DIAS

All India TEST – SERIES CSE – 2023

Paper-1 (Test-7)

Syllabus -: Full Syllabus

Instructions:-

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

Information:

Name of student:- PURURAJ SINGH SOLANKI

UPSC Roll no:-

Mobile Number 7726842413

Date of Submission :-

Dias Roll Number :-

Official use.

Q.No	1	2	3	4	5	6	7	8
Mark:	34	28	34		26	~~30~~		31

Total Marks	148/250

Signature of invigilator

Signature of Examiner

Section-A

1.(a) Explain the number of metal bonds in the following molecules which obey16/18 e rule. Draw their structures. **(10)**

(i) $Fe_3(CO)_{12}$ (crystal) .

(ii) $[(\eta^5 - Cp)Fe(CO)(\mu - CO)]_2$

(iii) $[Rh(COD)Cl]_2$

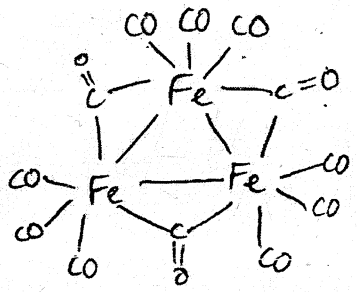
Number of metal bonds is given by EAN rule

(i) $Fe_3(CO)_{12}$

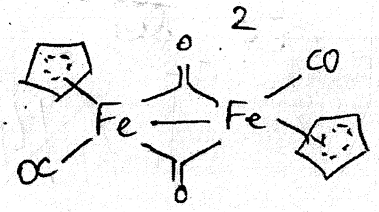
Total e^- = $18 \times 3 = 54$

present e^- = $12 \times 2 + 8 \times 3 = 48$

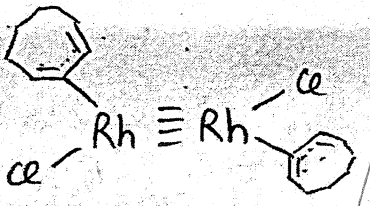
M-M bonds = $54 - 48/2 = 3$



(ii) $\frac{18 \times 2 - 5 \times 2 - 8 \times 2 - 4 \times 2}{2} = 1$ M-M bond



(iii) ~~$2 \times 10 = 10 \times 2 - 9 \times 2$~~ $\frac{18 \times 2 - 4 \times 2 - 8 \times 2 - 2}{2} = 4$

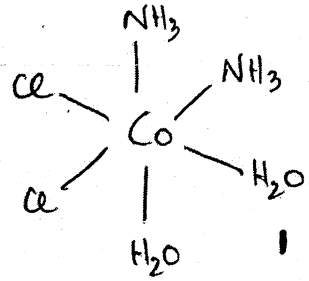


(b) Sketch all isomers of $[Co(NH_3)_2(H_2O)_2Cl_2]$ (10)

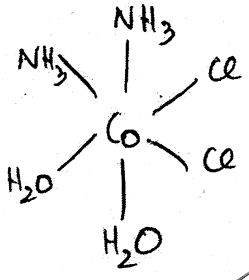
This is an Octahedral geometry Complex where oxidation state of Cobalt is given by

$$x - 2 = 0 \Rightarrow x = 2 \Rightarrow \boxed{Co^{2+}} \Rightarrow d^7 \text{ configuration}$$

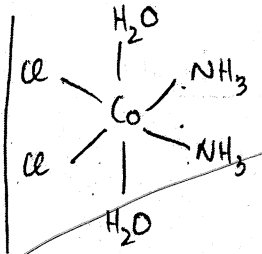
Isomerism arises due to different spatial arrangement of ligands around central Cobalt ~~ator~~ ion.



