DIAS

All India TEST – SERIES CSE – 2023

Test-9

Syllabus -: Full Syllabus Paper I

Instructions:-

1. Attempt five questions selecting at least one question from each section.
2. Question number 1and 5 are compulsory
3. Write answer in space provided for this purpose only.
4. Total time allowed is 3hr and Marks is 250.

Information:

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Date of Submission :- 29/08/23

Dias Roll Number :-

Official use.

Q.No	1	2	3	4	5	6	7	8
Marks	34	35	33		23	28		

Total Marks	153

200

Signature of invigilator

Signature of Examiner

Section -A

1.(a) (i) State and explain Heisenbrg's uncreatainty principle. Why is the not applicable to larger particles? (5)

Heisenberg's Unartainity principle states that there is always a ~~mmm~~ certain uncertainity in determination of position and momentum of a particle simultaneously, given by 50% of their real commutation value

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

Not applicable to large particles because uncertainity in one quantity gives neglegible uncertainity in other

Eg Cricket Ball $\Delta x = 0.1\,m$

$\therefore \Delta p_x = 3.31 \times 10^{-33}\ kg\,m\,s^{-1} \ll 10\ kg\,ms^{-1}$ momentum of ball.

(ii) When an electron was accelerated through a potential difference of 1.00 ± 0.01 kilovolt, what is the uncertainty of position of the electron along its line of projection? **(10)**

Given potential difference $V = 1.00 \pm 0.01$ KV

$\therefore$ Uncertainity in $V = 1.00 + 0.01 - (1.00 - 0.01)$

$= 0.02$ KV

Momentum (p) is related to V as: $\frac{p^2}{2m} = eV \rightarrow p = \sqrt{2meV}$

$\frac{2p\,dp}{2m} = e\,dV$ or $dp = \frac{me}{p}dV \Rightarrow dp = \sqrt{\frac{me}{2V}}\,dV$

Using Heisenberg Uncertainity principle

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

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

or $\boxed{\Delta x \geq \frac{h}{4\pi\sqrt{\frac{me}{2V}}\,\Delta V}}$

for electron - $m = 9.1 \times 10^{-31}$ kg

$e = 1.6 \times 10^{-19}$ C

$V = 1$ KV

$\therefore$ Minimum uncertainity in position $\boxed{\Delta x = 309.1 \text{ nm}}$

(b) Equilibrium constant Kp for dissociation of bromine atom $Br_2 \rightleftharpoons Br$ is 6×10^{-12} at 600 K and 10^{-7} AT 800 k. If this reaction is exo or endothermic? Calculate ΔG^0 for the dissociation reaction at 600 K? What will be formation constant at 800 K? What will be enthopy change at 600 K. **(15)**

Using Gibbs Helmoltz equation

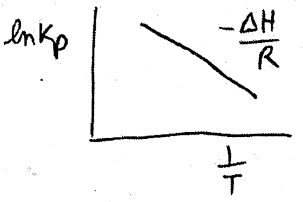
$$\boxed{\frac{d\left(\frac{G}{T}\right)}{dT} = -\frac{H}{T^2}} \quad -① \quad \text{or} \quad \frac{d\left(\frac{\Delta G}{T}\right)}{dT} = -\frac{\Delta H}{T^2}$$

At equilibrium $\Delta G = 0 \therefore \Delta G^\circ = -RT\ln K_p$

Hence $$\frac{d\left(-RT\ln K_p/T\right)}{dT} = -\frac{\Delta H}{T^2}$$

or $$\boxed{\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}} \quad -② \text{ Van't Hoff equation}$$

Integrating $$\ln K_p = -\frac{\Delta H}{RT} + C$$



(i) Given

K_p	T
6×10^{-12}	600K
10^{-7}	800K

as T increases, K_p increases

$\therefore$ Reaction has positive ΔH

Hence Reaction is endothermic

(ii) At equilibrium $\Delta G^\circ = -RT\ln K_p$

or at $T = 600K$, $K_p = 6\times10^{-12}$

$$\therefore \boxed{\Delta G^\circ = -128.89 \text{ KJ mol}^{-1}}$$

~~(iii) To calculate entropy~~

(iii) Formation Constant is given by reversing the reaction

$$2Br_{\bullet} \rightleftharpoons Br_2$$

Since $K_d = \frac{[Br_{\bullet}]^2}{[Br_2]}$

$$K_f = \frac{[Br_2]}{[Br_{\bullet}]^2} = \frac{1}{K_d}$$

$\therefore$ Formation Constant $= \frac{1}{10^{-7}} = \boxed{10^7}$

(iv) Using derivation above $\ln\left(\frac{K_{p_1}}{K_{p_2}}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

or $\Delta H = \frac{R \ln\left(\frac{K_{p_1}}{K_{p_2}}\right)}{R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$

