DIAS

All India TEST – SERIES CSE – 2023

Physical – 2

Syllabus –: Thermodynamics Phase, electrochemistry, kinetics

Instructions:-

1. Attempt five questions selecting atleast one question each section apart from question 1&5 which is compulsory.
2. Write answer in space provided for this purpose only.
3. Total time allowed is 3hr and Marks is 250.

Information:

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Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	24	X	36	33	35	20	X	X

Signature of invigilator

Signature of Examiner

148/250

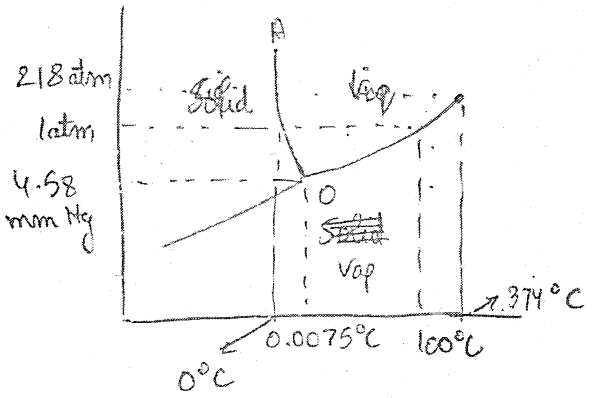
Overall Theory But revise Kinetics & Thermo

Section – A

Q1.(a) Compare and contrast the phase diagram of Water & carbon dioxide. (10)

Phase diagram of a substance depicts the phase transition processes and states of the substance at different P, T values

Water

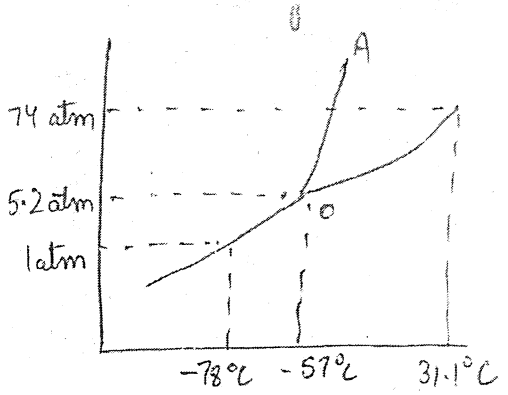


① At 1 atm, water is liquid at room temperature

② Curve OA → Fusion curve has negative slope means water expands on cooling i.e. ice has lower density than liquid water.

③ Higher critical temperature and pressure

Carbon dioxide



① At 1 atm, CO_2 is vapour at room temperature

② Curve OA → Fusion curve has positive slope, CO_2 contracts on cooling.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

③ Lower critical T, P.

(b) Write down Debye-Huckel limiting equation with symbolic significance and unit. Find the ionic strength of 0.01 mol L^{-1} aqueous solution of potassium Ferrocyanide. (10)

Debye-Huckel limiting equation relates the activity coefficient of a species with its ionic strength (i.e. ionic potential of a substance in solution)

Mathematically $\log \gamma_{\pm} = |Z_+ Z_-| A I^{1/2}$

$\gamma_{\pm}$ = Activity coefficient of a compound (unitless)

Z_+ and Z_- are charges on ionic species

A is Debye Huckel Constant = 0.509 $m^{-1/2}$ for water

I = Ionic strength = $\frac{\sum m_i z_i^2}{2}$ (unit = mol/L)

⇒ Significance

→ Applicable to dilute solutions

→ To find activity coefficient from concentration and formula unit

⇒ Ionic strength for 0.01 mol L^{-1} aq. solution of $K_4[Fe(CN)_6]$

$Z_+ = 1$ (K^+) $Z_- = (-4)$ ($[Fe(CN)_6]^{4-}$)

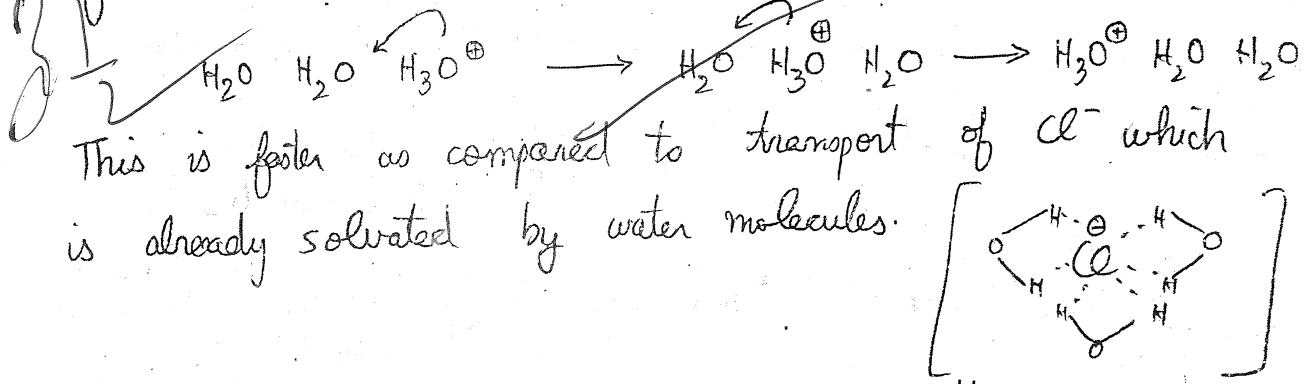
$m_+ = 4 \times 0.01 = 0.04$ mol L^{-1}, $m_- = 0.01$ mol L^{-1}

$$I = \frac{\sum m_i z_i^2}{2} = \frac{0.04 \times 1^2 + 0.01 \times (-4)^2}{2} = \boxed{0.34 \text{ mol } L^{-1}}$$

(c)(i) In an aqueous solution of HCl, the transport number of H^+ ion I is abnormally higher than Cl^- ion. Explain why. (5)

(ii) With increase of temperature of HCl (aq) solution, the transport number of the H^+ ion decreases, though its velocity increases. Explain with reason(S). (5)

(i) Transport number is contribution of an ionic species in total current passing through solution. It is abnormally high for $[H^+]$ due to Grotthus mechanism (proton jump from one water to another water molecule)



This is faster as compared to transport of Cl^- which is already solvated by water molecules.