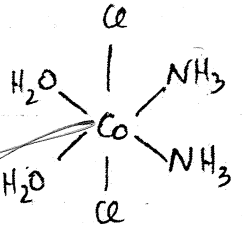
- all cis
- Optically active



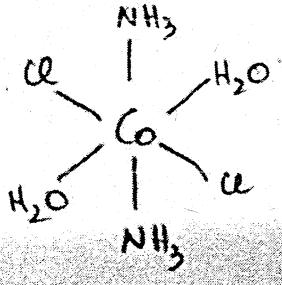
Enantiomeric pair



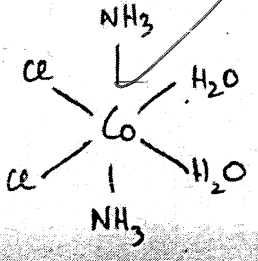
- H_2O trans rest cis



- Cl trans rest cis



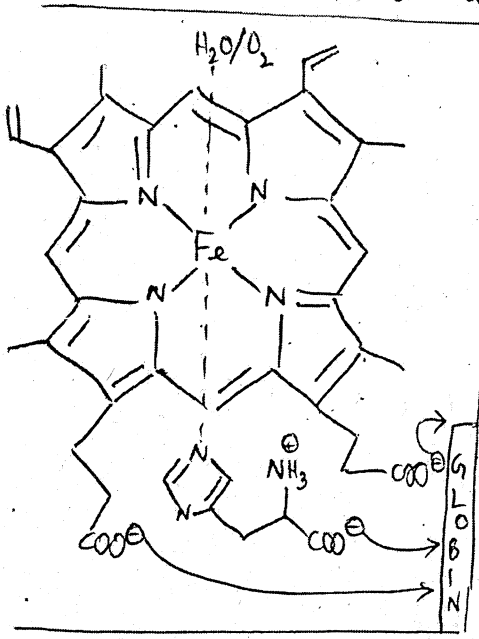
- all trans
- Optically inactive



- NH_3 trans, rest cis

(c) Write the names of macrocylic ligand present in hemoglobin. Explain the coordination of Fe, and its coordinating atoms. Give the importance of the coordination number of Fe and geometry of Fe. (10)

Hemoglobin is oxygen carrying protein present on red blood cells of mammals. It consists of Central Fe(II) coordinated to Heme prosthetic group



Coordination of Fe :-

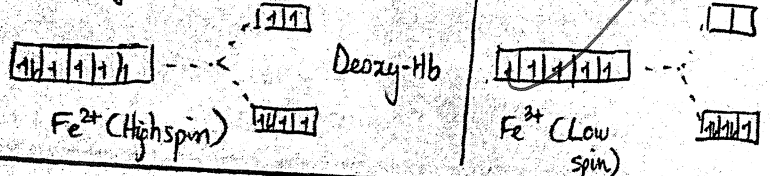
① Octahedral geometry with 4 planar positions occupied by Nitrogen from heme prosthetic group

② 5th position occupied by H_2O in deoxy-Hb, and by O_2 in Oxy-Hb

③ 6th position is occupied by N of imidazole from Histidine amino acid.

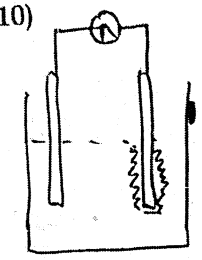
④ $COO^{\ominus}$ groups from heme prosthetic group and histidene bind to globin protein, which further contains 4 such Hb units in a tetrahedral fashion

⇒ Coordination number of Fe is 6 and geometry is octahedral as explained by CFT



(d) Given ,AgBr(s) + e⁻ ⟹ Ag⁺ + Br⁻ ; E^0_+ =0.071 V Ag⁺ + e⁻ ⟹ Ag(s) ; E^0_- = 0.799 V
Compute the solubility product expressed as AgBr(s) + e⁻ ⟹ Ag⁺ + Br⁻.

(10)



Electrochemical Cell at equilibrium is considered with following half cell reactions :-

Anode $Ag \rightleftharpoons Ag^+ + e^-$

Cathode $AgBr(s) + e^- \rightleftharpoons Ag + Br^-$

Net reaction $AgBr(s) \rightleftharpoons Ag^+ + Br^-$

Using Nernst Equation, E_{cell} is given by :-

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \log \frac{\prod[\text{products}]}{\prod[\text{reactants}]} \quad \text{— ①}$$

Since equilibrium cell $\therefore \Delta G_{rxn} = 0$, But $\Delta G = -nFE_{cell} \therefore E_{cell} = 0$ — ②

From ① and ②

$$0 = E^\circ_{AlO} + E^\circ_{ClR} - \frac{0.059}{1} \log \frac{[Ag^+][Br^-]}{1}$$

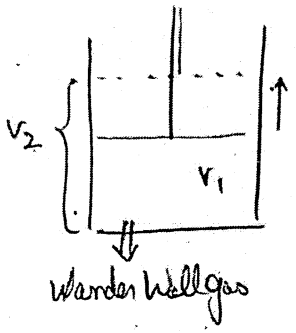
Given $E^\circ_{AlO} = -0.799$ V , $E^\circ_{ClR} = 0.071$ V , $[Ag^+][Br^-] = K_{sp}$

$$0 = -0.799 + 0.071 - 0.059 \log K_{sp}$$

$$\log K_{sp} = -12.388$$

or $\boxed{K_{sp} = 4.59 \times 10^{-13}\ M^2}$

(e) Deduce the expression for the work the work done W, change of internal energy ΔU and change of enthalpy ΔH for the reversible expansion from volume V_1 to volume V_2 for a van der Waals gas. (10)



Vander Waal gas follows.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad — ①$$

From Fast law of thermodynamics

$$\Delta U = q + w$$

$$dU = dq + dw \quad — ②$$

where $dw = -P_{ext}\,dV = -P\,dV$ for reversible process

Assume Constant T

$$dw = -\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right] dV$$

$$dw = \int_{V_1}^{V_2} \frac{n^2 a\, dV}{V^2} - \int_{V_1}^{V_2} \frac{nRT\, dV}{V - nb}$$

$$\boxed{W = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right)}$$

Now $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

Since $dT = 0$ (assume)

$$\therefore \quad dU = \left(\frac{\partial U}{\partial V}\right)_T dV \quad — ③$$