$\Delta H = 193.97 \text{ KJ mol}^{-1}$

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

$\therefore \Delta S = \frac{\Delta H - \Delta G}{T} \Rightarrow \boxed{\Delta S = 538.1 \text{ J mol}^{-1} \text{K}^{-1}}$

(c) Calculate the energy in Joule to disperse one spherical drop of radius 3.0 mm into spherical drops of radius 3.0×10^{-3} mm if the surface tension of the drop is 72.8 dynes cm^{-1}.
(10)

Surface energy is equal to energy required to increase surface area by 1 unit in presence of surface tension.

$$E = \gamma(\Delta A) \quad -①$$

where γ = Surface tension

ΔA = change in area.

Since spherical drop is broken into smaller drops, Volume remains same.

$$\frac{4}{3}\pi R_0^3 = N\,\frac{4}{3}\pi r^3$$

$$N\,(\text{Number of drops}) = \left(\frac{R}{r}\right)^3 = \left(\frac{3}{3\times10^{-3}}\right)^3$$

$$N = 10^9 \text{ drops} \quad -②$$

$$\Delta A = N \times \pi r^2 - \pi R^2 \quad -③$$

$$E = \gamma\pi\,(Nr^2 - R^2)$$

$$= 72.8 \times \pi\,(10^9 \times 9 \times 10^{-6} - 9) \text{ dyne cm}$$

E (Energy for dispersion) = 0.205 J

(d) Explain the criteria of equilibrium and spontaneity in terms of U, S, A and G. **(10)**

From reversible isothermal process we have $dW|_{rev} \geq dW|_{irrev}$

$\therefore dq|_{rev} \leq dq|_{irrev}$ — ①

(i) Spontaneity in terms of U

from 1st law $dU = TdS - PdV = dq_{rev} - PdV$

using ① $TdS \leq dU + PdV$

or $dU \geq TdS - PdV$ — ②

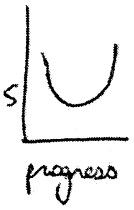
when $dS = dV = 0 \Rightarrow (dU)_{S,V} = 0$ (Equilibrium)

$\therefore$ Criteria for spontaneity is $\boxed{(dU)_{S,V} \geq 0}$

(ii) In terms of S

Using ② $TdS \leq dU + PdV$

or $\boxed{(dS)_{U,V} \leq 0}$ Equilibrium when $dS = 0$



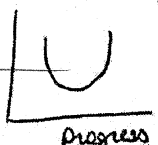
(iii) In terms of A where $dA = -PdV - SdT$

Since $dW|_{rev} \geq dW|_{irrev}$

$-PdV \geq dA + SdT$ or $dA \leq -PdV - SdT$

or $\boxed{(dA)_{V,T} \leq 0}$

$dA = 0$ at equilibrium



(iv) $\boxed{(dG)_{P,T} \leq 0}$ is criteria for spontaneity

2(a). Define dipole moment. (15)

Explain the following.

(i) Why is dipole moment of BF_3 zero?

(ii) Why is dipole moment of NH_3 greater than that of NF_3?

(iii) Why does SO_2 have dipole moment while CO_2 does not

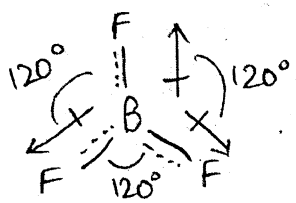
Dipole Moment refers to product of charge and the separation distance. It is a measure of molecular polarity.

Mathematically $\vec{\mu} = q \times \vec{d}$ Measured in Debye

$1D = 3.31 \times 10^{-30}$ Cm

(i) BF_3 - applying drago formula.

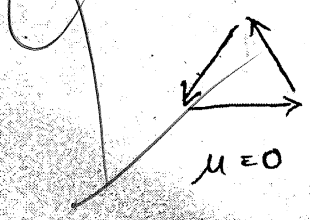
Electron pair (EP) = $\frac{3+3}{2} = 3 \Rightarrow sp^2$



Bond order = 1.33 (Back bonding)

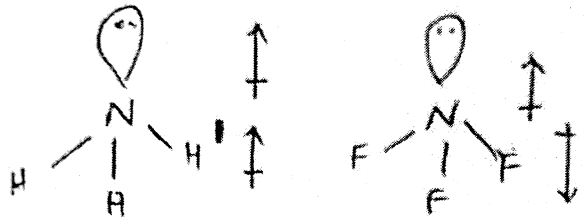
Since BF_3 molecule is symmetrical with all bond angles 120°, 3 dipole moments Cancel out