(ii) On increase in temperature, velocity of both H^+ and Cl^- ions increases due to additionally available thermal energy. Added to this, the solvation sphere of Cl^- ion becomes larger and solvation pull on it decreases. Its t_{Cl^-} increases

Since $t_{H^+} + t_{Cl^-} = 1$ increase in t_{Cl^-} reduces t_{H^+}.

H^+ ions move more haphazardly in all directions, reducing effective transport in a single direction.

(d)(I) Obtain the expression of e.m.f. (E) of the following galvanic cell in terms o fits standard e.m.f(E^0), molality of aqueous solution (m) of the electrolyte and its mean ionic activity coefficient ($\gamma_\pm$) :

$Zn \mid ZnCl_2 (aq, m) \mid AgCl, Ag$ (5)

(ii) The conductivity of $KClO_4$ (aq) solution, at 25 ^{0}C is 13.78 Ms m^{-1} when its concentration is 1.0 mmol dm^{-3}. Calculate its molar conductivity. (5)

(i) $Zn \mid ZnCl_2 (aq, m) \mid AgCl, Ag$.

Half Cell reactions anode $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode $2AgCl + 2e^- \rightarrow 2Ag + 2Cl^-$

Overall $2AgCl + Zn \rightarrow Zn^{2+} + 2Cl^- + 2Ag$

E_{cell} from Nernst equation $= E^\circ_{cell} - \frac{RT}{nF} \ln \frac{\prod [products]}{\prod [reactants]}$

$$E_{cell} = E^\circ_{Zn|Zn^{2+}} + E^\circ_{AgCl|Ag|Cl^-} - \frac{RT}{2F} \cdot \ln \left[\frac{[Zn^{2+}][Cl^-]^2}{1} \right]$$

$$= \left[E^\circ_{AgCl|Ag|Cl^-} - E^\circ_{Zn^{2+}|Zn} \right] - \frac{2.303RT}{2F} \log (4m^3 \gamma_+ \gamma_-^2)$$

Since $\gamma_+ \gamma_-^2 = \gamma_\pm^3$

$$E_{cell} = \left[E^\circ_{AgCl|Ag|Cl^-} - E^\circ_{Zn^{2+}|Zn} \right] - \frac{0.059}{2} \log (4m^3 \gamma_\pm^3)$$

(ii) Molar conductivity is case of conduction between 2 plates of unit distance with suffecient area to accomodate 1 Molar solution in between

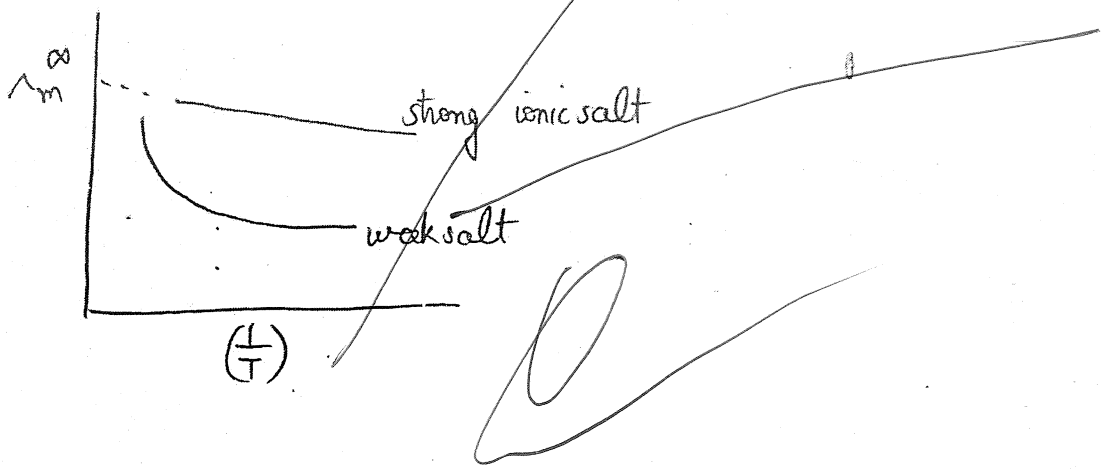
$\Lambda_m = \frac{\kappa}{c}$ κ = Conductivity = 13.78×10^{-5} S cm^{-1}

c = Concentration = 1×10^{-6} mol cm^{-3}

$$\Lambda_m = \frac{13.78 \times 10^{-5}}{10^{-6}} \text{ S cm}^2 \text{ mol}^{-1} \Rightarrow \Lambda_m = 137.8 \text{ S cm}^2 \text{ mol}^{-1}$$

(e) Conductivity of an ionic solution does not depend on its mass but depend on its temperature. Explain with reasons. (10)

