# DIAS

## All India TEST – SERIES CSE – 2020

## Physical – 2 (Test-2)

Syllabus -: Thermodynamics, Phase,Electro Chemistry and chemical kinetics.

## Instructions:-

1. Attempt all the questions
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 |
|---|---|---|---|---|---|
| Marks | 23 | 30 | 27 | 24 | 29 |

| Total Marks |
|---|
| 133/250 |

Signature of invigilator

Signature of Examiner

1. (a) Draw phase diagram of Mg – Al system with given information:

M.pt. of Mg: - 500°C  Eutectic 1:- 270°C (20%Mg)

M.pt. of Al:- 800°C  Eutectic 2:- 390°c (20%Al)

M.pt. of $Mg_3Al_2$ :- 600°C

Lable the area; lines and points with respect to phase and degree of freedom. **(20)**

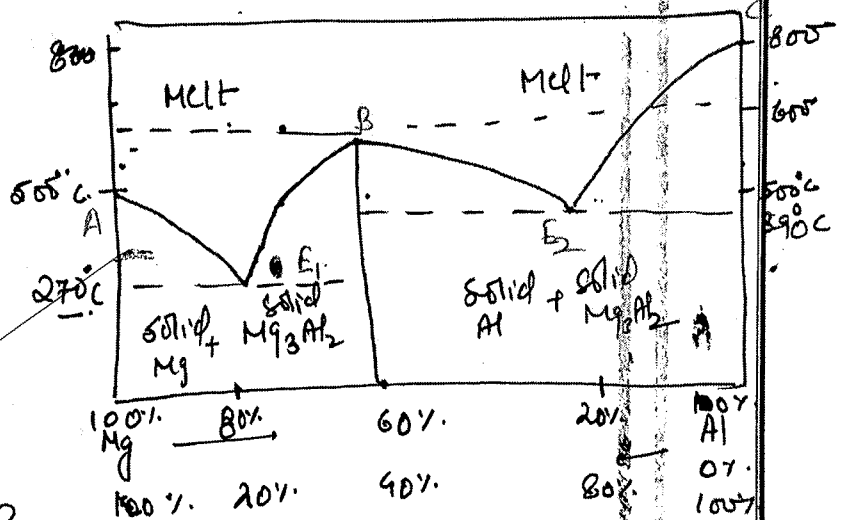
Mg-Al system – 2 component system.

According to Gibbs Rule

$F = C - P + 2$ .

$F = C - P + 1$ (when pressure is constant)

$\boxed{F = 3 - P}$




Phase diagram of $Mg_3Al_2$

It has 2 independent system.

1. Equilibrium between Mg & $Mg_3Al_2$

2. Equilibrium between $Mg_3Al_2$ & Al.

Areas.

$F = 3 - P$ { 1 phases exists } → $(F = 2)$

1. Above AE₁B.

Melt composition of (Mg) & ($Mg_3Al_2$) both will exist in liquid form.

• Area above $BE_2B$ — Melt + Al & $Mg_3Al_2$ — $F = 3-P$ — $F=2$ — Phase = 1

**Lines**

1. (AE) equilibrium between solid Mg & Melt + Mg & $Mg_3Al_2$.
$F = 3-P \Rightarrow P = 2$
$F=1$

2. $(E_1B)$ equilibrium between solid $Mg_3Al_2$ & Melt + Mg & $Mg_3Al_2$
$F = 3-P \Rightarrow P=2$ } 2 phases exist
$F=1$ So upon changing temperature graph will follow the $E_1B$ trajectory

3. Similarly lines $(BE_2)$ and $(E_2C)$ will have their corresponding equilibrium (as cases before). It just the equibilim will now be with Al & $Mg_3Al_2$

**Points**

1. $E_2$ - Eutectic Point 1
$F = 3-P \Rightarrow P=3$
$F=0$ } Three phases exist Melt / solid Mg & solid $Mg_3Al_2$
This the minimum temperature at which equilibrium can exist. Below that the only solid phase exists.

2. Similarly for point
$E_2 \Rightarrow F=0$

3. B Point (B)
Congruence Melting point. System shifts from 2 component system to (1) as only liquid and solid $Mg_3Al_2$ exists
$P=2$ ; $C=1$
$F=0$ (nonvariant point)

b) Determine number of components in each cases:-

(i) $PCl_5$: $PCl_3$; $Cl_2$ (ii) NaCl- KBr – $H_2O$

(iii) $CH_3COOH$ – $H_2O$ (iv) $H_2O$ at 373 K

(v) $CaCO_3$; $CO_2$ ; CaO (10)

(i) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$C = (N) - (R)$

Non constituents — i. Restricting Relationships

$C = 3 - 1 \Rightarrow 2$

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-OH - H_2O$

1. $CH_3-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H^{\oplus}$
2. $H^+ + OH^{\ominus} \rightleftharpoons H_2O$
3. Electroneutrality of solution

$C = 5 - 3 \Rightarrow (2)$

(iii) $CaCO_3$ : $CO_2$ : CaO

$CaCO_3 \rightleftharpoons CaO + CO_2$

$C = 3 - 1 \Rightarrow (2)$

(iv) $H_2O$ (373k)

$H_2O(l) \rightleftharpoons H_2O(g)$

2 phases.

