DIAS

All India TEST – SERIES CSE – 2024

Paper-1 (Test-7)

Syllabus -: Full Syllabus

Instructions:-

1. Attempt five questions selecting at least one questions 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 :- 09-09-24

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Official use.

Q.No	1	2	3	4	5	6	7	8
Marks	36	35	34	0	22	—	—	33

Total Marks	160/200

Signature of invigilator

Signature of Examiner

Section-A

1.(a) . The vapour pressure of ice $\rightleftharpoons$ water system at 0.0075^0 is 4.58 mm and at 0^0C is 79.80 mm of mercury. Calculate the molar heat of fusion of ice, given that the specific volumes of ice and water at 0^0C are 1.0907 cm^3 and 1.0001 cm^3, respectively. Density of mercury at 0^0C = 13.6 g cm^3. **(10)**

Vapour pressure is defined as the pressure exerted at the surface of liquid.

$$ice \rightleftharpoons water$$

$$\cancel{\Delta G} = dG_{ice} = dG_{water} \quad \text{(equilibrium)}$$

$$V_i dP - S_i dT = V_w dP - S_w dT \quad (\cancel{\text{since } dT = 0})$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{fusion}}{T_f \, \Delta V}} \quad \text{(i)}$$

$\Rightarrow$ $\Delta H_{fusion} = ?$

$\Delta V = +1.0907 - 1.0001 \ cm^3 = +0.0906 \ cm^3$

$$dP = \Delta P = \frac{(79.80 - 4.58)\,mm}{760\,mm} \times 1.01325 \times 10^5 \ Pa$$

$\Delta P = 1.02 \times 10^4 \ Pa$

$\Delta T = 0.0075 \ K$

Putting in (i) $\Rightarrow$ $$\frac{1.02 \times 10^4}{0.0075} = \frac{\Delta H_{fusion} \, (10^6)}{(\cancel{0.0075})(273)(0.0906)(18 \, g/mol)}$$

$$\boxed{\Delta H_{fusion} = 6.05 \ KJ/mol}$$

(b) For the electrochemical cell Cd. $CdCl_2$ $5/2H_2O$(aq) | AgCl(s), Ag, EMF at 0^0C and 25^0C is 0.6915 V and 0.6753 V. respectively. The cell reaction is Cd(s) + 2AgCl(s) + aq $\rightleftharpoons$ $CdCl_2.5H_2O$ (sat) + 2Ag(s). Calculate ΔG^0 , ΔS^0 and ΔH^0 at 25^0C. **(10)**

$$Cd(s) + 2AgCl(s) + H_2O \rightleftharpoons CdCl_2 \cdot 5H_2O(sat) + 2Ag(s)$$

Since, Anode ⇒ $Cd \longrightarrow Cd^{2+} + 2e^-$

Cathode $AgCl + e^- \longrightarrow Ag + Cl^-$

$\boxed{n=2}$

$\Delta G^\circ = -nFE^\circ_{cell}$ $[E^\circ_{cell} = 0.6753V]$ at 25°C

$\Delta G = (-2)(96500\ C/mol)(0.6753\ V)$

$\boxed{\Delta G^\circ = -130.332\ KJ}$

We know, $\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = -\Delta S^\circ$

$\Rightarrow \cancel{-}nF\frac{\partial \Delta E^\circ}{\partial T} = \cancel{-}\Delta S^\circ$

$\Delta S^\circ = -(2)(96500)\frac{(0.6915 - 0.6753)}{(-25)}$

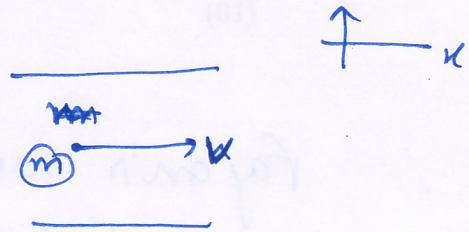
$\boxed{\Delta S^\circ = -125.06\ J/K}$

Since $\boxed{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$

$\Delta H^\circ = -130.325 + \left(\frac{298}{1000}\right)(-125.06)$ KJ

$\boxed{\Delta H^\circ = -167.6\ KJ}$

(c) Derive the expression for the linear momentum operator of particle moving in the x-direction. **(10)**



The expression can be derived using the energy operator being provided by ~~shcd~~ Schrodinger wave equation

Schrodinger wave equation:

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

$$\underbrace{-\frac{h^2}{8\pi^2 m}\frac{\partial^2 \psi}{\partial x^2}}_{\text{Kinetic energy term}} + V\psi = E\psi$$

Since $K.E = \frac{p^2}{2m}$ $\quad P = \sqrt{2mK.E}$

$\hat{P} = \sqrt{2m(K\hat{E})}$

Therefore, $\hat{P} = \sqrt{\cancel{2m}\left(-\frac{h^2}{8\pi^2 \cancel{m}}\right)\frac{\partial^2}{\partial x^2}}$

$\cancel{P = -i\frac{h}{2}}$ $\quad \boxed{\hat{P} = -ih\frac{\partial}{\partial x}}$

(d) State Fajan's rule. Which for the compounds in the pairs of compounds is more covalent: CuO or CuS; CuO or Cu_2O; AgCl or AgI; LiCl or KCl; LiI or LiF; $AlCl_3$ or $GaCl_3$; $PbCl_2$ or $PbCl_4$. **(10)**

Fajan's rule state that covalency depends upon polarisation of cation and polarisability of anion.

⇒ More the ionic potential $\left(\frac{\text{charge}}{\text{size}}\right)$ ⇒ more is cation's polarization

⇒ ~~No.~~ Larger the size of anion ⇒ more is anion's polarisability

Covalent

⇒ $CuO < CuS$ as $r_{S^{2-}} > r_{O^{2-}}$

⇒ $\overset{+1}{Cu_2}O < \overset{+2}{Cu}O$ as Cu^{2+} (charge) > Cu^{+} (charge)

⇒ $AgCl < AgI$ since $r_{I^-} > r_{Cl^-}$

⇒ $KCl < LiCl$ since $r_{Li^+} < r_{K^+}$

⇒ $LiI > LiF$ since $r_{I^-} > r_{F^-}$

⇒ $AlCl_3 > GaCl_3$ since $r_{Al^{3+}} < r_{Ga^{3+}}$

⇒ $PbCl_4 > PbCl_2$ since charge ($Pb^{4+} > Pb^{2+}$)

Usage of covalency is further show through valence bond theory for structural determinations.