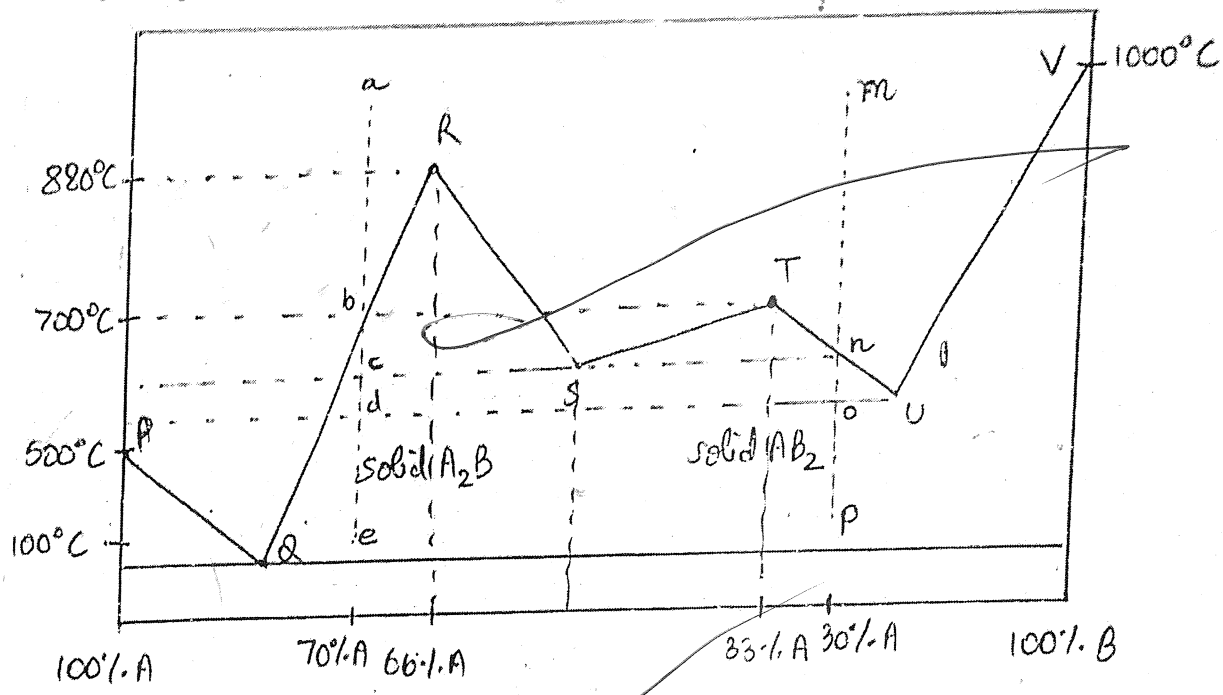
Conductivity of ionic solution is the ratio of Conductance and concentration. As Temperature increases, conductivity varies as



3(a) A & B from two solid A_2B melts at 880°C & AB_2 melts at 700°C. The melting point of A &B is 500°C & 1000°C. Sketch the phase diagram and discuss cooling behaviour of 70% & 30% A&B respectively from 900°C to 100°C. (15)

Given pure solids A and B react to give 2 new solids A_2B and AB_2 with % A as 66·% and 33·% respectively.

Phase diagram depicts the fusion behaviour of solids at varying temperatures along with reaction and product recovery.



Q is eutectic point for pure A and solid A_2B

S is eutectic point for solid A_2B and solid AB_2

U is eutectic point for solid AB_2 and pure solid B.

Melting behaviour of A_2 at 70% from 900°C to 100°C

ab – Homogenous liquid phase

bc – Separation of solid A_2B and melt

cd – separation of solid AB_2 and melt

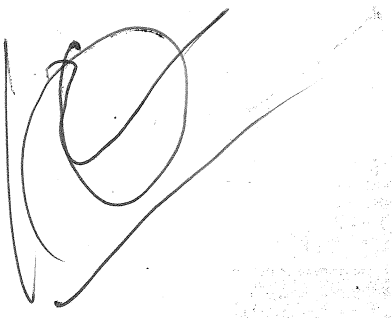
de – separation of melt and pure B

Melting behaviour of 30% A

mn – homogenous liquid phase

no – separate A_2B and melt

op – separate melt and pure B



(b) Discuss basic principle of amperometry? Draw amperometric titration curve of K_2SO_4 Vs Pb^{+2} at $E_{1/2}$ of Pb^{+2}. (15)

Amperometry involves titration processes where the end point is found by monitoring the diffusion current passing through solution.

⇒ Principle of amperometry

(a) Based on Concentration polarisation – concentration of ions changes around the electrode over time due to diffusion, this changes the reduction potential of electrode as per:

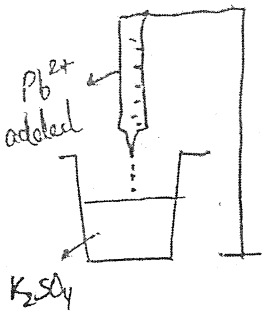
$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} + \frac{RT}{nF} \ln \frac{[M_{(a)}^{n+}]}{[M_{(s)}]}$$

(b) Half Wave potential, ($E_{1/2}$) – It is the potential at which diffusion current is half of the maximum value (i_d). It is specific to an ionic species and does not depend on Concentration

(c) For titration proceeding at $E_{1/2}$ of one species, diffusion current is only detected when that species is freely present in solution i.e. after the end point is reached. Further illustrated in $K_2SO_4 - Pb^{2+}$ titration.

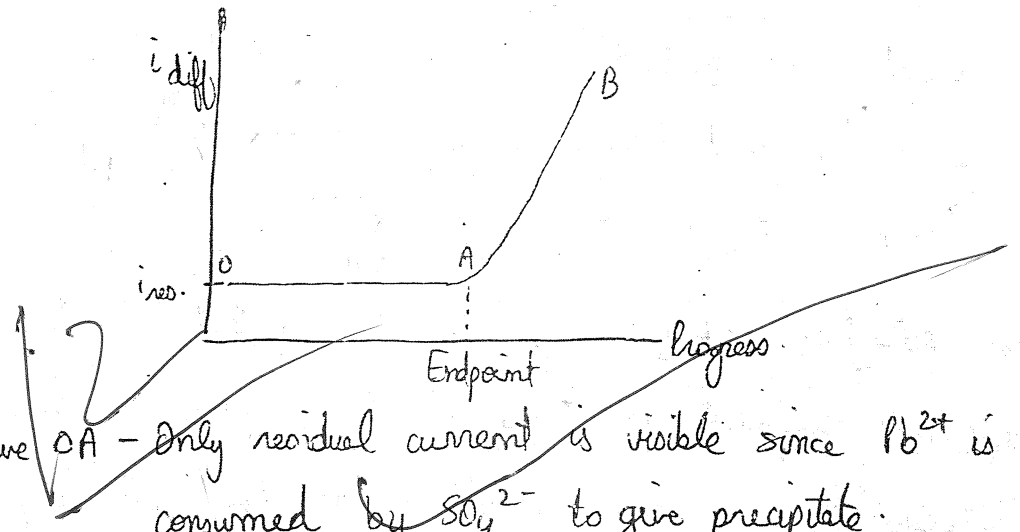
Reaction : $K_2SO_4 + Pb^{2+} \rightarrow PbSO_4\downarrow + 2K^+$