From Thermodynamic equation of state - I

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad — ④$$

Use in ③

$$dU = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

$$\int dU = \int_{V_1}^{V_2} \frac{an^2}{V^2} dV$$

$$\boxed{\Delta U = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)}$$

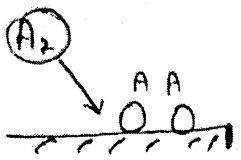
$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (\because dT = 0)$$

and $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = b - \frac{2a}{RT}$

$$\therefore \quad dH = \int \left(b - \frac{2a}{RT}\right) dP$$

$$\boxed{\Delta H = \left(b - \frac{2a}{RT}\right)(P_2 - P_1)}$$

2(a) For the dissociative chemisorptions of gaseous A_2 at pressure P $A_{2(g)} \rightleftharpoons 2\,A_{(ads)}$, derive equation for the fractional surface coverage (θ) using Langmuir theory. **(10)**



Surface chemisorption analysis using langmuir theory. $2S + A_2(g) \rightleftharpoons 2A(ads)$

where S = Surface active site

Fractional surface coverage = θ, Total sites = C_s

$\therefore [S] = C_s(1-\theta)$ — ①

$[A] = C_s\theta$ — ②

Since chemisorption here is dynamic equilibrium:

$Rate_{(adsorption)} = Rate_{(desorption)}$ — ③

$Rate_{ads} = K_a(P_{A_2})[C_s(1-\theta)]^2$ — ④

$Rate_{des} = K_d[C_s\theta]^2$ — ⑤

Equating ④ and ⑤

$K_a P_{A_2} C_s^2 (1-\theta)^2 = K_d C_s^2 \theta^2$

$\left(\frac{1-\theta}{\theta}\right)^2 = \left(\frac{1}{P_{A_2}}\right)\left(\frac{K_d}{K_a}\right)$

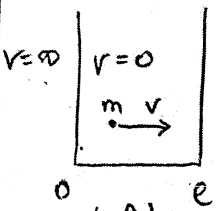
$K_{eq} = \frac{K_a}{K_d}$

$\left(\frac{1}{\theta} - 1\right)^2 = \left(\frac{1}{P_{A_2}}\right)\left(\frac{1}{K_{eq}}\right)$

$\frac{1}{\theta} = 1 + \sqrt{\frac{1}{P_{A_2} K_{eq}}}$

or $\boxed{\theta = \frac{\sqrt{P_{A_2} K_{eq}}}{1 + \sqrt{P_{A_2} K_{eq}}}}$

(b) Show that the function A $\sin \frac{n\pi x}{L}$ for a particle in a one - dimensional box of length L is not an eigenfuncation of the momentum operator, $\hat{P}_x = \frac{\hbar}{i}\frac{d}{dx}$, but it is so of p^2. Discuss the significance of the result. (10)



A function is said to be eigenfunction of an operator when operation of later on the former yields an eigen value with regeneration of the eigenfunction.

$$\psi_n = A \sin\left(\frac{n\pi x}{e}\right), \quad \hat{P}_x = +\frac{\hbar}{i}\frac{d}{dx}$$

$$\hat{P}_x \psi_n = \frac{\hbar}{i} A \frac{d}{dx}\left[\sin\left(\frac{n\pi x}{e}\right)\right] = \frac{\hbar}{i} A \left(\frac{n\pi}{e}\right) \cos\left(\frac{n\pi x}{e}\right)$$

Here ψ_n is not regenerated ∴ not an eigenfunction of $\hat{P}_x$

Consider $\hat{P}_x^2 = -\hbar^2 \frac{d^2}{dx^2}$

$$\hat{P}_x^2 \psi_n = -\hbar^2 A \frac{d^2}{dx^2}\left[\sin\left(\frac{n\pi x}{e}\right)\right] = +\hbar^2 A \left(\frac{n\pi}{e}\right)^2 \sin\left(\frac{n\pi x}{e}\right)$$

Thus $\boxed{\hat{P}_x^2 \psi_n = \hbar^2 \left(\frac{n\pi}{e}\right)^2 \psi_n}$ satisfies $\boxed{\hat{A}\psi = a\psi}$

Significance

→ Since momentum corresponding to a given energy gives 2 values (positive and negative) no uniqueness of eigenvalue

→ However $P_x^2 = 2mE$, unique value of energy gives unique P_x^2 value

Thus P_x^2 follows the eigen criteria.

(c) Using a radiation source of 250 W at 250 nm, a compound was irradiated for 90 mins. 40% of the light was reflected off and the rest was absorbed by the compound. After irradiation, 0.02 moles of the compound was found to have decomposed. Calculate the quantum yield for the decomposition. **(10)**

Quantum yield is defined as amount of decomposed material relative to the amount of photochemical radiation it absorbs to do so.