(d)Calculate the lattice energy of cesium iodide which crystallizes in the cesium chloride structure and has an interionic distance of 395 pm. The Madelung constant and the Born exponent for CsI are 1.76 and 12, respectively. **(10)**

Born lande equation provides for the formulation of lattice energy

such that $U_c = \frac{Z_+ Z_- e^2}{4\pi\epsilon_0 r} N_0 A \left(1 - \frac{1}{n}\right)$ —(i)

where A = Madlung const

n = Born exponent

r = Interionic distance

Putting the values in (i)

$$U_c = \frac{(1)(-1)(1.6\times10^{-19})^2 (6.022\times10^{23})(1.76)}{(4\pi\epsilon_0)(395\times10^{-12}\,m)}\left(1-\frac{1}{12}\right)$$

$$U_c = -0.566\times10^{6}\ KJ/mol$$

$$\boxed{U_c = -566\ KJ/mol}$$

Further, lattice enthalpy depends upon the charge and size such that

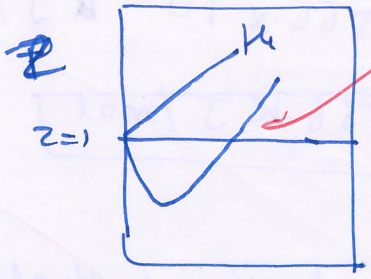
$$\boxed{\begin{array}{l} U_c \propto Z_+ Z_- \\ U_c \propto \frac{1}{r} \end{array}}$$

(e)(i) Inert gases have closed shells. Why do they liquify. **(5)**

Liquification depends upon the intermolecular attraction between the molecules/atoms.

Despite having closed shell configuration, inert gases do have appreciable force of interaction such that below critical temperature and at certain pressure, they can be liquified

(compressibility factor)



~~Though, the~~ For liquification $Z \neq 1$

(ii) The electronegativities of A, B and C are 1.0, 2.5 and 3.0, respectively. Predict the type of bonding in AC and BC. **(5)**

Using formula to calculate % ionic character

% ionic (Pauling's) $= 16|X_A - X_B| + 3.5(X_A - X_B)^2$

For AB $\Rightarrow$ $16(1.5) + 3.5(1.5)^2 = 31.875\%$

For BC $\Rightarrow$ $16(0.5) + 3.5(0.5)^2 = 9.875\%$

For AC $\Rightarrow$ $16(2) + 3.5(2)^2 = 46\%$

AC has much larger % ionic character than BC

BC is ~~du~~ predominantly of covalent nature, while AC is much more ionic in nature.

2(a)Discuss the MO energy level diagram of NF molecule. How it differ from NO^- molecule in the terms of bonding. **(15)**

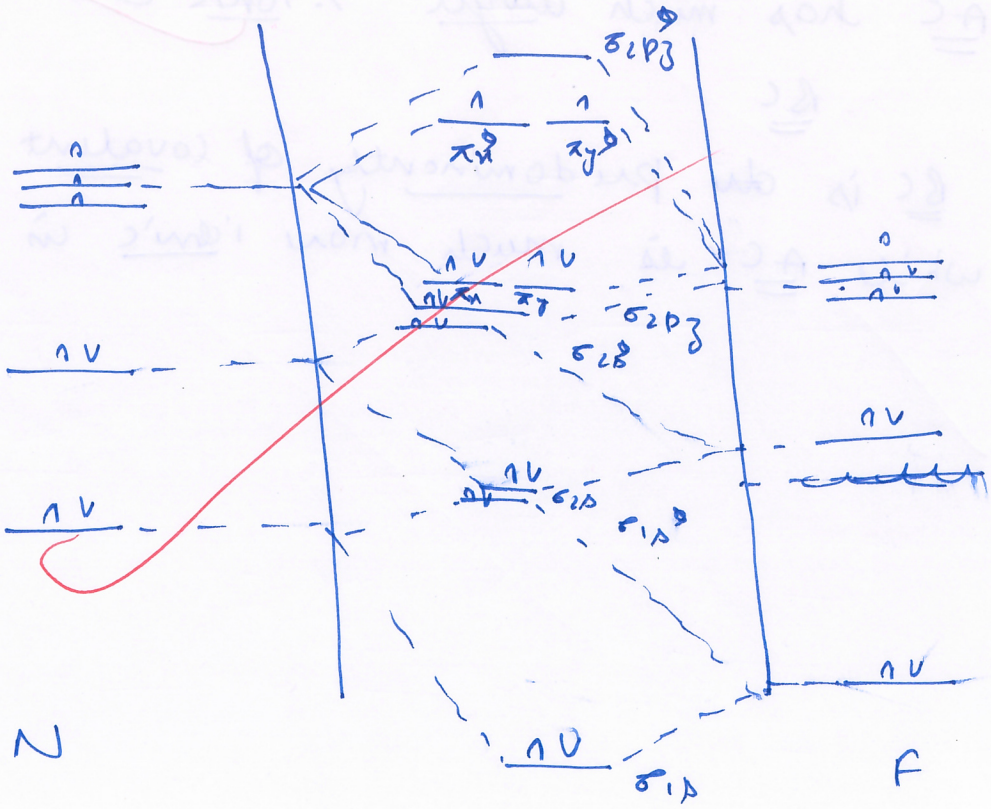
MO diagram is obtained through MOT which involves intermixing of orbitals and generation of equal number of bonding and non-bonding orbitals.