$C = 2 - 1 \Rightarrow (1)$

Component

(v) NaCl - KBr - $H_2O$

1. $Na^+ + K^+ \rightleftharpoons Cl^- + Br^{\ominus}$

Electroneutrality of solution must be maintained.

$C = 3 - 1 = (2)$

c) The conversion of $O_3$ and $O_2$ catalysed by $N_2O_5$ the proposed mechanism is

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{k_2} N_2O_5$$

$$NO_2 + O_3 \xrightarrow{k_3} NO_3 + O_2$$

$$2NO_3 \xrightarrow{k_4} NO_2 + O_2 + NO_2$$

Show that - $A\dfrac{-d[O_3]}{dt} = \left\{2\left(\dfrac{k_1}{k_2}\right)^2 K_3^2 K_4\right\}^{1/3} [N_2O_5]^{2/3}[O_3]^{2/3}$ **[15]**

The Rate of the reaction can be studied with the help of Chemical kinetics and using the steady state Approximation. In which the Rate of formation of intermediates is taken as zero or negligible.

$$+\frac{d[O_3]}{dt} = -k_3[NO_2][O_3].$$

using steady state Approx on $[NO_2]$

$$\frac{d[NO_2]}{dt} = -k_3[NO_2][O_3] - k_2[NO_2][NO_3] + k_1[N_2O_5] + 2k_4[NO_3].$$

$$\Rightarrow [NO_2] = \frac{k_1[N_2O_5] + 2k_4[NO_3]}{k_3[O_3] + k_2[NO_3]}$$

using steady state Approximation on $[NO_3]$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_3][NO_2] + k_3[NO_2][O_3] - 2k_4[NO_3]$$

$$0 \quad [NO_3] = \frac{k_1[N_2O_5] + k_3[NO_2][O_3]}{2k_4 + k_2[NO_2]}$$

$$0 = -k_3[NO_2][O_3] - k_2[NO_2][NO_3] + k_1[N_2O_5] + 2k_4[NO_2]$$

$$= -k_3[NO_2][O_3]$$

(d) Show that for first order reaction $t_{99.9\%} = 10t_{1/2}$. **(5)**

first order reaction follow the following rate law

$$A \xrightarrow{k} P$$

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

: k - rate constant
[A] - concentration of A

Upon integrating

$$k = \frac{[A]_t = [A]_0 e^{-kt}}{}$$

: $[A]_0$ - initial conc.
$[A]_t$ - conc. at time t

$t_{1/2}$ is the time the concentration of [A] becomes half of initial concentration

$$\frac{[A]_0}{2} = [A]_0 e^{-kt} \Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

$t_{99.9} \Rightarrow [A]_t = 0.001 [A]_0$

$$0.001 [A]_0 = [A]_0 e^{-kt}$$

$$\ln(0.001) = \ln e^{-kt} \Rightarrow t_{99.9} = \frac{-\ln(0.001)}{k}$$

$$\frac{t_{99.9}}{t_{1/2}} = \frac{-\ln(0.001)}{\ln 2} = \frac{9.96}{\sim 10}$$

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**2.** (a) Derive, the equation of liquid junction potential (LJP) of a concentration call given below. Ag ; AgCl |HCl ($a_2$): HCl ($a_1$) |AgCl;Ag. $\left[12\frac{1}{2}\right]$

Liquid junction potential can be calculated by using a Concentration Electrolytic cell. First with transference and then using the same cell without transference by using a salt bridge.

$E_{WT}$: EMF with Transference

$E_{WOT}$: EMF without Transference

$$LJP = E_{WT} - E_{WOT}$$

potential at the junction of layer in transference cell

Ag | AgCl | HCl ($a_2$) : HCl ($a_1$) | AgCl : Ag

Anode $Ag(s) + Cl^-_{(a_1)} \rightleftharpoons AgCl(s) + e^{\ominus}$

$t_+ H^+(a_2) \rightleftharpoons t_+ H^+(a_1)$

Migration of (H) due to consumption of $Cl^-_{(a_1)}$

Cathode $AgCl + e^{\ominus} \rightleftharpoons Ag + Cl^-(a_1)$

$t_- Cl^-(a_1) \rightleftharpoons t_- Cl^-(a_2)$

$Cl^-(a_2) + t_+ H^+(a_2) \rightleftharpoons t_+ H^+(a_1) + Cl^-(a_1) + t_- Cl^-(a_2) + t_- Cl^-(a_1)$