Mathematically $\phi = \left[\frac{-\frac{d[R]}{dt}}{Ia}\right]$ — ①

Ia (Radiation absorbed in moles) = Moles of photons absorbed

Total Energy absorbed = (Power of source) × (time) × (absorption efficiency) — ②

Total moles of photons absorbed (n) is given by

$N\frac{hc}{\lambda}$ = Power × t × efficiency

$\therefore N = \left(\frac{\lambda}{hc}\right)$(Power)(time)(efficiency) $\quad n = \frac{N}{N_A}$ (Avogadro)

$\phi = \left(\frac{\text{Moles decomposed}}{n}\right) \frac{(\text{mol})0.02 \times 6.626\times10^{-34}\,\text{J s} \times 3\times10^{8}\,\text{m s}^{-1} \times N_A}{250\times10^{-9} \times 250\,\text{J s}^{-1} \times 90 \times 60\,\text{s} \times 0.4 \times \text{m}}$

$\boxed{\phi = 1.77\,\%}$

(d) (i) Applying the law of equipartition of energy, estimate the energy of H_2 molecule assuming that all the degrees of freedom are excited and contribute towards the energy of the molecule. Give the statement of the law. (5)

Equipartition of energy states that the molecular energy is divided or partitioned into its degrees of freedom (dof) with respective contributions of $\frac{KT}{2}$, $\frac{KT}{2}$ and KT per molecule in translational, rotational and vibrational freedoms.

H_2 – Bimolecular	dof		Energy
Translational	3	$\Rightarrow$	$3KT/2$
Rotational	3	$\Rightarrow$	$3KT/2$
Vibrational	3	$\Rightarrow$	$3KT$

Total energy of H_2 ~~atom~~ molecule is $\boxed{6KT}$

(e) Justify the following statements : (10)

(i) The net entropy of the Universe increases.

(ii) X rays are used for diffraction by crystals

(i) Considering a path from point A to point B thermodynamically

A $\xrightarrow{\text{reversible}}$ B

A ← irreversible ← B

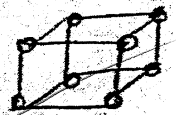
It is derived that $\Delta S_{A\to B} > \int_A^B \frac{dq_{rev}}{T}$

Clausius inequality

By assuming universe as an isolated system, we infer that dq_{univ} is zero. RHS becomes zero which leaves us with $\boxed{\Delta S_{univ} > 0}$

Hence Net entropy of universe increases.

(ii). Diffraction study of crystals requires interaction of incident Radiation with the crystal sites, this is possible only when the crystal unit all dimensions are comparable with the wavelength of incoming radiation. Hence x-ray is used due to wavelength in Å.



X Ray – most suitable wavelength

radiation passes through without diffraction

radiation is too big to interact with crystal

3(a) What is virial equation of state for real gases? Express van der Waals equation in the from of virial equation. Discuss the physical significance of virial coefficients. (15)

→ Virial equation of state describes the gaseous behaviour for a Real gas by making correction to ideal gas law using certain Coefficients.

→ Compressibility factor Z is defined as PV_m/RT. It is 1 for ideal gas but it is an infinite expansion series for Virial equation

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \cdots \quad — (1)$$

→ Another equation to describe Real gas behaviour is given by Vander Wall as :-

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad — (2)$$

Rearranging (2)

$$P = \left(\frac{RT}{V_m - b}\right) - \frac{a}{V_m^2}$$

$$\frac{PV_m}{RT} = \left(\frac{V_m}{V_m - b}\right) - \frac{a}{V_m RT} = \frac{1}{\left(1 - b/V_m\right)} - \frac{a}{V_m RT}$$

Since $\frac{PV_m}{RT} = Z$ $\therefore$ $Z = \left(1 - b/V_m\right)^{-1} - \frac{a}{V_m RT}$ — (3)

Using the relation $(1+x)^{-1} = 1 - x + \frac{x^2}{1} - \frac{x^3}{1} + \ldots$

where $x \ll 1$ [true because here $b \ll V_m \Rightarrow \frac{b}{V_m} \ll 1$]

Re writing ③

$$Z = 1 + \left(\frac{b}{V_m}\right) + \frac{1}{1}\left(\frac{b}{V_m}\right)^2 + \frac{1}{1}\left(\frac{b}{V_m}\right)^3 + \ldots - \frac{a}{V_m RT} \quad 1$$

$$Z = 1 + \left(\frac{1}{V_m}\right)\left(b - \frac{a}{RT}\right) + \left(\frac{b^2}{1}\right)\left(\frac{1}{V_m^2}\right) \ldots\ldots - ④$$

Comparing ④ with Virial equation of state

we have $\boxed{B = b - \frac{a}{RT} \quad | \quad C = b^2}$

Higher terms are not important due to very small magnitude

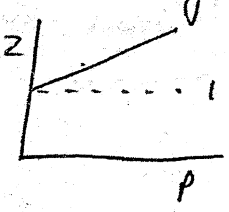
Physical significance of Virial Coefficients

→ At some particular temperature, for appreciable range of pressure a real gas shows ideal behaviour. This is boyle Temperature (T_B)

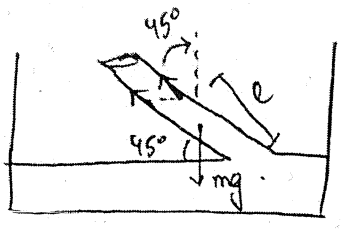
Here $Z = 1$ ∴ B should be 0, C is already very small.