MO for $\boxed{NF}$

$N = 1s^2 2s^2 2p^3$

$F = 1s^2 2s^2 2p^5$

Total electrons $\Rightarrow 16$



$\boxed{\text{Bonding}} = \left(\frac{2-0}{2}\right)\sigma + \left(\frac{4-2}{2}\right)\pi$

$= \boxed{1\sigma + 1\pi}$

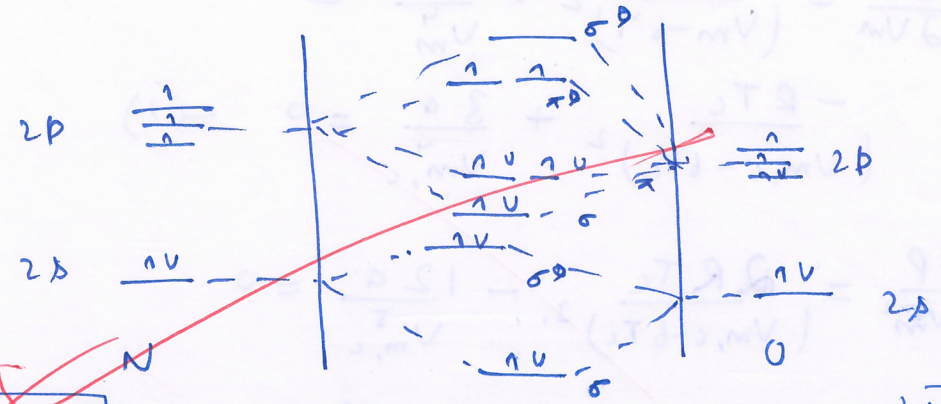
Thus, first bond is $\underline{\sigma}$ and other one is $\underline{\pi}$

$\boxed{N \leftarrow F}$

MO for $\boxed{NO^-}$

$N = 1s^2\, 2s^2\, 2p^3$

$O = 1s^2\, 2s^2\, 2p^4$



$\boxed{\text{Bonding}} \Rightarrow \left(\frac{2-0}{2}\right)\sigma + \left(\frac{4-2}{2}\right)\pi = \boxed{1\sigma + 1\pi}$

$[N \xleftarrow[\sigma]{\pi} O]^- \rightleftharpoons [{}^-N = O]$

$\boxed{\text{Differences}} \Rightarrow$ $\underline{NO^-}$ is more polar than $\underline{NF}$

$\Rightarrow$ Resonance is a possibility in NO^- $\boxed{N \leftarrow O^- \leftrightarrow {}^-N = O}$ but not in $\underline{NF}$

(b)(i) A certain gas has the equation of state . **(10)**

$$P = \frac{RT}{V_m - bT} - \frac{a}{V_m^3}$$

Where a and b are constants characteristic of the gas. Show that

$$a = \frac{4RT_cV_c^2}{3}, \quad b = \frac{V_c}{2T_c}$$

~~Fat~~ Critical temperature is that one, above which gas cannot be liquified, whatever may be the pressure.

We know, $\left.\frac{\partial P}{\partial V_m}\right|_{T=T_c} = 0$ $\quad \left.\frac{\partial^2 P}{\partial V_m^2}\right|_{T=T_c} = 0$

Thus,

$$\frac{\partial P}{\partial V_m} = \frac{-RT}{(V_m - bT)^2} + \frac{3a}{V_m^4} = 0 \quad \text{at } T = T_c$$

$$\frac{-RT_c}{(V_{m,c} - bT_c)^2} + \frac{3a}{V_{m,c}^4} = 0 \quad -(i)$$

Also

$$\frac{\partial^2 P}{\partial V_m^2} = \frac{2RT_c}{(V_{m,c} - bT_c)^3} - \frac{12a}{V_{m,c}^5} = 0$$

$$\frac{RT_c}{(V_{m,c} - bT_c)^2} = \frac{3a}{V_{m,c}^4} \quad \text{and} \quad \frac{12a}{V_{m,c}^5} = \frac{2RT_c}{(V_{m,c} - bT_c)^3}$$

$$\Rightarrow \frac{4\cancel{RT_c}}{(V_{m,c} - bT_c)^2 V_{m,c}} = \frac{2\cancel{RT_c}}{(V_{m,c} - bT_c)^3}$$

$$2(V_{m,c} - bT_c) = V_{m,c} \Rightarrow \boxed{b = \frac{V_{m,c}}{2T_c}}$$

Further

$$\frac{4RT_c}{(V_{m,c})^2} = \frac{3a}{V_{m,c}^4} \Rightarrow \boxed{a = \frac{4RT_cV_{m,c}^2}{3}}$$

(ii) Obtain the reduce from of the above equation of state. (10)

Reduced form is defined as any unit divided by its critical term.

Let $\Phi = \frac{P}{P_c}$ $\Theta = \frac{T}{T_c}$ $\pi = \frac{V}{V_{m,c}}$

$$P_c = \frac{RT_c}{V_{m,c} - bT_c} - \frac{a}{V_{m,c}^2}$$

$$P_c = \frac{2RT_c}{V_{m,c}} - \frac{4RT_c}{3V_{m,c}} = \frac{2RT_c}{3V_{m,c}}$$

Putting in main equation

$$\Phi P_c = \frac{R\Theta T_c}{\pi V_{m,c} - b\Theta T_c} - \frac{a}{\pi^3 V_{m,c}^2}$$

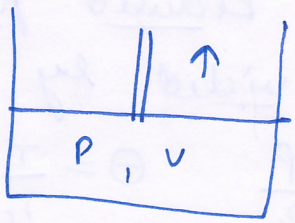
$$\Phi\left(\frac{2R\cancel{T_c}}{3\cancel{V_{m,c}}}\right) = \frac{R\Theta\cancel{T_c}}{\pi\cancel{V_{m,c}} - \Theta\frac{\cancel{V_{m,c}}}{2}} - \frac{4R\cancel{T_c}}{3\pi^3\cancel{V_{m,c}}}$$

$$\boxed{\frac{2R\Phi}{3} = \left(\frac{2R\Theta}{2\pi - \Theta}\right) - \frac{4R}{3\pi^3}}$$