Yellow colour ppt



Any additional Pb^{2+} added after end point will give a Rise in diffusion current since $E_{1/2}$ is set for Pb^{2+}

Amperometric analysis



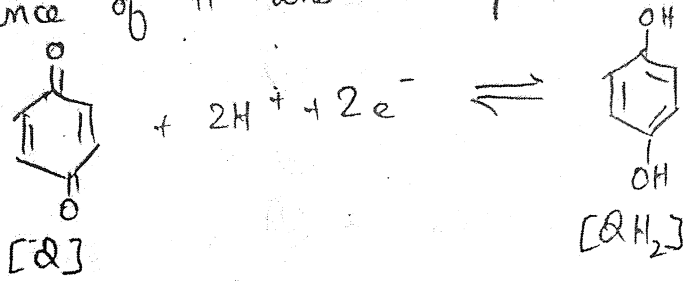
Curve OA - Only residual current is visible since Pb^{2+} is continuously consumed by SO_4^{2-} to give precipitate.

Point A - achievement of End point

Curve AB - Change in diffusion current owing to addition of Pb^{2+}.

(c) Discuss the principle and working of quinhydrone electrode. Why its fails miserably above pH = 10. (10)

Quinhydrone electrode is a type of indicator electrode for presence of H^+ ions and pH calculation



$$[Q] + 2H^+ + 2e^- \rightleftharpoons [QH_2]$$

$$QH_2 \overset{K_1}{\rightleftharpoons} [QH^-] + H^+ \quad -(1)$$

$$QH^- \overset{K_2}{\rightleftharpoons} [Q^{2-}] + H^+ \quad -(2)$$

$$[Q] = [QH_2] + [QH^-] + [Q^{2-}]$$

Using nernst equation

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln \frac{[QH_2]}{[H^+]^2 [Q]} \quad -(3)$$

Using (1) and (2)

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln \frac{[QH_2]}{[H^+]^2 [QH_2]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)}$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln \frac{1}{([H^+]^2 + K_1[H^+] + K_1K_2)}} \quad -(4)$$

Principle - quinhydrone dissociates as per (1) and (2) and attains equilibrium. Its working is based on pH values.

(a) at $pH < 8$ $K_1[H^+] + K_1K_2 \ll [H^+]^2 \Rightarrow E_{cell} = E^\circ_{cell} - \frac{RT}{F} pH$ (normal case)

(b) $8 < pH < 10$ $K_1[H^+] + [H^+]^2 > K_1K_2 \Rightarrow$ slight deviation

(c) $pH > 10$ $K_1K_2 > K_1[H^+] + [H^+]^2 \Rightarrow E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln\left(\frac{1}{K_1K_2}\right)$

The electrode fails to estimate pH and thus fails.

(d) The following data were obtained for the reaction A + B → products. Derive the rate law. (10)

[A]	[B]	Rate	
Mole dm^{-3}	Mole dm^{-3}	Mole $dm^{-3} s^{-1}$	
6.0×10^{-3}	1.0×10^{-3}	0.012	— (a)
6.0×10^{-3}	2.0×10^{-3}	0.024	— (b)
2.0×10^{-3}	1.5×10^{-3}	0.002	— (c)
4.0×10^{-3}	1.5×10^{-3}	0.008	— (d)

Rate law for A + B → products can be taken as

$$r = K [A]^{\alpha} [B]^{\beta}$$

Taking (a) and (b) – when [B] doubles, rate also doubles at constant [A]

i.e. $r_1 = K [A]^{\alpha} [B]^{\beta}$

$r_2 = 2r_1 = K [A]^{\alpha} [2B]^{\beta}$

$2 = 2^{\beta}$ or $\boxed{\beta = 1}$

Taking (c) and (d) – when [A] doubles, rate increases 4 times at constant [B]

i.e. $r_1 = K [A]^{\alpha} [B]$

$r_2 = 4r_1 = K [2A]^{\alpha} [B]$

dividing both $\Rightarrow 4 = 2^{\alpha}$ or $\boxed{\alpha = 2}$

Hence final rate law is

$$\boxed{\text{rate} = K [A]^2 [B]^1}$$

4(a) Why is to incorrect to apply the formula (15)

$\text{Ln}\left(\frac{P_2}{P_2}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ to the graphite diamond system

Graphite $\rightleftharpoons$ diamond

Using classius relation

$\mu_{graphite} = \mu_{diamond}$ at equilibrium

$V_{grap}\,dP - SdT|_{grap} = VdP - SdT|_{diamond}$ — ①

$(V_{graphite} - V_{diamond})\,dP = (S_{grap} - S_{diam})\,dT$

or $\frac{dP}{dT} = \frac{(S_{grap} - S_{diam})}{(V_{grap} - V_{diam})}$ — ②

Using thermodynamic relation $\Delta G = \Delta H - T\Delta S = 0$ at equilibrium

$\therefore \Delta S = \frac{\Delta H}{T}$ — ③

$$\boxed{\frac{dP}{dT} = \frac{(\Delta H_{grap \to diam})}{T\,\Delta V_{grap \to diam}}} \quad \text{— ④}$$

Since diamond and graphite are solids, their ΔV cannot be written as $\left(\frac{RT}{P}\right)$ as this is only applicable to ideal gas and not solids.

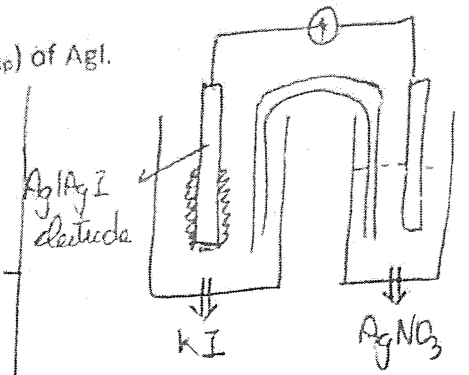
$\therefore \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ which is derived by integrating

$\frac{dP}{dT} = \frac{P\Delta H}{RT^2}$ is not applicable.