∴ $b - \frac{a}{RT_B} = 0$ or $\boxed{T_B = \frac{a}{bR}}$

→ Since B, C, D ... are all positive, Z of Virial gas is always higher than 1, hence Z vs P for virial gas is



(b) A capillary tube of radius 0.001 cm is inclined at an angle of 45^0 to the surface of liquid. The liquid wets the wall of the tube. Calculate the distance along the capillary to the meniscus of the liquid if the density of the liquid is 0.85 g cm^{-3} and the surface tension is 36 dynes cm^{-1}. **(10)**



Capillary action due to wetting property of liquid causes it to rise up the capillary.

Force due to Surface tension on the liquid meniscus is $S \times (2\pi r)$ — ① [∵ Angle of Contact is 0 - wetting liquid]

This force balances the gravitational force arising out of risen liquid column.

Gravitational force = $mg = \pi r^2 \ell \rho g$

where ℓ = distance along capillary.

Equating forces in vertical direction

$$S(2\pi r)\sin(45^0) = \pi r^2 \ell \rho g.$$

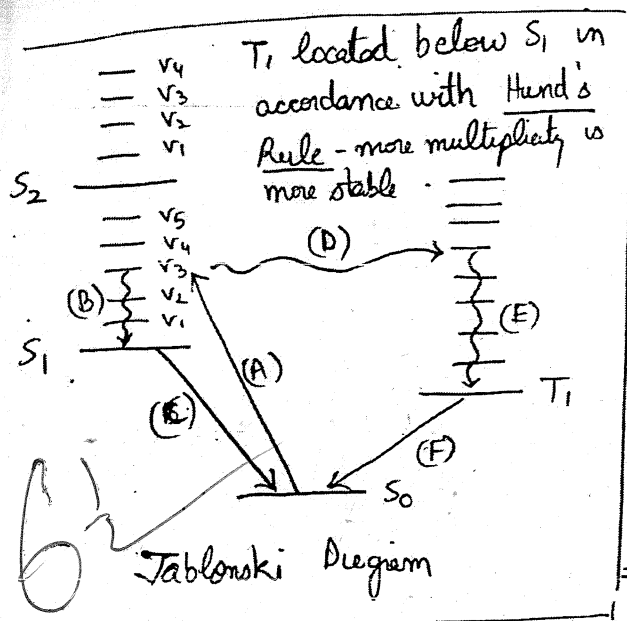
$$\frac{2S\sin(45^0)}{\rho g r} = \ell$$

$$\therefore \ell = \frac{2 \times 36 \text{ dyne cm}^{-1} \times 1}{\sqrt{2} \times 0.85 \text{ gcm}^{-3} \times 980 \text{ cms}^{-1} \times 0.001 \text{ cm}}$$

Distance along the capillary = 61.118 cm

(c) The average lifetime of phosphorescence is higher than fluorescence. Explain with Jablonsky diagram. (10)

Jablonsky diagram is representation of possible electronic transitions in a photo active molecule due to electromagnetic radiation.



Jablonski Diagram

(A) initial excitation
(B) Vibrational Relaxation
(C) Fluorescence
(D) Internal Conversion ($S_1 v_j \rightarrow T_1 v_k$)
(E) vibrational Relaxation
(F) Phosphorescence

⇒ Fluorescence (represented by transition C in diagram) refers to relaxation from excited singlet state (S_1) back to ground state S_0. As depicted, it is a high energy transition compared to Phosphorescence (shown by F).

⇒ Using Heisenberg Uncertainity Principle

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

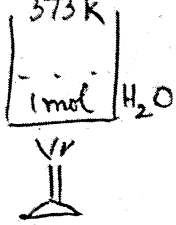
Since $\Delta E_{flu} > \Delta E_{phos}$

$$\Delta t_{phos} > \Delta t_{flu}$$

Hence average lifetime of phosphorescence (0.1–100 ms) is higher than fluorescence (< 0.01 ms). This property is utilised in night vision watches.

(d) 18.0 g of liquid water vaporizes at 1 bar and 373 k. Calculate q, w, ΔU, ΔH, ΔS, ΔA and ΔG (in SI units) for this process. given, latent heat of vaporization of liquid water at 1 bar and 373 K is 540 cal g^{-1}. (15)

1bar (1 atmosphere)



Water vaporisation process at constant pressure takes in latent heat without change in system Temperature. Assuming ideal gas behaviour for water vapor produced.