Further, law of corresponding state states that if two gases have same reduced pressure and volume, they'll have same reduced temperature

(c)(i) Proved that if free energy change of a system decreases then entropy of universe increases at constant temperature and pressure. **(10)**

Provided, constant T
Constant P



(A)

We know,

$\Delta \cancel{S_{surrounding}} =$

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$

For a simple system (A)

$q_{system} = -q_{surrounding}$

$\Delta S_{universe} = \Delta S_{system} + \frac{q_{surrounding}}{T}$

$\Delta S_{universe} = \Delta S_{system} - \frac{q_{system}}{T}$

$\Delta S_{universe} = \frac{T\Delta S_{sys} - q_{sys}}{T}$

Since, $T\Delta S_{sy} - q_{sys} = -\Delta G_{sys}$ at Constant Pressure

$$\boxed{\Delta S_{universe} = -\frac{\Delta G_{sys}}{T}}$$

Thus, as free energy change of system decreases, the entropy of universe increases. This is also a measure of $\boxed{\text{spontaneity}}$

(ii) A Carnot engine converts one-sixth of heat input into work. When the temperature of the sink is reduced by 62^0 C, its efficiency is doubled. Find the temperature of the source and the sink. **(5)**

Carnot cycle involves two isothermal and two adibatic events, in a cyclic manner, alternatively.

$\eta = 1 - \frac{T_2}{T_1}$ where, T_2 = Temp. of sink
T_1 = Temp. of source
η = efficiency

Provided $\eta = \frac{(-W)}{q} = \frac{1}{6} = 1 - \frac{T_2}{T_1}$

$\frac{1}{6} = 1 - \frac{T_2}{T_1}$

$\cancel{6 = T_1 + 6T_2}$

$\frac{T_2}{T_1} = \frac{5}{6}$

$\frac{1}{3} = 1 - \frac{T_2 - 62}{T_1}$

$\frac{2}{3} = \frac{T_2}{T_1} - \frac{62}{T_1}$

$\frac{2}{3} - \frac{5}{6} = -\frac{62}{T_1}$

$T_1 = 62 \times 6$ °C

$\boxed{T_1 = 372\,K}$ of source

$\boxed{T_2 = 310\,K}$ of sink

3(a) Define "Partial molar property". What is its physical significance? Derive the relationship for chemical potential in the terms of partial molar enthalpy . **(10)**

'Partial molar property' is defined as the change in any thermodynamic quantity with respect to change in composition of any one quantity, keeping other ~~var~~ factors as constant

$$\mu_i = \left(\frac{\partial X}{\partial n_i}\right)_{\cancel{i \neq j},\, T, P, n_j\, (i \neq j)}$$

Physical significance ⇒ Helps in determining the contribution of any particular quantity towards the reaction or overall composition. It helps in understanding "activity" of specific component

Relationship of μ with ΔH_m

Since,

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

$$\frac{\partial \Delta h}{\partial n} = \frac{\partial \Delta H}{\partial n} - \frac{\partial T\Delta S}{\partial n}$$

$$\Rightarrow \Delta \mu_i = \Delta H_{,m} - T\Delta S_{,m}$$

$$\Rightarrow \boxed{\mu_i = H_{,m}}$$

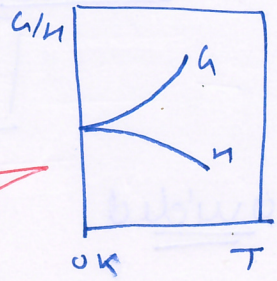
$$\boxed{\mu_i dn = dH}$$ at constant entropy

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j\, i \neq j}$$

(b) Explain the Nernst heat theorem. How does it lead to the enunciation of the Third law of thermodynamics. **(10)**

Nernst heat theorem states that as the temperature approaches $\boxed{0K}$, the difference between free energy and enthalpy, approaches zero.

i.e. $G - H = T\left(\frac{\partial G}{\partial T}\right)_P = 0$



$\boxed{\text{Third law}}$

Entropy of a well-defined crystalline solid is zero at zero Kelvin

Explanation by Nernst Theorem.

as $G - H = 0$

$\left(\frac{\partial G}{\partial T}\right)_P = -S = 0$

$\boxed{S = 0}$

Further $\left(\frac{\partial H}{\partial T}\right)_P = C_P = 0$ $\boxed{C_P = 0}$

Thus, nernst law provides that motion ceases to exists at 0K, which provides a base for third law of thermodynamics

(c)(i) Calculate the entropy change accompanying the conversion of 1 mole of ice at 273.1 K and 1 atm pressure into steam at 373.1 K and 1 atm pressure, given that at 273.1 K, the molar heat of fusion of ice ,ΔH_{fus}, is 6.00 kJ mol^{-1} and 373.1 K the molar heat of vaporization of water, ΔH_{vap}, is 40.60 kJ mol^{-1}. Also assume that the molar heat capacity. C_p, in the temperature range 373.1 – 273.1 K remains constant at 75.2 J K^{-1} mol^{-1}. **(15)**

Entropy is a measure of randomness (freely available work)

$$dS = \frac{dq_{rev}}{T}$$

Provided,

$$H_2O(s) \underset{273.1K}{} \overset{a}{\rightleftharpoons} H_2O(l) \underset{273.1K}{} \overset{b}{\longrightarrow} H_2O(l) \underset{373.1K}{} \overset{c}{\rightleftharpoons} H_2O(g) \underset{373.1K}{}$$

For (a)

$$\Delta S_{fus} = \frac{\Delta H_f}{T}$$

$$\Delta S_{fusion} = \frac{6}{273.1} \text{ kJ/mol/K}$$

$$\Delta S_f = 21.96 \text{ J/mol-K}$$

For (b)

$$dS = \frac{dq}{T} = \frac{n C_p dT}{T}$$

$$\therefore \Delta S = n C_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_b = (75.2) \ln\left(\frac{373.2}{273.1}\right)$$

$$\Delta S_b = 23.46 \text{ J/mol-K}$$

For Path (C)