$t_+ HCl(a_2) \rightleftharpoons t_+ HCl(a_1)$

$E_{WT} = E^{\circ}_{WT} - \frac{RT}{nF} \ln \left(\frac{a_{HCl_1}}{a_{HCl_2}}\right)^{t_+}$ ($E^{\circ}_{WT} = 0$)

$E_{WT} = \frac{t_+ RT}{F} \ln \left(\frac{a_1}{a_2}\right)^2$ or $E_{WT} = \frac{t_+ RT}{F} \ln \left(\frac{a_2}{a_1}\right)^2$

$\Rightarrow E_{WT} = 2t_+ \frac{RT}{F} \ln \left(\frac{a_2}{a_1}\right)$

without transference

$Cl^-(a_2) \rightleftharpoons Cl^-(a_1)$

$E_{WOT} = -\frac{RT}{nF} \ln \left(\frac{a_1}{a_2}\right)$

$E_{WOT} = \frac{1}{F} \frac{RT}{F} \ln \left(\frac{a_2}{a_1}\right)$

$LJP = \left(2t_+ - 1\right) \left(\frac{RT}{F}\right) \ln \left(\frac{a_2}{a_1}\right)$

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b) For a sequential reaction given below; derive the relation for concentration if [B] if $[B]_0 = [C]_0 = 0$ and $[A] = [A]_0$ Also shown that maximum conc. Of [B] is at $t_{max} = \frac{k_2}{k_2 - k_1} \ln(k_2/k_1)$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$[A]_0 \quad 0 \quad 0$

$[A]_t \quad [B]_t \quad [C]_t$

$$-\frac{d[A]}{dt} = k_1[A] \Rightarrow [\dot{A}] = -k_1[A] \quad -(1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$= [\dot{B}] = k_1[A] - k_2[B] \quad -(2)$$

$$\frac{d[C]}{dt} = k_2[B] \Rightarrow [\dot{C}] = k_2[B] \quad -(3)$$

Taking double derivative of equation (2)

$$[\ddot{B}] = k_1[\dot{A}] - k_2[\dot{B}]$$

$$[\dot{B}] = k_1[A] - k_2[B]$$

$$[A]_t + [B]_t + [C]_t = [A]_0$$

$$[A] = [A]_0 - [B] - [C]$$

using initial condition

$$[\dot{B}] = k_1[[A]_0 - [B] - [C]] - k_2[B]$$

$$[\dot{B}] = k_1[A]_0 - k_1[B] - k_1[C] - k_2[B]$$

$$[\ddot{B}] = 0 - k_1\dot{B} - k_1\dot{C} - k_2\dot{B}$$

$$\ddot{B} + k_1\dot{C} + (k_1 + k_2)\dot{B} = 0$$

$$\boxed{\ddot{B} + k_1k_2[B] + (k_1 + k_2)\dot{B} = 0} \quad -(4)$$

$[12\frac{1}{2}]$

Equation (4) is a double differential equation

$$[B] = c_1e^{-k_1t} + c_2e^{-k_2t}$$

at $t=0$ $[B] = 0$ / $[\dot{B}] = 0$

$$[B] = c_1 = -c_2$$

$$c_1 = \frac{k_1[A]_0}{k_1 - k_2}$$

$$\boxed{[B] = -\frac{k_1[A]_0}{k_1 - k_2}\left(e^{-k_1t} - e^{-k_2t}\right)} \quad -(5)$$

To find maximum conc. of (B) taking derivative of equation (5) wrt to time

$$\frac{d[B]}{dt} = 0$$

$$\Rightarrow \left(-k_1e^{-kt} - (-k_2)e^{-k_2t}\right) = 0$$

$$k_1e^{-kt} - k_2e^{-k_2t} = 0$$

$$\ln k_1 - k_1t_{max} - \ln k_2 + k_2t = 0$$

$$t_{max}(k_2 - k_1) = \ln(k_2/k_1)$$

$$\boxed{t_{max} = \frac{1}{k_2 - k_1}\ln(k_2/k_1)}$$

c) Discuss physical significances of $\mu_{JT}$ joule Thompson coefficient. $\left[12\frac{1}{2}\right]$

Joule Thomphson experiment is the expansion of gas against vaccum under adiabatic conditions. It is an isoenthalpic process and in this experiment a quanity $\mu_{JT}$ is defined as change in temperature per change in pressure at constant enthalpy