$\therefore$ Resultant $\mu = 0$



(ii) NH_3 - $\frac{5+3}{2} = 4 \Rightarrow sp^3$

NF_3 - $\frac{5+3}{2} = 4 \Rightarrow sp^3$



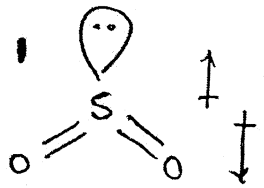
As shown, since electronegativity order is $H < N < F$, dipoles add up in NH_3 but tend to cancel out in NF_3 ∴ NH_3 has higher dipole moment than NF_3

(11)

SO_2

$EP = \frac{6}{2} = 3 \Rightarrow \boxed{sp^2}$

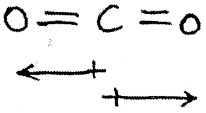
1 lone pair



$\mu_{SO_2} \neq 0$ Since dipoles do not cancel out.

CO_2

$EP = \frac{4}{2} = 2 = \boxed{sp}$



Exactly cancel out ∴ $\boxed{\mu_{CO_2} = 0}$

∴ SO_2 has dipole moment but CO_2 does not.

(b) Show that (20)

(i) $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$

(ii) $C_p - C_v = \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_T$

(i) This relation is Thermodynamic equation of State - I derived by utilisation of Entropy as a state function

From Ist law $dU = \partial q + \partial W$ — ①

Since $\partial q = TdS$, $\partial W = -PdV$

$\therefore dU = TdS - PdV$ — ②

Now: $U = f(V, T)$ $\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ — ③

Putting ③ in ② and rearranging

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \left[\frac{P}{T} + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad — ④$$

$$= M dT + N dV$$

Since S is state function $\left.\frac{\partial M}{\partial V}\right|_T = \left.\frac{\partial N}{\partial T}\right|_V$ — ⑤

$$\therefore \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{T^2}P + \frac{1}{T}\left(\frac{\partial^2 U}{\partial V \partial T}\right) - \frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T$$

Multiplying by T^2 we get

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$$

(ii) This equation is used to relate heat capacities at constant Volume and pressure.

From I^{st} Law $\quad dU = TdS - PdV \quad -①$

Since $H = U + PV \quad \therefore \quad dH = TdS + VdP \quad -②$

Since $U = f(V,T)$ and $H = f(P,T)$

$\therefore \quad dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP$ and $dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ $\quad -③$

Subtracting ① from ② and using expressions from ③

$$C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP - C_v dT - \left(\frac{\partial U}{\partial V}\right)_T dV = VdP + PdV$$

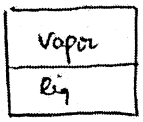
or $$(C_p - C_v)dT = VdP + PdV + \left(\frac{\partial U}{\partial V}\right)_T dV - \left(\frac{\partial H}{\partial P}\right)_T dP$$

In most physical processes, Pressure is kept constant $\therefore dP = 0$

$$\therefore \quad C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

or $$\boxed{C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P}$$

(c) (i) The vapour pressure of water at 298 K and 308 K are 3167 Pa and 5599 Pa respectively. Calculate the enthalpy of vaporisation of water. (10)



For vapor - liquid equilibrium

$$\mu_l = \mu_{vapor}$$

$$V dP - S dT\big|_{liq} = V dP - S dT\big|_{vap}$$

or $$\boxed{\frac{dP}{dT} = \frac{\Delta S_{liq \to vap}}{\Delta V_{liq \to vap}}} \quad — (1)$$

At equilibrium $\Delta G = 0 = \Delta H - T\Delta S \therefore \Delta S = \frac{\Delta H_{vap}}{T}$ — (2)

also $\Delta V_{liq \to vap} \sim V_{vapor}$ since $V_{liq} \ll V_{vap}$.

$$V_{vapor} = \frac{RT}{P} \quad — (3)$$

Using (3), (2) in (1)

$$\frac{dP}{dT} = \frac{P \Delta H_{vap}}{RT^2} \Rightarrow \text{Integrating } \boxed{\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \quad — (4)$$

Given $P_2 = 5599$ Pa, $P_1 = 3167$ Pa, $T_2 = 308$ K, $T_1 = 298$ K

$$\therefore \Delta H_{vap} = \frac{R \ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\boxed{\Delta H_{vaporisation\ of\ water} = 43.48 \text{ KJ mol}^{-1}}$$

(ii) Define excess free energy. What is its significance? (5)

Excess free energy refers to difference in the free energies of mixing 2 or more real gases to the case of mixing where they are considered ideal