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

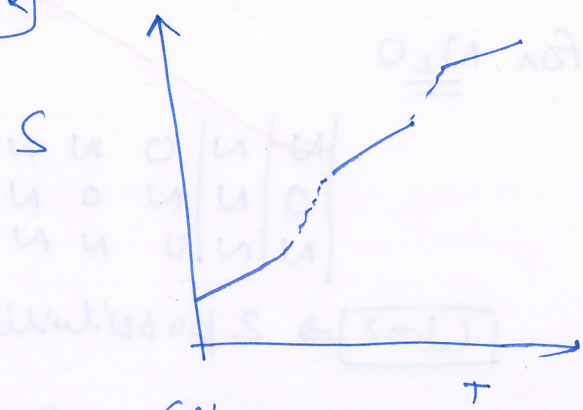
$$= \frac{40.60}{373.1} \text{ kJ/mol-K}$$

$$\Delta S_{vap} = 108.8 \text{ J/mol-K}$$

Total entropy change

$$\Delta S \Rightarrow \Delta S_f + \Delta S_v + \Delta S_b$$

$$\boxed{\Delta S = 154.23 \text{ J/Kmol K}}$$



(Phase change process)

(ii) What is residual entropy. Determine residual entropy of N_2O. **(5)**

Residual entropy is the entropy that exists at $\boxed{0K}$, which goes against the 3rd law of thermodynamics (stating impossibility)

$$\boxed{S_m = R \ln W}$$

S_m = molar entropy

W = possible randomness

For N_2O

N	N	O	N	N	O
O	N	N	O	N	N
N	N	O	N	N	O

$\boxed{W=2} \Rightarrow$ 2 possibilities of arrangement

Thus, $S_m = 8.314 \ln 2$ J/K/mol

$$\boxed{S_m = 5.76 \text{ J/K-mol}}$$

(d) Integrate the van't Hoff equation for temperature dependence of equilibrium constant and determine Intergration constant. **(10)**

Van't Hoff equation provides for variation of thermodynamic equilibrium with change in enthalpy.

Since, $\Delta G^\circ = -RT \ln K_{eq}$ (at equilibrium)

$$\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} = -R\frac{\partial \ln K_{eq}}{\partial T}$$

Also, $\left(\frac{\partial \Delta G^\circ/T}{T}\right) = \frac{-\Delta H^\circ}{T^2}$ (Gibbs - Helmoltz Equation)

Thus, $$\frac{\partial \ln K_{eq}}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

$$\partial \ln K_{eq} = \frac{\Delta H^\circ}{RT^2}\, dT$$

Integrating, $$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + I$$

Since $\Delta G^\circ = -RT \ln K_{eq}$.

$$-\frac{\Delta G^\circ}{RT} + \frac{\Delta H^\circ}{RT} = I$$

$$I = \frac{-\Delta G^\circ + \Delta H^\circ}{RT} = \frac{T\Delta S^\circ}{RT}$$

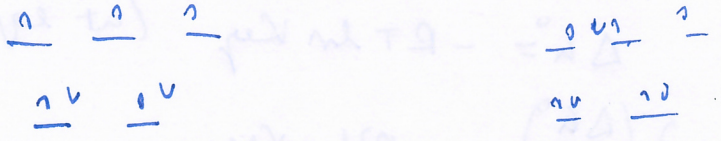
$$\boxed{I = \frac{\Delta S^\circ}{R}}$$

[since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

4(a)(i) . Why does Co(II) from tetrahedral complexes more readily than Ni(II) ? **(5)**

Co (II) = $3d^7$

~~Co~~ Ni (II) = $3d^8$



(ii) Why are Fe(II) complexes less stable that Zn(II) or Fe(III) complexes **(5)**

=) $Fe^{2+} = 3d^6\ 4p^2$

(b) A dark green compound $Co(NH_3)_3(H_2O)Br_3$ in solution turns red on standing. Its conductivity increases from 151 to 363 $cm^2.ohm^{-1}\ eq^{-1}$. One mole of bromide per mole of the green compound can be precipitated by $AgNO_3$. (a) what is the most probable structure of the green compounds, and optical isomers, if any. (b) What is the most probable structure of the red compound? Give the structures and optical isomers, if any. **(10)**

Given $[Co(NH_3)_3Br_2(H_2O)]^{+1}Br^-$

$\Rightarrow$ ~~$\{Co(NH_3)_3Br_3\}$~~ Co

$[Co(NH_3)_3(H_2O)]Br_3$

(c) A conductivity cell, when filled with an aqueous solution of 0.02 M KCl at 25^0C, had a resistance of 250 ohm, Its resistance, when filled with 6×10^{-5} M NH_4OH solution was 10^5 ohm. The specific conductance of 0.02 M KCl was 0.277 S m^{-1}. The molar ionic conductance's at infinite dilution of NH_4^+ and OH^- ions are 73.4×10^{-4} and 198.0×10^{-4} S m^2 mol^{-1}, respectively. Calculate the degree of dissociation of 6×10^{-5} M NH_4OH solution. **(10)**

$\cancel{\lambda = \kappa \times K}$

$\lambda =$ $\quad K = G = K \frac{A}{l}$

$\Rightarrow \frac{R}{a} = \frac{1}{K}\frac{l}{A}$ $\quad \frac{Gl^2}{n} = \frac{K}{C}$