(b) The emf of the cell :

$Ag|AgI||(0.05\ M\ KI)||0.05\ M\ AgNO_3|Ag$

is 0.788 V. Calculate the concentration solubility product (K_{sp}) of AgI.



Given $E_{cell} = 0.788\ V$

Half cell reactions

Anode $\quad Ag + I^- \longrightarrow AgI + e$

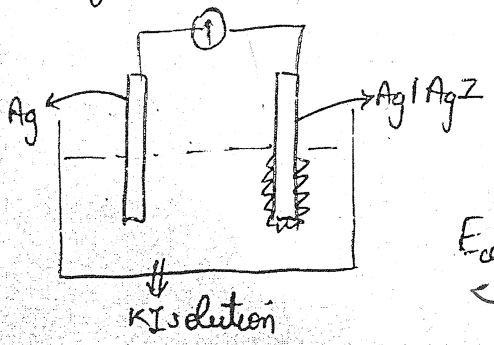
Cathode $\quad Ag^+ + e^- \longrightarrow Ag.$

$$E_{anode} = E^\circ_{Ag|I^-|AgI} - \frac{RT}{F} \ln \frac{1}{[I^-]_a} \quad — (1)$$

$$E_{cathode} = E^\circ_{Ag^+|Ag} - \frac{RT}{F} \ln \frac{1}{[Ag^+]_c} \quad — (2)$$

In order to find K_{sp}, we need another expression for $E^\circ_{Ag|I^-|AgI}$

We consider an equilibrium cell separately with following half reactions



Anode $\quad Ag \longrightarrow Ag^+ + e^-$

Cathode $\quad AgI + e^- \longrightarrow Ag + I^-$

$$E_{cell} = E_{anode} + E_{cathode}$$

$$= E^\circ_{Ag|Ag^+} - \frac{RT}{F} \ln [Ag^+] + E^\circ_{AgI|Ag|I^-} - \frac{RT}{F} \ln [I^-] \quad — (3)$$

Since it is equilibrium cell $\Delta G = 0$

But $\Delta G = -nFE_{cell}$ $\quad \therefore \boxed{E_{cell} = 0} \quad — (4)$

Using ③ and ④

$$E_{cell} = 0 - E^\circ_{Ag|Ag^+} + E^\circ_{Ag_2|Ag|I^-} - \frac{RT}{F} \ln [Ag^+][Cl^-]$$

But $[Ag^+][Cl^-] = K_{sp}$ (solubility product)

Hence $\boxed{E^\circ_{Ag_2|Ag|I^-} = E^\circ_{Ag^+|Ag} + \frac{RT}{F} \ln K_{sp}}$ — ⑤

Using ⑤ in ① and writing $E_{cell} = E_{cathode} + E_{anode}$

$$E_{cell} = E^\circ_{Ag^+|Ag} - \left[E^\circ_{Ag^+|Ag} + \frac{RT}{F} \ln K_{sp} \right] - \frac{RT}{F} \ln \frac{1}{[Ag^+]_c [I^-]_a}$$

$$0.788 = -\frac{RT}{F} \ln \left(\frac{K_{sp}}{[Ag^+]_c [I^-]_a} \right)$$

$$0.788 = -0.059 \ln \left(\frac{K_{sp}}{(0.05)(0.05)\,M^2} \right)$$

$$4.4 \times 10^{-14} = \frac{K_{sp}}{(0.05)^2\,M^2}$$

or $\boxed{K_{sp} = 1.1 \times 10^{-16}\,M^2}$

(c) For the reaction : $A + B \rightarrow P$; (20)

(i) Derive the expression of rate constant (k) where reaction is first order with respect to each A and B and initial concentrations of A and B are 'a' and 'b' respectively.

(ii) Calculate the rate constant of above reaction, when 'a' = 0.075 mol L^{-1}; 'b' = 0.050 mol L^{-1} and concentration of B = 0.020 mol L^{-1} after 1 h.

(i) Given $A + B \rightarrow P$

$t=0 \quad a \quad b \quad 0$

$t \quad a-x \quad b-x \quad x \quad -①$

$$\text{rate} = -\frac{d[A]}{dt} = k_2[A][B] \quad -②$$

Using ① in ②

$$-\frac{d(a-x)}{dt} = k_2(a-x)(b-x) \Rightarrow \frac{dx}{dt} = k_2(a-x)(b-x)$$

$$\int_{x=0}^{x} \frac{dx}{(a-x)(b-x)} = \int_{t=0}^{t} k_2\,dt \Rightarrow \text{using partial fractions}$$

$$\frac{1}{(b-a)}\left[\frac{1}{a-x} - \frac{1}{b-x}\right] = \frac{1}{(a-x)(b-x)}$$

$$\frac{1}{b-a}\left[\int_0^x \frac{dx}{(a-x)} - \frac{dx}{(b-x)}\right] = \int_0^t k_2\,dt$$

$$\frac{1}{(b-a)}\left[\ln\left(\frac{a-x}{a}\right) - \ln\left(\frac{b-x}{b}\right)\right] = k_2 t$$

$$\boxed{\frac{(-1)}{(b-a)} \ln\left[\frac{b(a-x)}{a(b-x)}\right] = k_2 t}$$ or $$\boxed{k\,(\text{rate constant}) = \frac{(-1)}{t(b-a)} \ln\left[\frac{b(a-x)}{a(b-x)}\right]} \quad -⑤$$

$$\boxed{k = \frac{1}{t(a-b)} \ln\left[\frac{b}{a}\frac{(a-x)}{(b-x)}\right]} \quad -③$$

(ii) Given $[B] = 0.02$ mol L^{-1} after 1h, $a = 0.075$ mol L^{-1}, $b = 0.05$ mol