Mathematically $\Delta G_E = \sum x_i \ln \gamma_i$

where x_i = mole fraction of gas i

γ_i = activity coefficient of gas i

ΔG_E significance

→ Represents deviation of gaseous mixing from ideality

→ As from formula, when gases are completely ideal,

$\gamma_i = 1$ and $\boxed{\Delta G_E = 0}$

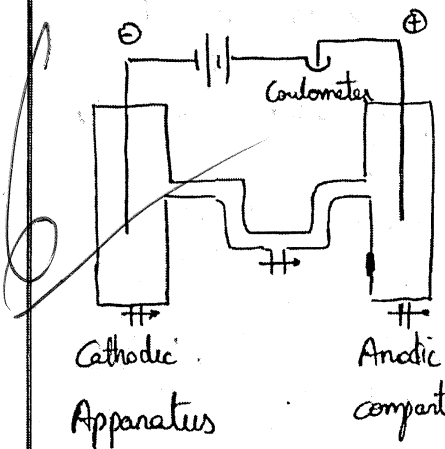
3(a) (i) Define transport number of anion and describe how it is measured. (10)

Transport number of anion is understood as fraction of the system current contributed by transport of that anion within solution.

Mathematically for salt A^+B^-

$t_{A^+} + t_{B^-} = 1$ or t_{B^-} (transport no of anion $= 1 - t_{A^+}$)

Measurement of t_{B^-}



→ Total current of cell is measured by Ag deposition in Coulometer (Moles $= \frac{m_{Ag}}{108}$)

→ Solutions from all 3 compartments are analysed till the compositions become stable.

→ Analysis of anodic compartment

ⓐ Salt concentration before electrolysis = a moles per ml

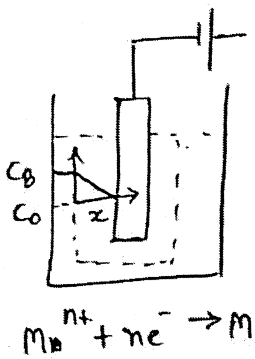
ⓑ Salt concentration after electrolysis = K moles per ml.

ⓒ Change in concentration is due to anion migration

$$\therefore t_{B^-} = \frac{(K-a)}{\left(\frac{m_{Ag}}{108}\right)}$$

(ii) Explain the basis of polarography. How is it used in diffusion measurements? (10)

Polarography refers to electrolysis of small amount of electroactive species using a micropolarisable electrode and a standard electrode. It is Based on Concentration polarisation

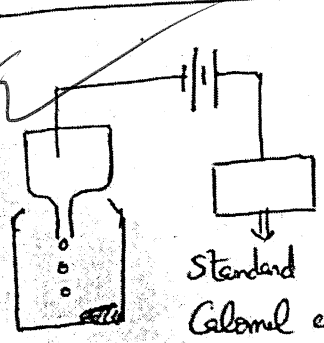


Concentration of ions in immediate electrode vicinity is lesser than bulk concentration C_B

$\therefore$ Gives rise to diffusion current $\boxed{i = k(C_B - C_0)}$

When $C_0 = 0 \rightarrow$ limiting diffusion current $\boxed{i_d = kC_B}$

Using polarography in diffusion measurement (Dropping Mercury electrode)



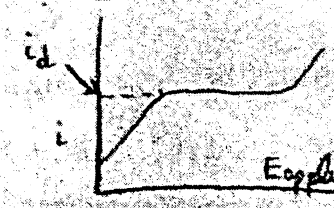
Diagram

For dropping mercury electrode, following experimental relation holds.

$$\boxed{i_d = (607\, D\, n^{1/2}\, m^{2/3}\, t^{1/6})\, C_B}$$

where D = Diffusion Constant in $cm^2 s^{-1}$

When C_B is known, m (mercury flow rate) and n (valency) are known and limiting current is observed, D can be calculated.

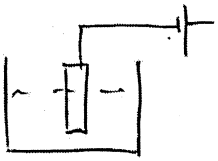


i_d is detected by sudden jump in electrode potential

(iii) What is the principle behind ion selective electrode and how is it used as a reference electrode? **(10)**

Ion selective electrode indicates the presence of a particular ionic species by measuring cell potential in terms of its concentration. Example - Metal-metal ion electrode, H_2 gas electrode etc.

Principle behind ion selective electrode

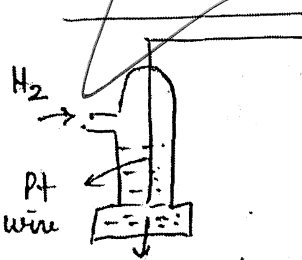


Half Cell reaction $M^{n+} + ne^- \rightarrow M$

$$E_{cell} = E^\circ_{cathode\ reduction} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

or $$\boxed{E_{cathode} = E^\circ_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}]}$$ electrode gives potential based on $[M^{n+}]$

Ion selective electrode as reference electrode - Case of H_2 electrode



Half cell reaction $H_2 \rightleftharpoons 2H^+ + 2e^- \rightarrow H_2$

$$E_{H^+/H_2} = \underbrace{E^\circ_{H^+/H_2}}_{\text{assumed } 0} - \frac{RT}{2F} \ln \frac{1}{[H^+]^2}$$

$$\therefore \boxed{E_{H^+/H_2} = -0.059\ pH}$$

This electrode can be coupled with another electrode as reference.