(I) q (Heat) $= mL$ where m = mass of water
L = Latent heat

$q = 18\,g \times 540\,cal\,g^{-1}\,mol^{-1} \times 1/4.18\,J\,cal^{-1}$

$\boxed{q = 1.937\ KJ\ mol^{-1}}$ Here $q = 1.937$ KJ itself

(II) $W = \int -P_{ext}\,dV = -P_{ext}\int dV$

or $W = -P_{ext}(V_{vapor} - V_{liq})$

Since $V_{vap} \gg V_{liq}$

$W = -P_{ext}\,V_{vapor} = -nRT$ (ideal gas law)

$W = -1 \times 8.314\ JK^{-1}\,mol^{-1} \times 373\ K$

$\boxed{W = -3.101\ KJ\,mol^{-1}}$ negative since expansion against external pressure

(III) $\Delta U = q + W = 1.937 - 3.101 = \boxed{-1.164\ KJ\,mol^{-1}}$

(III) ΔU (internal energy change) is solely Temperature dependent for ideal gas. Since $dT = 0$, $\boxed{\Delta U = 0}$

(IV) $\Delta H = \Delta U + \Delta PV = \Delta U + nR\Delta T$

Since $\Delta T = 0$, Both ΔU and $\boxed{\Delta H = 0}$ ΔH are equal to $-1.164\ KJ\ mol^{-1}$

(V) $\Delta S_{(sys)} = \frac{q_{rev}}{T} = \frac{1.937\ KJ mol^{-1}}{373\ K}$

$$\boxed{\Delta S_{sys} = 5.193\ J\ mol^{-1} k^{-1}}$$

$$\Delta S_{surr} = -\frac{q_{rev}}{T} \qquad \Delta S_{univ} = 0$$

(VI) $\Delta A = \Delta U - T\Delta S$ (Work function) $= -1.164 - 1.937$

~~$0 = TAS_{sys}$~~

$$\boxed{\Delta A = -q_{rev} = -1.937\ KJ mol^{-1}}$$

$$\boxed{\Delta A = -3.101\ KJ\ mol^{-1}}$$ — equal to work done.

(VII) $\Delta G = \Delta H - T\Delta S = \Delta A$

$$\boxed{\Delta G = -3.101\ KJ\ mol^{-1}}$$

4(a). An ideal gas follows two different routes to change its state from X to Z: (10)

5(a) Arrange the following metal compounds in the increasing order of their molar extinction coefficient values. Explain the reasons. **(10)**

$KMnO_4$, $[Co(NH_3)_6]^{2+}$, $[MnBr_4]^{2-}$ and $[CoCl_4]^{2-}$

Extinction coefficient values are directly related to lability of complexes.

* $KMnO_4$ - d^0
* $[Co(NH_3)_6]^{2+}$ - d^7 - low spin
* $[MnBr_4]^{2-}$ - d^5 - high spin
* $[CoCl_4]^{2-}$ - d^7 - high spin

Using CFAE explanation, d^0 is inert

d^7 (low spin) less labile than d^7 (high spin)

d^5 (high spin) ~~most labile~~.

∴ Molar extinction coefficient order.

~~$[MnBr_4]^{2-}$~~ $KMnO_4 < [Co(NH_3)_6]^{2+} < [CoCl_4]^{2-} < [MnBr_4]^{2-}$

(b) Iodine and bromine are added to a solution containing I^- and Br^- ions. What reaction would occur? Explain. **(10)**

$I_2 + 2e^- \rightarrow 2I^-$, $E^0 = +0.54$ V

$Br_2 + 2e^- \rightarrow 2Br^-$, $E^0 = +1.08$ V

Standard Reduction potential values help decide the half cell reactions in a cell. More positive standard reduction potential indicates better reaction feasibility. Since

$\Delta G = -nFE^\circ$ when E is more positive, ΔG is more negative

Since $E^\circ_{Br_2|Br^-} > E^\circ_{I_2|I^-}$, Br_2 reduction will be coupled with I^- oxidation for overall positive cell constant.

Anode $2I^- \longrightarrow I_2 + 2e^-$ $E^\circ = -0.54$ V

Cathode $Br_2 + 2e^- \rightarrow 2Br^-$ $E^\circ = +1.08$ V

Net Reaction $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$ $\boxed{E^\circ_{cell} = 0.54\ V}$

$\Delta G_{reaction} = -2 \times 96500\ C \times 0.54V$

$\Delta G_{reaction} = -104.2$ KJ – Highly favoured reaction

(c) A dilute solution of KCl was placed between two Pt electrodes 10 cm apart, across which a potential difference of 6.0 V was applied. What will be the velocity of K^+ ion? Given : molar ionic conductivity of K^+ ion at this dilution and at experimental temperature is 73.52×10^{-4} S m^2 mol^{-1}. **(10)**