But $[B] = b - x \Rightarrow x = b - [B] = 0.05 - 0.02$

$$\boxed{x = 0.03 \text{ mol } L^{-1}} \quad -④$$

Replacing x, a, b, t in (3)

$$K = \frac{1}{t}\frac{(-1)}{(b-a)} \ln\left[\frac{b}{a}\frac{(a-x)}{(b-x)}\right]$$

$$= \frac{1}{1\,hr}\frac{1}{(-0.05+0.075)\,mol\,L^{-1}} \ln\left[\frac{0.05}{0.075}\frac{(0.075-0.03)}{(0.05-0.03)}\right]$$

$$= (L\,mol^{-1}\,hr^{-1})\left(\frac{+1}{0.025}\right)\ln(1.5)$$

$$\boxed{K = 16.2\ L\,mol^{-1}\,hr^{-1}}$$

12

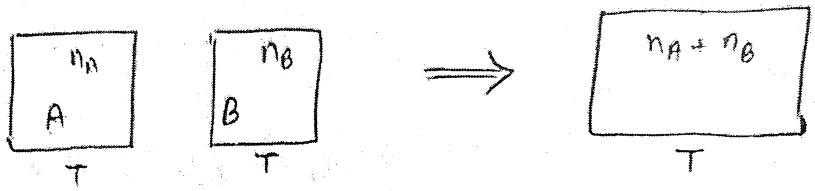
(3)

mol

Section – B

5(a) Show that the molar free energy of mixing ΔG_{mix} in a binary ideal gas mixture is minimum when the two gases are present in the equimolar ratio. (15)

Mixing of 2 ideal gases A and B initially present seperately at T, P



Initially $\mu_{A,i} = \mu_A^\circ + RT \ln\left(\frac{P}{P_\circ}\right)$

$\mu_{B,i} = \mu_B^\circ + RT \ln\left(\frac{P}{P_\circ}\right)$ — (1)

where μ_A, μ_B are chemical potentials for A, B

$P_\circ$ is standard pressure, P is system pressure.

After mixing Mole fractions $x_A = \frac{n_A}{n_A + n_B}$, $x_B = \frac{n_B}{n_A + n_B}$ — (2)

Partial pressure = Total pressure × mole fraction

$\therefore P_A = P x_A$, $B_B = P x_B$ — (3)

$\mu_{A,f} = \mu_A^\circ + RT \ln\left(\frac{P_A}{P_\circ}\right)$

$\mu_{B,f} = \mu_B^\circ + RT \ln\left(\frac{P_B}{P_\circ}\right)$ — (4)

Free energy $\Delta G_{mixing} = (\mu_{A,f} + \mu_{B,f}) - (\mu_{A,i} + \mu_{B,i})$

$= (n_A \mu_{A,f} + n_B \mu_{B,f}) - (n_A \mu_{A,i} + n_B \mu_{B,i})$

$$\Delta G_{mix} = n_A\left[\mu_A^\circ + RT\ln\left(\frac{x_A P_A}{P_0}\right) - \mu_A^\circ - RT\ln\left(\frac{P}{P_0}\right)\right]$$

$$+ n_B\left[\mu_B^\circ + RT\ln\left(\frac{x_B P}{P_0}\right) - \mu_B^\circ - RT\ln\left(\frac{P}{P_0}\right)\right]$$

$$\Delta G_{mix} = \left[n_A \ln x_A + n_B \ln x_B\right] RT$$

$\Rightarrow \Delta G_{mix,m}$ (molar energy of mixing)

$$= \frac{RT\left[n_A \ln x_A + n_B \ln x_B\right]}{(n_A + n_B)} = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\therefore \boxed{\Delta G_{mix,m} = RT(x_A \ln x_A + x_B \ln x_B)} \quad \text{— (5)}$$

$\Rightarrow$ Maximum value of $\Delta G_{mix,m}$ is found by differentiating (5) wrt x_A

Replacing $x_B = 1 - x_A$ in (5)

$$\frac{d\Delta G_{mix,m}}{dx_A} = \frac{RT\, d\left[x_A \ln x_A + (1-x_A)\ln(1-x_A)\right]}{dx_A}$$

$$= RT\left[\ln x_A + 1 - \ln(1-x_A) - 1\right]$$

For maxima $\frac{d\Delta G_{mix,m}}{dx_A} = 0 \Rightarrow \ln x_A = \ln(1-x_A)$

possible only when $x_A = 1 - x_A$

or $\boxed{x_A = \frac{1}{2},\ x_B = \frac{1}{2}}$

Equimolar ratio proved

(b) Calculate the standard enthalpy change at 473 K for the reaction $CO + \frac{1}{2} O_2 \rightarrow CO_2$; The standard heat of formation at 298 K are -110.5 KJ/mol and -393.5 KJ/mol respectively. The heat capacities of CO;CO_2 and O_2 over the 298 K to 473 K are given by the equations:- (15)

$Cp(CO) = (26.53 + 7.70 \times 10^{-3}) T - 1.17 \times 10^{-6} T^2) J K^{-1} mol^{-1}$

$Cp(CO_2) = 26.78 + 42.26 \times 10^{-3} T - 14.23 \times 10^{-6} T^2) J K^{-1} mol^{-1}$

$Cp(O_2)$ $25.52 + 13.60 \times 10^{-3} T - 4.27 \times 10^{-6} T^2) J K^{-1} mol^{-1}$.

$CO + \frac{1}{2} O_2 \longrightarrow CO_2$ given Cp values for all 3, $\Delta H_f^\circ (CO)$, $\Delta H_f^\circ (CO_2)$

From definition of enthalpy

$$\int_{H_1}^{H_2} dH = n \int_{T_1}^{T_2} Cp\, dT$$

$$\boxed{H_2 - H_1 = n \int_{T_1}^{T_2} Cp\, dT} \quad \text{— (1)}$$

Thus to find Standard enthalpy change at 473K, it is required to take all species at 473K from 298K and then react them at 473K.