(b) State the essential conditions for hybridisation. Show diagrammatically the possible geometries from hybridisation of s, p, and d orbitals. Give examples. (10)

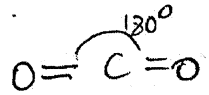
Hybridisation is a hypothetical concept used to explain covalent bonding by stable orbitals. Its essential conditions are:-

① Combining orbitals must be of similar energy.

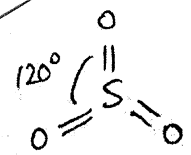
② Resultant hybrid orbitals have better directional property and energy density. Hence they only form sigma bonds, not π.

s, p, d orbital hybridisation → possible geometries

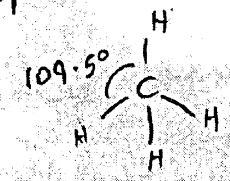
① sp - linear eg CO_2



② sp^2 - trigonal eg SO_3

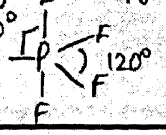


③ sp^3 - tetrahedral eg CH_4



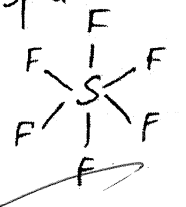
④ sp^3d - Trigonal bipyramidal

longer axial bonds



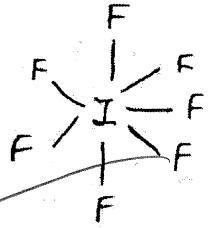
$(sp^2 + pd_{z^2})$

⑤ sp^3d^2 - Octahedral



all bonds equivalent

⑥ sp^3d^3 - pentagonal bipyramidal



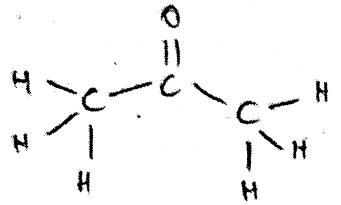
longer axial bonds

(c) Calculate Parachor of (i) CH_3COCH_3 (ii) Benzene if Parachor of C: 8.6; H: 15.7; O: 19.8; Single bond O; Double bond 19.9, 6-membered ring: 1.4. **(10)**

Parachor refers to Molar Volume at unit Surface tension for a liquid.

$$P = \frac{M\gamma^{1/4}}{(\rho_e - \rho_{vapr})} \sim \frac{M\gamma^{1/4}}{\rho_e} \quad (\rho_{vapr} \ll \rho_{liq})$$

It is additive property i.e. atoms and bonding interaction contributions are added to get molecule Parachor.

(i) 

3 'C' $\Rightarrow 8.6 \times 3 = 25.8$

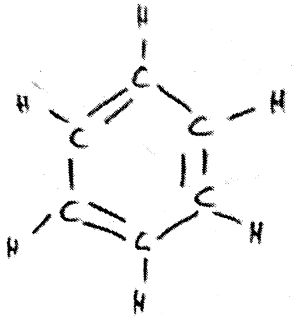
6 'H' $\Rightarrow 15.7 \times 6 = 94.2$

1 'O' $\Rightarrow 19.8 \times 1 = 19.8$

Single bonds 8 $= 0$

1 Double bond $\Rightarrow 1 \times 19.9 = 19.9$

Parachor of acetone = **159.7**

(ii) 

6 'C' $\Rightarrow 8.6 \times 6 = 51.6$

6 'H' $\Rightarrow 15.7 \times 6 = 94.2$

9 Single bonds $\rightarrow 0$

3 Double bond $\Rightarrow 3 \times 19.9 = 59.7$

6-membered ring $\rightarrow 1.4$

Parachor of Benzene = **206.9**

Section-B

5(a) In $[Fe(NO)(CN)_5]^{2-}$, $[Co(NO)(en)_2Cl]^{+}$ and $[Ru(NO)(OH)NO_2)_4]^{2-}$ explain angle (<) M – N – O if they all follow 18 e rule. **(10)**

$[Fe(NO)(CN)_5]^{2-}$ $\quad x + 12 + 2 = 18$

$x = 4 \quad \therefore \quad Fe^{4+}$

$[Co(NO)(en)_2Cl]^{+}$ $\quad x + 12 - 1 = 18$

$x = 7 \quad \therefore \quad Co^{2+}$

$[Ru(NO)(OH)(NO_2)_4]^{2-}$ $\quad x + 12 + 2 = 18$

$x = 4 \quad \therefore \quad Ru^{4+}$

M–N–O bond is linear but undergoes bending when Metal has back donation tendency – depends on charge and principal quantum number.