Ionic mobility is defined as velocity of an ion per unit potential gradient

Mathematically Ionic mobility $= \dfrac{V_{ion}}{(V/\ell)}$ — ①

Ionic mobility can also be expressed in terms of molar conductivity as Ionic mobility $(U_i) = \dfrac{\Lambda_{m,i}}{Z_i F}$ — ②

For $K^\oplus$ given $\Lambda_{m,K^+} = 73.52 \times 10^{-4}\ S m^2 mol^{-1}$

$Z_{K^+} = +1$, $F = 96500\ C$

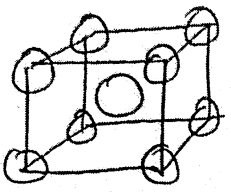
$V = 6V$, $\ell = 10\ cm = 0.1\ m$

Equating ① and ②

$$\frac{V_{ion}}{V/\ell} = \frac{\Lambda_{m,i}}{Z_i F} \quad \text{or} \quad \boxed{V_{ion} = \frac{V \Lambda_{m,i}}{\ell Z_i F}}$$

Using above values Velocity of K^+ ion is $\boxed{4.57\ \mu m s^{-1}}$

(d) An element exists in the bcc structure where cell edge is 2.88 Å. The density of this element is 7.20 g cm^{-3}. How many atoms does 104 g of the element contain? **(10)**



BCC cubic lattice has 8 atoms at all vertices and one central atom

$$2 = \frac{1}{8} \times 8 + 1 = 2 \text{ (atoms per unit cell)} \quad \text{— ①}$$

Given $\rho = 7.20\ g\,cm^{-3}$ (density)

Volume of 104g of the element $= \frac{104\ g}{7.2\ g\,cm^{-3}} = 14.44\ cm^{+3}$ — ②

Volume of single unit cell $= a^3$ where a = cell edge $= 2.88$ Å — ③

Total number of unit cells present $= \frac{14.44\ cm^3}{a^3}$ — ④

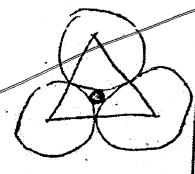
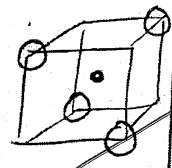
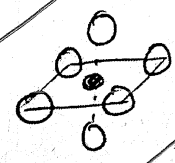
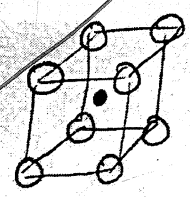
But every unit cell has 2 atoms

$\therefore$ Total atoms in 104 g of element $= \frac{14.44\ cm^3}{a^3} \times 2$

$$\boxed{\text{Total atoms} = 12.089 \times 10^{23}}$$

(e) How the concept of radius ratio governs the coordination number of the ions in a compound? Illustrate with suitable examples. (10)

Radius Ratio Rule relates the ratio of cation and anionic radii to the Coordination number of their compound. It does so by identifying what size of cation can suitably be accomodated within the void space created by anions.

Radius Ratio Range $\left(\frac{r_c}{r_A}\right)$	Coordination Number	Example
0.155 - 0.225	3 	
0.225 - 0.414	4 	ZnS crystal
0.414 - 0.732	6 	NaCl crystal (FCC lattice)
0.732 - 1.0	8 	CsCl crystal (BCC lattice)

8(a). What are meant by phase, component and degree of freedom? Define Gibbs phase rule. A saturated solution of sodium sulphate with excess salt is at equilibrium with its vapour in a close vessel. How many phases, components and degrees of freedom are there in the system? (10)

Phase refers to a homogenous entity which is distinct from its surroundings seperated by a visible boundary.

- Component refers to total number of minimum independent constituents required to completely describe the state of a system at equilibrium
- Degree of freedom are the total number of variables which can be varied independently to alter the state of system
- Gibbs Phase Rule - relates the total phases (P), components (C) and degree of freedoms (F) of a system

It is given by $F = 2 + C - P$

2 represents Temperature and Pressure variables

In case of system with reaction or some additional restriction like equimolar mixture, constant Temperature, azeotrope etc

Phase rule modifies as $F = 2 + C - P - r$

r is total restrictions

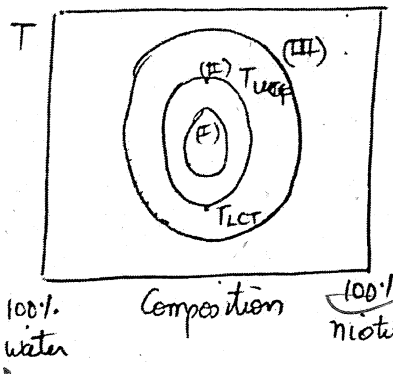
For Na_2SO_4 solution – C = $Na_2SO_4(s)$, Na^+, SO_4^{2-}, $H_2O(l)$, $H_2O(v)$ = 5 r = 2 $H_2O \rightleftharpoons H_2O(v)$, $Na_2SO_4 \rightleftharpoons Na^+ + SO_4^{2-}$

P = 3 F = 2 + C – P – r = 2 + 5 – 3 – 2 = 2 = Degree of Freedom

(b) The nicotine–water system exhibits two critical solution temperatures. What is the effect of external pressure on the system? **(10)**

Nicotine water system ordinarily forms a partially misible solution. However above a certain T called Upper

Consolute Temperature) and also below at certain TC called lower Consolute Temperature), this system forms a completely miscible solution.