For the above reaction

$$\Delta H = \Sigma H_{f,\text{products}} - \Sigma H_{f,\text{reactants}}$$

$$= H_{f,CO_2} - \left[H_{f,CO} + \left(\frac{H_{f,O_2}}{2} \right) \right] \text{ at 473K} \quad \text{— (2)}$$

using (1) in (2)

$$\Delta H_{\text{reaction},473K} = \left(\Delta H_{f,CO_2|298K} - \left[\Delta H_{f,CO|298K} + \frac{\Delta H_{f,O_2|298K}}{2} \right] \right) \quad \text{— (3)}$$

$$+ \int_{298K = T_1}^{473K = T_2} \left(C_{p,CO_2} - C_{p,CO} - \frac{C_{p,O_2}}{2} \right) dT$$

$$\Delta H_{f,473K} = \left[-393.5 - \left(-110.5 + \frac{0}{2}\right)\right] + \int_{298K}^{473K} \left[-12.51 + 27.76 \times 10^{-3} T + (-10.925 \times 10^{-6}) T^2\right] dT \quad \text{— (4)}$$

(4) is obtained by putting Cp expressions in (3) and simplifying

$$\Delta H_{f,473K} = -283 \text{ KJ mol}^{-1} + (-12.51) \times 175 \text{ J mol}^{-1} + \frac{27.76 \times 10^{-3}}{2}\left[473^2 - 298^2\right] \text{ J mol}^{-1} + \frac{(-10.925 \times 10^{-6})}{3}\left[473^3 - 298^3\right]$$

$$\boxed{\Delta H_{f,473K} = -283.605 \text{ KJ mol}^{-1}}$$

(c) Compare the thermodynamic efficiency to be expected (a) when a engine operate between 1000 K and 300 K (b) when an engine operate between 1000K and 600 k and waste heat passed to another engine working between 600 K & 300 K. (10)

Thermodynamic efficiency of heat engine is defined as

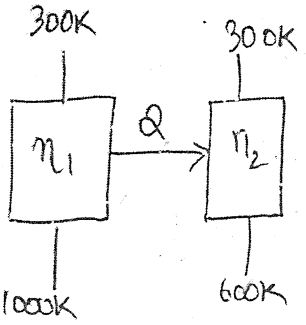
$\eta = 1 - \frac{T_2}{T_1}$ T_2 = Temperature of sink

T_1 = T of source

(a) $T_2 = 300K$ $T_1 = 1000K$

$\eta_1 = 1 - \frac{300}{1000} = 0.7$ or 70 % efficiency

(b)



Efficiency for engine 1 = $\eta_1 = \frac{W_1}{Q_1} = 1 - \frac{300}{1000} = 0.7$ — ①

Q_2 = heat wasted = $Q_1 - W_1$ which goes to engine 2

Now efficiency for engine 2 = $\eta_2 = \frac{W_2}{Q_2} = 1 - \frac{300}{600} = 0.5$ — ②

Overall efficiency = $\frac{W_1 + W_2}{Q_1} = \frac{W_1}{Q_1} + \frac{W_2}{Q_2} = \frac{W_1}{Q_1} + \frac{\eta_2 Q_2}{Q_1}$

Using ① and ②

Overall efficiency = $\eta_1 + \eta_2\left(\frac{Q_2}{Q_1}\right) = \eta_1 + \eta_2\left(\frac{Q_1 - W_1}{Q_1}\right)$

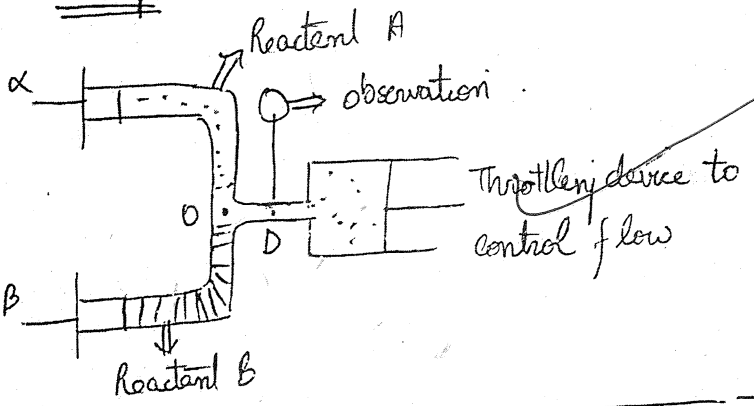
$= \eta_1 + \eta_2(1 - \eta_1) = \boxed{\eta_1 + \eta_2 - \eta_1\eta_2}$

Efficiency = $0.7 + 0.5 - 0.35 = \boxed{0.85}$

(d) Discuss stop-flow method to study kinetics of fast reaction.

Fast reaction kinetics are difficult to study by normal methods due to steep gradients of yield and poor observation. Hence stop-flow method is used.

Setup



Working

① Reactants A and B are present in 2 U-shaped tubes meeting at point O

② Flow rates of reactants are controlled by throttling devices α and β.

③ Mixing of 2 reactants and fast reactions occurs at D. Since mixture essentially stops at D for analysis, it is called stop flow method.

④ Spectroscopic technique is used to find Concentration gradient

⇒ Utility - Biochemical reactions and pharmaceutical development.

6(a) one mole of methane gas obeying vanderwall nature is compressed isothermally and reversibly from 1 atom to 400 atm at 0^0 C what amount of heat must be removed during such compression in order to ensure isothermal nature of the process.(a =2.264 atml^2/mol ; you can make necessary assumption for calculation by specifying the same). (10)

Given isothermal compression of a Vander wall gas following $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$ (Given 1 mol of CH_4)

Using Ist law of thermodynamics

$dU = \partial q + \partial w$ — ①

By defination $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ — ②

From Thermodynamic Equation of state I

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

$$= T \frac{\partial}{\partial T}\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]_V - P$$

$$= \frac{RT}{V_m - b} - P$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2} \quad \text{— ③}$$

Since $dT = 0$, using ③ in ②

$$dU = \frac{a}{V_m^2} dV \quad \text{— ④}$$

From ① , $\partial q = dU - \partial w$

$$\partial q = \frac{a}{V_m^2} dV + P dV$$

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

or $dq = \left(\frac{RT}{V_m - b}\right) dV$

For VWG $\frac{dP}{dT} = \frac{V_m - b}{T} + \frac{2a}{RT^2}$

(b) The decomposition of HI (g) to H_2 (g) and I_2 (g) is a second-order reaction. The half-line of the reaction is found to be 13.5 min, when the initial pressure of HI (g) is 1.0 bar. (15)