Highest donation tendency of Co^{2+}, lowest in Ru^{4+}

High nuclear charge.

$\therefore$ Order of donation $Co^{2+} > Fe^{4+} > Ru^{4+}$

Bond angle order is given by $[Co(NO)(en)_2Cl]^{+} > [Fe(NO)(CN)_5]^{2-} > [Ru(NO)(OH)(NO_2)_4]^{2-}$

(b) The following data are obtained for the decomposition of an organic compound. Find the order of the reaction and also the rate constant. **(10)**

Initial conc.(a_0) M	0.5	1.0	2.0
Half life period(s)	4000	2000	1000

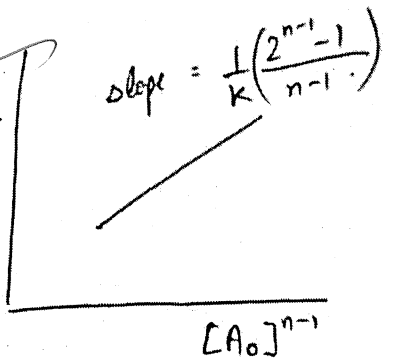
From data, it is clear that as initial concentration doubles half life period becomes half, indicates inverse relation.

For reaction $A \rightarrow$ products

$$-\frac{d[A]}{dt} = K[A]^n \quad \text{— ①}$$

$$-\int_{[A_0]}^{[A_0]/2} \frac{d[A]}{[A]^n} = \int_0^{t_{1/2}} K\,dt$$

$$-\frac{1}{(1-n)}\left[\frac{2^{n-1}}{[A_0]^{n-1}} - \frac{1}{[A_0]^{n-1}}\right] = K t_{1/2}$$



or $$\boxed{t_{1/2} = \frac{1}{K}\left(\frac{2^{(n-1)}-1}{n-1}\right)\frac{1}{[A_0]^{n-1}}} \quad \text{— ②}$$

For above data to fit the above relation, only possible choice is $n = 2$ → putting in ②

$$\boxed{t_{1/2} = \frac{1}{K[A_0]}} \quad \therefore \text{ Order of Reaction} = \boxed{2}$$

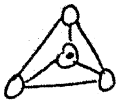
$$\Rightarrow \text{Rate Constant } K = \frac{1}{t_{1/2}[A_0]} = \frac{1}{(0.5 \times 4000)\,Ms}$$

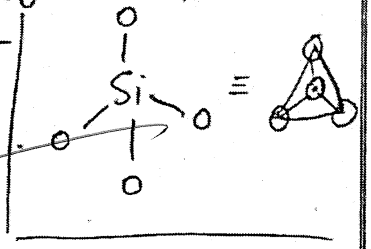
$$\boxed{K = 5 \times 10^{-4}\ M^{-1}s^{-1}}$$

(c) Write the structures of different types of silicates. **(10)**

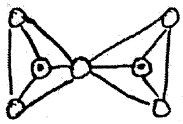
Silicates are naturally occuring tetrahedral arrangements of SiO_4^{4-} units in diverse fashions, giving different types.

① Orthosilicate - simplest silicate - unit formula SiO_4^{4-}



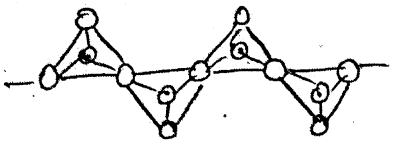


② Pyrosilicate - Combination of 2 orthosilicates

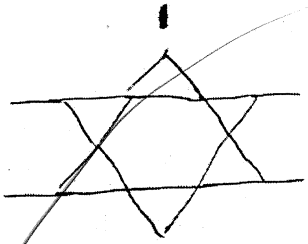


$Si_2O_7^{6-}$ eg $Sc_2Si_2O_7$

③ Chain silicates - extension of pyrosilicate

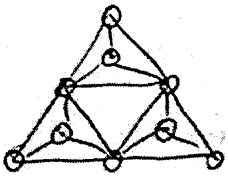


Pyroxene type SiO_3^{2-}

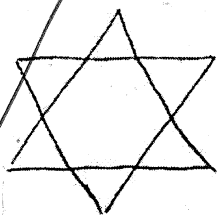


Amphibole type $Si_4O_{11}^{6-}$

④ Cyclic silicates



$(SiO_3^{2-})_3$

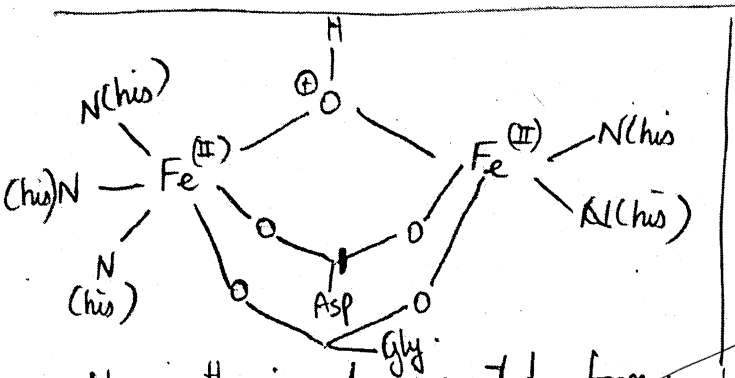


$(SiO_3^{2-})^6$

⑤ Sheet Silicates - expansion of amphibole type.