$\Rightarrow$

$\lambda_{KCl} = K \times h$

$\lambda_{NaOH} \rightarrow K \times h$

$\lambda_{NH_4OH} = ?$

λ $\quad \alpha = \frac{\Lambda}{\Lambda_\infty}$

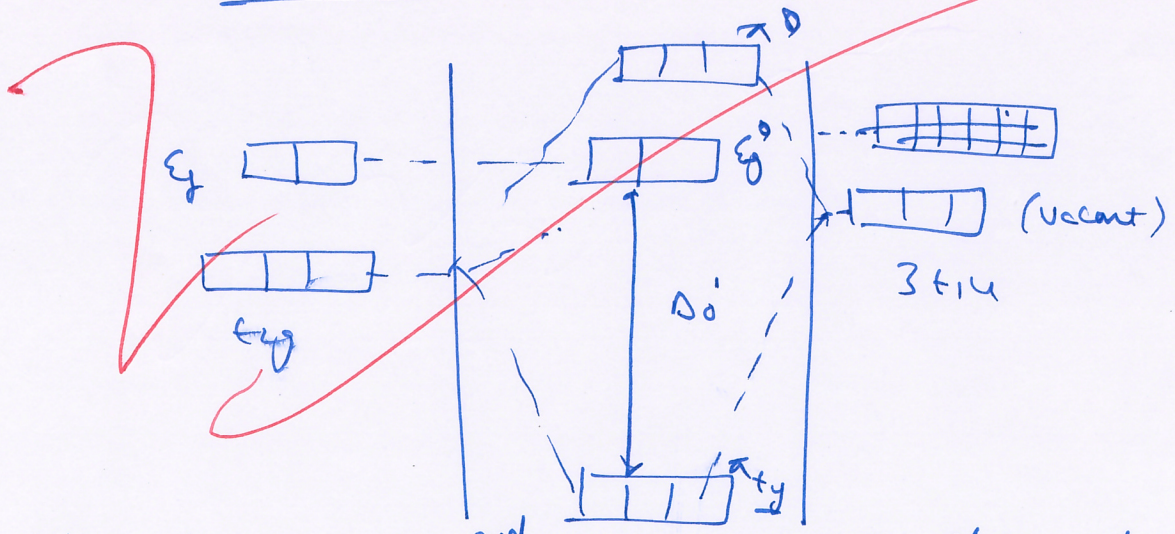
$\Rightarrow \frac{\lambda}{C}$

Section- B

5.(a) 'Although trialkyl phosphines, arsines and stibines are weak σ donors, yet they from kinetically stable complexes with transitional metal ions.' Why is it so? **(10)**

Kinetic stability is measured through inertness of a complex to resist substitution of ligand at 25°C.

$P(R)_3$, stibines and arsines have vacant d/π^* orbitals which facilitates back-bonding from the central atom. Thus the overall stability increases. Due to rise in bond strength (double bond character) ⇒ Kinetic stability is observed.

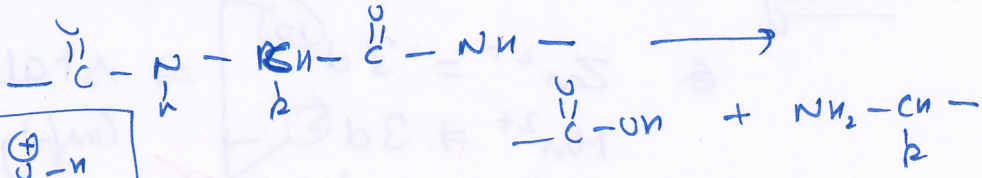


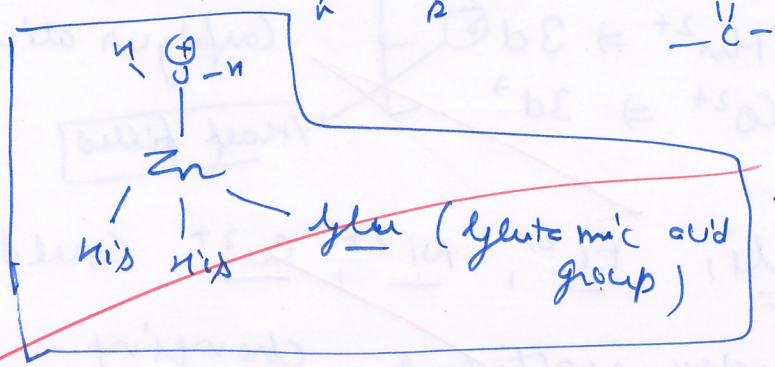
Since Δ_o increases and M ⇄ L bond is observed.

(b)(i) Discuss probable difference present in carboxypeptidase and carbonic anhydrase. **(5)**

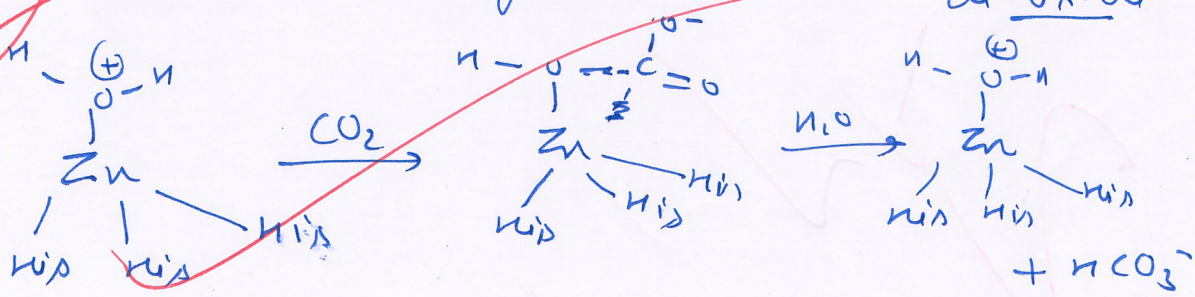
Both involve usage of zinc metal

carboxypeptidase ⇒ facilitates hydrolysis of peptide bond (terminal)





Carbonic Anhydrase ⇒ facilitates hydration and dehydration of carbon di-oxide



$$CO_2 + OH^- \xrightleftharpoons{CA} HCO_3^-$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

(ii) Common ion in enzyme system are those that have low site preference such as Co^{+2}, Zn^{+2}, Mn^{+2} rather than Fe^{+2}, Ni^{+2} and Cu^{+2}. Explain? **(5)**

Since, Mn^{2+}, Zn^{2+}, Co^{2+} do not undergo redox reactions readily due to

$Zn^{2+} = 3d^{10}$ → Fully filled

$Mn^{2+} \Rightarrow 3d^{5}$ → Half filled

$Co^{2+} \Rightarrow 3d^{7}$

$\Rightarrow$ stable configurations

While, Fe^{2+}, Ni^{2+}, Cu^{2+} could undergo redox reactions, changing their oxidation state.

