overset{\cdot}{C} - \overset{\cdot}{O} - \overset{\cdot}{H} + \overset{\cdot}{H}^{2} \overset{\cdot}{O} \rightarrow -\overset{\cdot}{C} - \overset{\cdot}{C} - \overset{\cdot}{C} + \overset{\cdot}{H}^{2} \overset{\cdot}{O}$			

#### 4. Mechanism for the acidic Dehydration of alcohols to give alkenes (At 443 K)

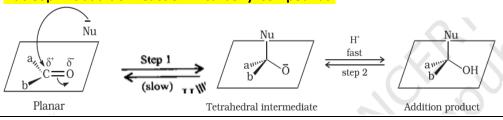
Step 1: Formation of protonated alcohol.	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
<b>Step 2:</b> Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Step 3: Formation of ethene by elimination of a proton	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

#### 5. Mechanism for the acidic Dehydration of alcohols to give ethers (At 413K)

(ii) 
$$CH^3CH^3 - \dot{O}$$
: +  $CH^3 - \dot{C}H^3 - \dot{O}$   $\stackrel{H}{\sim}$   $CH^3CH^3 - \dot{O}$   $\stackrel{H}{\sim}$   $CH^3CH^3 + H^3O$ 

(iii) 
$$CH_3CH_2 \stackrel{\circ}{>} - CH_2CH_3 \longrightarrow CH_3CH_2 - O - CH_2CH_3 + H^{\dagger}$$

#### 6. Nucleophilic addition reaction in carbonyl compounds.



# **BIOMOLECULES**

Carbohydrates are class	ified on the basis of their behavior on hydrolysis :	
Monosaccharides:	A carbohydrate that cannot be hydrolyzed further to give simpler unit of	
ivioriosaccitariaes.	examples are glucose, fructose, ribose, etc.	
Oligosaccharides:	Carbohydrates that yield two to ten monosaccharide units, on hydrolysis. For	
Ongosacchariacs.	example, sucrose , Maltose and Lactose	
Polysaccharides:	Carbohydrates which yield more than 10 of monosaccharide units on	
	hydrolysis are called polysaccharides. Some common examples are starch,	
	cellulose, glycogen, gums, etc.	
Reducing sugars:	All those carbohydrates which reduce Fehling's solution and Tollens' reagent are	
	referred to as reducing sugars. Examples: All monosaccharides, Maltose and Lactose.	
Non-reducing	In disaccharides, if the reducing groups of monosaccharides i.e., aldehydes or	
sugars:	ketone groups are bonded, these are non-reducing sugars e.g. Starch, Sucrose	
Anomers:	$\alpha$ & $\beta$ - Glucose , which differ in the orientation of – OH group at $C_1$ .	
Proteins:	proteins are polymer of $\alpha$ - amino acids , joined by peptide bonds . They also	
	known as polyamides.	
Types of Proteins:	(i) Fibrous proteins:- The polypeptide chains run parallel and are held by H-	
	bond or disulphide linkage , Insoluble in water Eg : Keratin ,Myocin	
	(ii) Globular proteins:- Polypeptides coil around to give a spherical shape, Soluble	
	in water Eg : Insulin ,Albumins	
Structure and shape	Primary structure: It is a specific sequence of amino acids	
of Proteins:	<ul> <li>2) Secondary structure: It represent shape ie. α - halix and β- pleated sheet.</li> </ul>	
	i) $\alpha$ - halix: polypeptide chain twisted in to a right handed screw by	
	forming H-bonds b/w NH group and >C=O grup.	
	ii) β- pleated sheet: peptide chains laid side by side and held together by H-bonds	
	3) <b>Tertiary structure:</b> It represent further folding of the secondary structure. It	
	gives rise to two major molecular shapes viz. fibrous and globular.	
	4) Quaternary structure of proteins: composed of two or more	
	polypeptide chains referred to as sub-units. The spatial arrangement of these	
	subunits with respect to each other.	
Denaturation of	Disturbing the $2^0$ and $3^0$ structures of proteins by heating or changing pH. eg:	
proteins	coagulation of egg white on boiling .	
Nucleic acids	Polymer of nucleotides linked by phosphodiester linkage -3' 5' linkage	
Nucleotide	Each nucleotide contains N-base, Sugar and Phosphate.	
Nucleoside	Contains N-base & Sugar.	
Double helical	Two strand of DNA coiled around each other and held together by H-bonds	
structure of DNA	b/w pairs of bases. Such as – C=G–, and –A =T–	
	Purines: Adinine & Guanine And Pyrimidines: Cytosine, Uracil & Thymine	
DNA	N-Bases : A,G ,C &T, Double helix, Contains 2-deoxy ribose	
DINA	sugar, Transfer heredity characters.	
DNIA	,	
RNA	N-Bases: A,G C & U, Single helix, Contains Ribose sugar, Helps	
0	in proteins synthesis.	
Preparation of Glucose	(I) From Cane sugar: (Sucrose):	
	When sucrose is hydrotysed by boiling with dil HCl or dil H <sub>2</sub> SO <sub>4</sub> in alcoholic solution	
	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^*} C_6H_{12}O_6 + C_6H_{12}O_6$	
	Sucrose Glucose Fractose	
	(II) From Starch:	
	Commercially Glucose is obtained by hydrolysis of starch by boiling it with dil H <sub>2</sub> SO <sub>4</sub> at 393 K	
	$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^*} nC_6H_{12}O_6$	
	Starch Starch	
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