(d) Describe the active ligand environment around the coordination sphere of each iron in hemerythirn in the de-oxygenated from. **(10)**

Hemerythrin is a connective tissue used for oxygen transport in many invertebrates. It has 2 Fe ~~atoms~~ Cations in its active site



Hemerythrin - deoxygenated form.

(I) Fe^{2+} on left side

→ Present in d^6 configuration,

→ Coordination number is 6 - 3 positions are occupied by N atoms of histidine amino acids, other 3 are occupied by Oxygen from bridges.

(II) Fe^{2+} on right side

→ Coordination number only 5 - becomes 6 in Oxygenated form

→ 2 Positions by 'N' from histidines, 3 from 'O' of bridges.

* Bridges have Asp, Gly amino acids.

⇒ Both Fe^{2+} convert to Fe^{3+} in oxygenated form.

(e) Glowing of fireflies is a result of combination of chemical and physical processes. Explain with reasons. **(10)**

Glowing of fireflies is explained by photochemical reactions. Electrocyclic Ring closing and ring opening reaction causes the glow.

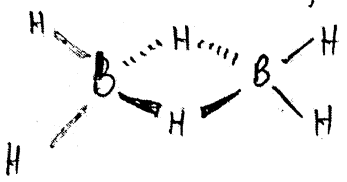
6(a). State the method of preparation of diborane from BF_3. Draw its structure and discuss its bonding. What happens when diborane is reacted with (i) water (ii) excess ammonia at low temperature. (10)

Diborane is type of Boron - hydrogen Compound with special type of bonding to satisfy its Octet.

→ Preparation from BF_3

$$2BF_3 + 6H_2 \longrightarrow B_2H_6 + 6HF$$

→ Structure and bonding

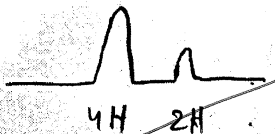


4 Hydrogens on external side contribute 2 electrons, but middle 2 H are shared via Banana Bonds

- This is also explained from chlorination

$$B_2H_6 \xrightarrow{4 \text{ times } Cl_2} B_2H_2Cl_4 \xrightarrow[\Delta]{Cl_2} 2BCl_3$$

- High energy per unit mass indicates restricted rotation - confirming banana bonds using NMR.



→ Reactions of B_2H_6

(i) $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

(ii) $B_2H_6 + NH_3$ (excess) $\xrightarrow[T]{\text{low}} [BH_2(NH_3)_2]^{\oplus} BH_4^{\ominus} \longrightarrow B_3N_3H_6$

Borazene

(b) Atomic radii of two of the lanthanides are considerably higher than the other lanthanides. identify those two lanthanides and explain the observation. (10)

Lanthanides atomic radii are governed by Lanthanide Contraction - which gives a regular decrement in size from La → Gd → Lu. due to increase in atomic charge but poor shielding of 4f electrons.

⇒ Atomic Radii of Lanthanum ($_{57}La$) and Cerium ($_{58}Ce$) are considerably higher than others (117 and 114 pm).

⇒ They are at the very beginning of lanthanoide series and have 0 and 2 f orbitals respectively. low number of f orbitals cause very small contraction barrier.

⇒ But later lanthanides having higher number of f orbitals show increased contraction due to poor shielding and thus have smaller sizes.

(c) A complex with the formula $CoCl_3\ 4NH_3$ gives precipitate with $AgNO_3$ with reference to one chloride ion. Answer the following: (10)

(i) What is the primary valency of cobalt?

(ii) What is the secondary valency of cobalt?

(iii) Draw the possible geometrical isomers of the compound.