(c) What are shortcomings of Lindemann theory? How are they overcome in Hinselwood theory. **(10)**

Lindemann theory provides for dimerisation

$$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} A^*$$

$$A^* + A \xrightarrow{k_2} A_2$$

$$\text{rate} = k_2 [A^*][A]$$

$$\frac{d[A^*]}{dt} = k_1[A] - k_1'[A^*] - k_2[A^*][A]$$

$$[A^*] = \frac{k_1[A]}{k_1' + k_2[A]}$$

$$\boxed{\text{rate} = \frac{k_2 k_1 [A]^2}{k_1' + k_2[A]}}$$

at lesser $[A]$ rate $\propto [A]^2$ (Bimolecular)

greater $[A]$ rate $\propto [A]$ (unimolecular)

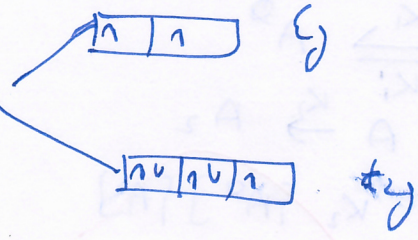
Shortcomings

- Through this method further polymerization may be possible (Eg) $\boxed{A^* + A_2 \rightarrow A_3}$
- Do not well provides for intermediate mechanism between bimolecular and unimolecular.

(d) (i) The magnetic moment of $[CoNCS)_4]^{2-}$ is 4.4 BM. Discuss. **(5)**

$Co^{2+} = 3d^7$

Since NCS⁻ is a weak field ligand

Co^{3+} - - 

$\mu = \sqrt{(3)(5)}$ B.M.
(spin only)

$= 3.87$ B.M

But, slightly greater magnetic moment may exist due to orbital movement of e⁻.

(ii) Explain why $[Co(CN)_6]^{3-}$ is inert but $[CoBr_6]^{3-}$ is a labile complex. **(5)**

Inertness and lability depends on the value of octahedral splitting.

For,

$[Co(CN)_6]^{3-}$

Since CN^- is a strong field ligand

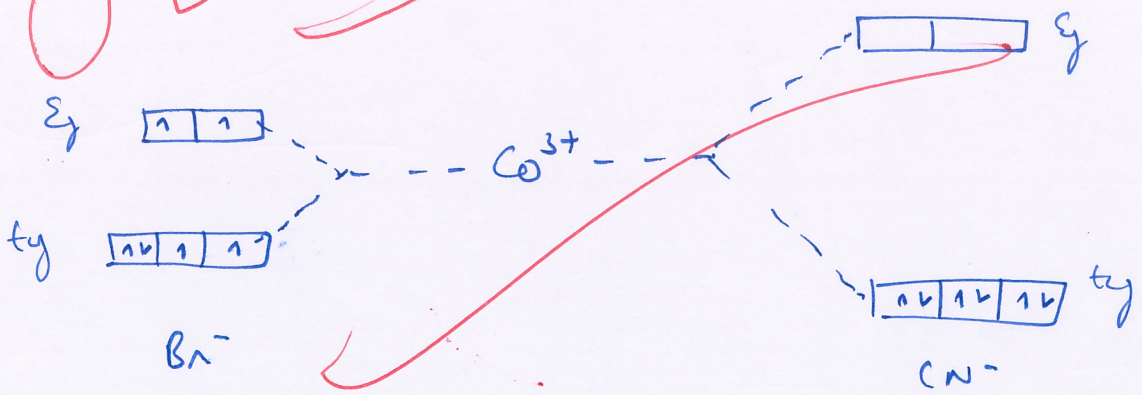
$Co = 3d^6$

$[Co(Br)_6]^{3-}$

Br^- is a weak field ligand

3

$\boxed{\text{splitting differences}}$



CFSE $\Rightarrow -0.4\Delta_o$

CFSE $\Rightarrow -2.4\Delta_o$

Thus, $(CFSE)_{[Co(CN)_6]^{3-}} > (CFSE)_{[CoBr_6]^{3-}}$

(ii)) Show that in a first order reaction, the time required for completion of 99% reaction is 10 times of the half-life ($t_{1/2}$) of the reaction. **(5)**

For a first order reaction

$$A \xrightarrow{k} P$$

$$-\frac{d[A]}{dt} = k[A]$$

where k = rate constant
t = time.

$$[A] = [A_0] \exp(-kt)$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k}} = \boxed{\frac{0.693}{k}}$$

For $t_{99\%}$ ⇒ ~~Let~~ $[A] = 1$ $[A]_0 = 100$

$$t_{99\%} = \frac{\ln(100)}{k} = \frac{4.6}{k}$$

Thus, time required is not 10 times but 6.63 times

3½

8(a) Name one nonmetallic polymer which exhibits super conductance at low temperatures. Discuss the preparation and structure of this polymer. **(10)**

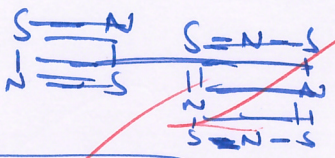
One such non-metallic polymer is $(SN)_x$ (polythioazyl)

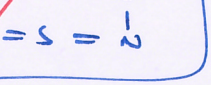
Since, S and N have little electronegativity difference, Katenation property is observed.

Preparation

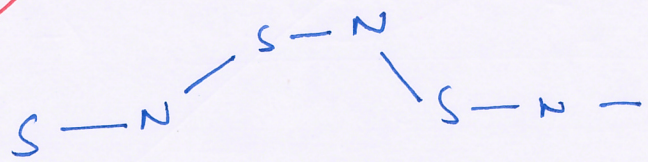
$$S_4N_4 \xrightarrow[\text{High T, P}]{\text{Ag-glass}} S_2N_2 \xrightarrow[\text{days}]{\text{Several}} (SN)_x$$

(Polymer)





Structure



Parallel stacking is observed with continuous chains.