(i) Calculate the half-life when the initial pressure of HI (g) is 0.1 bar

(ii) Calculate the reaction time required for the pressure of HI (g) to fall from 1.0 bar to 0.1 bar.

$$HI \longrightarrow H_2 + I_2$$

$$\text{rate} = K[HI]^2 \quad \text{— ①}$$

(i) $$-\frac{d[HI]}{dt} = K[HI]^2 \quad \text{— ②}$$

$$-\int_{[HI]_0}^{[HI]} \frac{d[HI]}{[HI]^2} = \int_0^t K\,dt$$

$$\boxed{\frac{1}{[HI]} - \frac{1}{[HI]_0} = Kt} \quad \text{— ③}$$

Half life occurs when $[HI] = \frac{[HI]_0}{2}$ — using in ③

$$\frac{1}{[HI]_0} = K t_{1/2} \Rightarrow t_{1/2} = \frac{1}{K[HI]_0}$$

$$t_{1/2} = \frac{1}{K_p P_0} \quad \text{— ④}$$

given ~~$K_p = 13.5$ min~~ ~~$P_0 = 0.1$ b~~ $t_{1/2} = 13.5$ min when $P_0 = 1$ bar

$$\therefore K_p = \frac{1}{13.5} \text{ min}^{-1}\text{ bar}^{-1}$$

Using K_p in ④ for $P_0 = 0.1$ bar

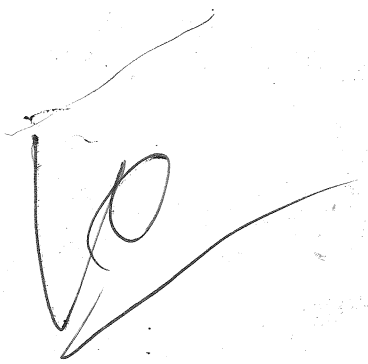
$$t_{1/2} = \frac{1}{\left(\frac{1}{13.5}\right) \text{min}^{-1}\text{bar}^{-1} \times 0.1 \text{ bar}} \Rightarrow \boxed{t_{1/2} = \text{~~135~~} 135 \text{ min}}$$

(ii) Using (3)

$P_{HZ} = 0.1$ bar, $P_{o_{HI}} = 1$ bar

$$\left[\frac{1}{0.1} - \frac{1}{1}\right] \text{bar}^{-1} = \frac{1}{13.5} \text{min}^{-1}\text{bar}^{-1} \times t$$

$$\boxed{t = 121.5 \text{ min}}$$



(c) Discuss effect of ionic strength on the rate constant of reaction. (15)

For a reaction $A + B \rightarrow$ products

Using activated complex theory

$$A + B \rightleftharpoons (AB)^{\#} \longrightarrow \text{products}$$

Rate of reaction = (Rate of decomposition) × (Conc. of $(AB)^{\#}$)

$$= \left(\frac{RT}{N_o h}\right) \times [AB^{\#}]$$

Using equilibrium correlation $K_{eq} = \dfrac{[AB^{\#}]}{[A][B]}$

$$\text{Rate of reaction} = \left(\frac{RT}{N_o h}\right) K_{eq} [A][B] = K[A][B]$$

$$\therefore \boxed{\text{Rate Constant } (K) = \frac{RT}{N_o h} K_{eq}}$$

Now $K_{eq} = \exp\left(-\dfrac{\Delta G^{o\#}}{RT}\right) = \exp\left(\dfrac{T\Delta S^{o\#} - \Delta U^{o\#} - \Delta nRT}{RT}\right)$

$$K_{eq} = \exp\left(\frac{\Delta S^{o\#}}{R} - \frac{\Delta U^{o\#}}{RT} - \Delta n_g\right)$$

Using $K = \dfrac{RT}{N_o h} \exp\left(\dfrac{\Delta G^{o\#}}{R}\right) \exp\left(-\dfrac{\Delta U^{o\#}}{RT}\right) \exp(-\Delta n_g)$

$$\frac{d \ln K}{dT} = \frac{1}{T^2} + \frac{\Delta U^{o\#}}{RT^2} = \frac{E_a}{RT^2}$$

or $\boxed{\Delta U^{o\#} = E_a - R}$

Finally $\boxed{K = \dfrac{RT}{N_o h} \exp(1 - \Delta n_g) \exp\left(\dfrac{\Delta S^{o\#}}{R}\right) \exp\left(-\dfrac{E_a}{RT}\right)}$

(d) The rates of a reaction starting with initial concentration 2×10^{-3} mol L^{-1} and 1×10^{-3} mol L^{-1} are equal to 2.40×10^{-4} mol L^{-1} s^{-1} and 0.6×10^{-4} mol L^{-1} s^{-1}, respectively. Calculate the order of thereaction with respect to the reactant and the rate constant. (10)

Order of a reactant is equal to the power of its concentration appearing in the rate law.

Here assume $\text{Rate} = K[A]^{\alpha}[B]^{\beta} \ldots$

For reaction $A + B + \ldots \longrightarrow$ products

Given Rate becomes 4 times when concentration of A is increased by factor of 2.

$2.4 \times 10^{-4}\ \text{mol}\ L^{-1} s^{-1} = K(2 \times 10^{-3})^{\alpha}[B]^{\beta} \ldots$ — (1)

$0.6 \times 10^{-4}\ \text{mol}\ L^{-1} s^{-1} = K(1 \times 10^{-3})^{\alpha}[B]^{\beta} \ldots$ — (2)

Dividing (1) and (2)

$4 = 2^{\alpha}$ or $\boxed{\alpha = 2}$

Hence order of reaction with respect to [A] is 2.

Since no further data is mentioned we assume $A \longrightarrow$ products as the reaction

Thus $\text{Rate} = 2.4 \times 10^{-4}\ \text{mol}\ L^{-1} s^{-1} = K(2 \times 10^{-3})^{2}$

or $\boxed{K(\text{Rate Constant}) = 60\ \text{mol}^{-1} L^{-1} s^{-1}}$