- 3 separate curves are considered for 3 pressures $P_I > P_{II} > P_{III}$
- As pressure increases the oval size reduces such that ~~both~~ UCT reduces and LCT increases. This occurs because higher pressure leads to better solubility of both solutions into each other. Thus temperature increase needed to increase mutual solubility reduces. Similarly temperature decrease for better hydrogen bonding increases to higher value.

(c) Give brief account on inter halogen compounds and discuss molecular structure of IF_7. (10)

Interhalogen Compounds are compounds formed among different halogen species. They are mostly of the forms XX'_7, XX'_5, XX'_3, XX'.

Inter halogen compounds are formed due to :-

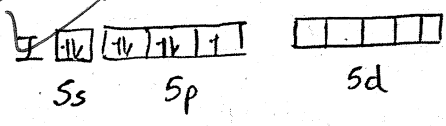
① Better stability due to electronegativity difference between different halogens

② In case of Iodine compounds, Fluorine causes better contraction of 5d orbital causing better overlap and maximum I-F compounds.

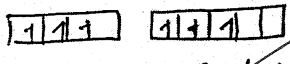
* Reactivity order depends on Electronegativity difference and steric Repulsion

$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF > IF_3 > IF$

⇒ IF_7 - structure

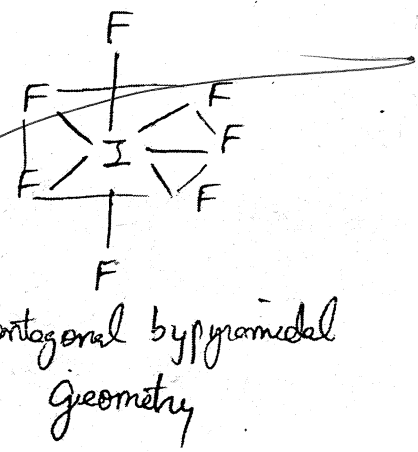


I(excited)



Now 7 F can form Covalent bonds.

in sp^3d^3 hybridised orbitals



Pentagonal bypyramidal Geometry

(d) Localized accumulation of aluminium in the brain is responsible for Alzheimer's disease. Why? (10)

Aluminium accumulation reduces enzyme activity in brain and affects the $Na^+ - K^+$ pumps in the nerve synapses. This causes neural signal leakage in

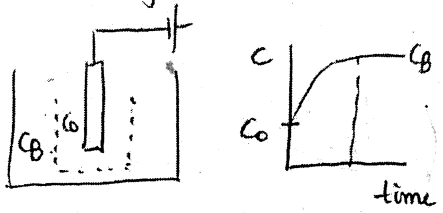
brain causing distorted memory and paralysis symbols, leading to Alzaimer disease. 1/2

most imp. fact "Till date Medical Science has no Concrete evidence that Al^{+3} deposites is responsible" 1

(e) Discuss the working of a polarography. Define $E_{1/2}$ and i_d and mention their application in chemical analysis. **(10)**

Polarography refers to electrolysis of a small amount of electrolyte using a standard electrode along with a micro polarisable electrode. 1

⇒ Working of Polarography



Based on Concentration polarisation i.e. Concentration of electrolyte reduces around electrode with time

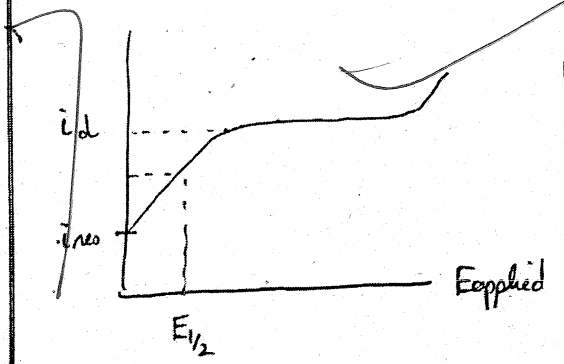
This results in formation of diffusion current (i).

$i = K(C_B - C_o)$ when $C_o = 0$, $i = i_d$ (diffusion limiting current)

$i_d = K C_B$.

Electrode follows $E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} + \frac{RT}{nF} \log\left(\frac{i_d - i}{K}\right)$

$E_{(applied)} \propto i_{(diffusion\ current)}$



when C_o approaches 0, E spikes up and this situation gives i_d.

When $i = i_{d/2}$, $E_{applied}$ is equal to $E_{1/2}$ or half wave potential

This is characteristic property of a particular electrolyte and helps in electrolyte estimation in ionic mixture.

i_d is used for finding Diffusion Coefficient corresponding to that electrolyte.