(b) 0.50 g of benzoic acid was subjected to combustion in a bomb calorimeter when the temperature of the calorimeter system (including water) was found to rise by 0.55^{0}C. Calculate the enthalpy of combustion of benzoic acid. The C calorimeter constant was found to be 23.85 Kj K^{-1}. **(10)**

Bomb calorimeter is used to calculate internal energy of any reaction

$$\Delta U = C\,\theta\,\frac{M}{m}$$

C = Calorimeter constant

θ = Temperature change

M = molar mass

m = mass provided

ΔU = internal energy change

$$\Delta U = -(23.85)(0.55)\frac{(122)}{(0.5)}\ KJ$$

$$\Delta U = -3200.6\ KJ$$

we know, $\Delta H = \Delta U + \Delta n_g RT$

(enthalpy of combustion)

$$C_6H_5COOH_{(s)} + \frac{15}{2}O_{2(g)} \longrightarrow 7CO_{2(g)} + 3H_2O_{(l)}$$

$$\Delta n_g = 7 - 7.5 = -0.5$$

$$\Delta H = (-3200.6\ KJ) - (0.5)\frac{(8.314)(298)}{1000}\ KJ$$

$$\boxed{\Delta H = -3201.8\ KJ}$$

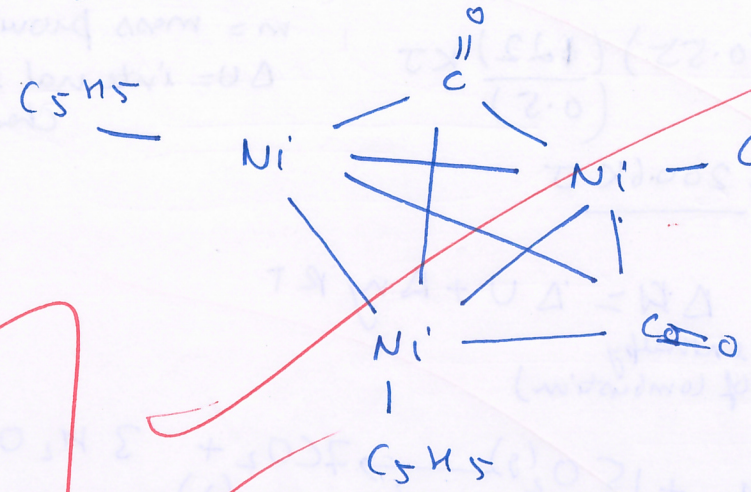
(c)) The compound $[Ni_3(C_5H_5)_3(CO)_2]$ has a single CO stretching absorption at 1761 cm^{-1}. The IR data indicate that all C_5H_5 ligands are pentahapto and probably in identical environments:

On the basis of these data, propose a structure.

Does the electron count for each metal in the structure agree with the $18e^-$ rule?. **(10)**

Provided, C_5H_5 are equally situated and also CO is equally situated

Possible structure



Checking for $18e^-$ rule $\Rightarrow \dfrac{(3)(10) + 3(15) + (2)(2) + 6}{3}$

$= 18.33\ e^-$

Thus, not being followed.

(d) Many actinoid oxides are non-stoichiometric but few lanthanoid oxides are non-stoichiometric. **(10)**

Actinoids could exist in number of oxidation states, which gives rise to several crystal defects, ~~non~~ stoichiometric in nature, such as Metal deficiency defect.

While for lanthanides, +3 oxidation state is predominately present, with little chances of conversion to other oxidation states.

Thus, no stoichiometric defect is observed in lanthanoid crystal. Thus it remains in stoichiometric proportions.

(e) A flask of 4 dm^3 capacity contains O_2 at 101.325 kPa and 298 K. The gas pressure is reduced to 0.19 Pa by attaching the flask to a pump. Assuming ideal behavior, answer the following:

What will be the volume of the gas which is left behind?

What amount of O_2 and the corresponding number of molecules are left behind in the flask ?

If now, 2 g of N_2 is introduced, what will be the pressure of the flask?. **(10)**

(#) Provided, ideal gas.

$\cancel{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$ $\quad n_i = \frac{P_1V_1}{RT_1}$ $\quad n_f = \frac{P_2V_2}{RT_2}$

$n_i = \frac{(1\ atm)(4\ l)}{(0.0821\ atm\ l/K/mol)(298)} = 0.16\ moles$ —(i)

$\cancel{n_f = \frac{(0.19)}{(101.325)(10^3)}}$ $\quad n_f = \frac{(0.19)(4)}{(101.325)(1000)(0.0821)(298)} = 3\times10^{-7}$ moles

(i) Volume of gas left behind ⇒ $V_2 = 4\ dm^3$

$\cancel{P_1V_1 = P_2V_2}$

$\cancel{(4)(101.325)(1000) = (0.19)\ V_2}$

$\cancel{V_2 = 2.13\times10^6\ dm^3}$

(ii) moles of O_2 from (i) = 0.16 moles to 3×10^{-7} moles

No. of molecules = $0.16 \times 6.022\times10^{23}$ = 8.96×10^{16} molecules

~~(iii) Total moles now ⇒ $\frac{2}{28} \Rightarrow \frac{1}{14}$ moles + 0.16 moles~~

~~= 0.23 moles~~

~~Thus pressure ⇒ $\frac{P_2}{P_1} = \frac{n_2}{n_1}$~~

~~$\frac{P_2}{0.19} = \frac{0.23}{0.16} = 0.27\ P_2$~~

Pressure : $P = \frac{(\frac{1}{14})(0.0821)(298)}{4\ (dm^3)} = 0.43\ atm$

$V_2 = 4\ dm^3$ | $n = 3\times10^{-7}$ | $P_2 = 0.43$ atm