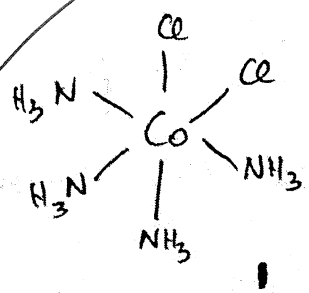
$CoCl_3 \cdot 4NH_3$ gives 1 mol of AgCl precipitate, This indicates that only 2 out of 3 chlorine form part of Coordination sphere Hence structure of this isomer is $[Co\,Cl_2(NH_3)_4]^{+1}Cl^{-1}$

Co^{+3} is d^6 configuration → d^2sp^3

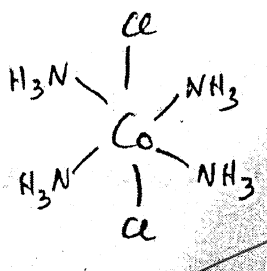
(i) Primary valency is defined as total ~~ligands in coordination sphere i.e. 6~~ oxidation state of Mental ion i-e. (+3)

(ii) Secondary valency is equal to total charge of Coordination sphere i-e. (+1)

(iii) Possible geometrical isomers



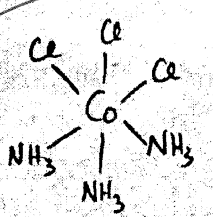
Cis isomer



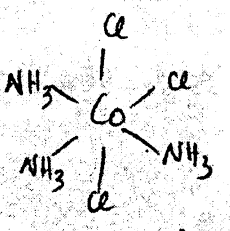
Trans isomer

If neutral Coordination sphere Case is also considered.

i-e. $[Co\,Cl_3(NH_3)_3] \cdot NH_3$



Fac isomer



Meridional isomer

(d) Which of the function(s) is/are eigenfuncation(s) of the operator $\frac{d^2}{dx^2}$? Find its eigenvalue(s) also (10)

(i) $6\cos(4x)$ (ii) $5x^2$ (iii) $3e^{-5x}$ (iv) $\ln(2x)$ (v) $\sin(3x)$

Eigenfunction of any operator means that after operation, the function is regenerated along with an eigenvalue.

i.e. $\hat{A}\psi = a\psi$ where ψ = wavefunction, a = eigenvalue

$\hat{A}$ = eigenfunction.

(i) $\psi = 6\cos(4x)$

$$\frac{d}{dx}\left(\frac{d}{dx}[6\cos(4x)]\right) = \frac{d}{dx}(-24\sin(4x)) = -96\cos(4x)$$

$$= (-16)(\psi)$$

∴ It is eigenfunction with eigenvalue $= (-16)$

(ii) $\frac{d}{dx^2}(5x^2) = 10 \neq a \times (5x^2)$ ∴ Not an eigenfunction

(iii) $\psi = 3e^{(-5x)}$. $\frac{d^2}{dx^2} = 25 \times 3e^{(-5x)}$ ∴ It is eigenfunction

Eigenvalue $= 25$

(iv) $\psi = \ln(2x)$ $\frac{d^2}{dx^2} = -\frac{1}{x^2} \neq a\ln(2x)$ ∴ Not an eigenfunction

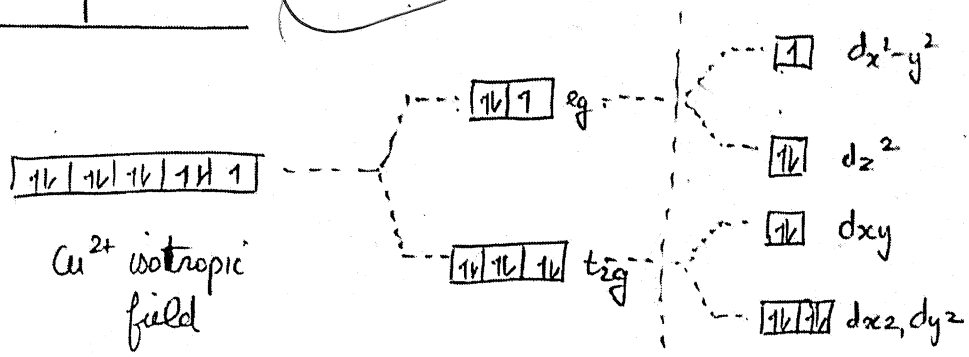
(v) $\psi = \sin(3x)$ $\frac{d^2}{dx^2} = -9\sin(3x)$ ∴ It is eigenfunction

Eigenvalue $= (-9)$

(e) The crystal structure of CuF_2 revealed that the Cu^{2+} ion is six coordinated wherein four Cu-F bond distances are of 1.93 Å. Explain. **(10)**

CuF_2 has Cu^{2+} present in d^9 configuration. Since its eg orbitals are asymmetrically filled, it shows strong Jahn-Teller Distortion to lower degeneracy, increase asymmetry and get stabilisation.

CFT explanation



→ Consider 3 eg electrons, 2 of them wish to reside in $d_{x^2-y^2}$ due to angular momentum spread in 3 directions. However this causes repulsion from F^- in 4 directions ∴ To avoid instability 2 electrons occupy d_{z^2} and 1 electron in $d_{x^2-y^2}$.

→ 2 d_{z^2} electrons repel electrons of incoming ligands along z, leading to longer axial bonds than 4 equatorial ones.