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H} \Rightarrow \mu_{JT} = \left(\frac{\Delta T}{\Delta P}\right)_H$$

Since Joule Thompson experiment is an expansion process

$$\mu_{JT} = \left(\frac{\Delta H\, T}{\Delta P}\right)_H \xrightarrow{\Delta P < 0} \boxed{\mu_{JT}} = \left(-\frac{\Delta T}{|\Delta P|}\right)_H \quad \text{--- (1)}$$

from eq (1) Physical significance of $\mu_{JT}$ can be understood

if $\mu_{JT} > 0 \Rightarrow \Delta T < 0$ } that means expansion will lead to temperature decrease (Normal gases at room temp)

if $\mu_{JT} < 0 \Rightarrow \Delta T > 0$ } Heating effect will be observed during expan (Hydrogen & helium at room temp)

if $\mu_{JT} = 0 \Rightarrow \Delta T = 0$ } no temp change?

- This principle is utilized in the cooling process of an airconditioner

d) $K_p$ of a reaction increases 3 times by increasing temperature from 427° C to 627°C the calculate $\Delta H^\circ$ reaction. $\left[12\frac{1}{2}\right]$

Using relationship between Gibbs energy and rate constant—

$\Delta G = \Delta G^\circ + RT\ln(Q)$

Since the reaction is at equilibrium i.e $k_p$

$\Delta G = 0 \Rightarrow \boxed{\Delta G^\circ = -RT\ln k_p}$ — (1)

$\ln k_p = \frac{-\Delta G^\circ}{RT}$

$\Rightarrow d(\ln k_p) = -\frac{1}{R} d\left(\frac{\Delta G^\circ}{T}\right)$ { using Gibbs-Helmholtz relation $d\left(\frac{\Delta G^\circ}{T}\right) = -\frac{\Delta H^\circ_{rxn}}{T^2}$

$\boxed{d(\ln k_p) = \frac{\Delta H^\circ_{rxn}}{RT^2}}$ — (2)

upon integrating equation (1)

$\ln\left(\frac{k_{p_2}}{k_{p_1}}\right) = \frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln(3) = \frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{700} - \frac{1}{900}\right)$

$\ln 3 \times 8.314\ (J/mol\,K) = \Delta H^\circ_{rxn}\left(8.17 \times 10^{-4}\right)$

$32.23\ kJ/mol = \Delta H^\circ_{rxn}$

$\boxed{\Delta H^\circ_{rxn} = 32.23\ kJ/mol}$

3. (a) The rate constant of a reaction change by 2% when its temperature is raised by 0.1°C. The standard enthalpy of the reaction at this temperature is 121.6 KJ/ mol. Find the energy of activation for the reverse reaction. **[10]**

Temperature dependence of rate constant is given by Arrhenius equation

$$\ln K = \frac{E_a}{RT^2} \Rightarrow \boxed{K = A e^{-E_a/RT}} \quad -(1)$$

K: Rate constant
A: frequency factor
$E_a$ - activation energy
T: Temperature
R: Universal gas constant

Rate constant increased by 2% upon 0.1° increase in temperature

$$\rightarrow 1.02K = A e^{\frac{-E_a}{R(T+0.1)}} \quad -(2)$$

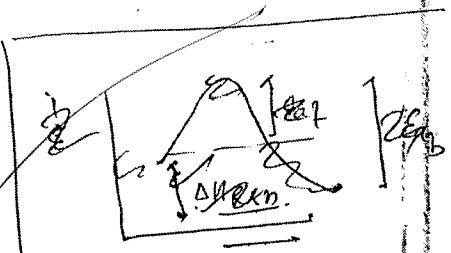
Dividing both the equation

$$1.02 = \frac{e^{-E_a/R(T+0.1)}}{e^{-E_a/R(1/T)}}$$

$$1.02 = e^{-E_a/R\left(\frac{1}{T+0.1} - \frac{1}{T}\right)}$$

$$1.02 = e^{-E_a/R\left(\frac{-0.1}{(T)(T+0.1)}\right)}$$

$$\boxed{E_a = 146.20\ KJ/mol}$$

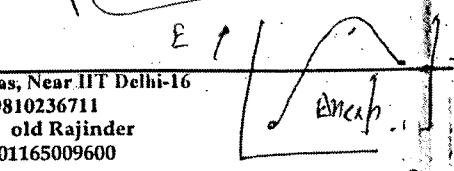



$$\Delta H = E_{af} - E_{ab}$$

$$121.6 = 146.20 - E_{ab}$$

$$E_a = 146.20 - 121.6\ KJ/mol$$

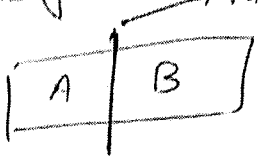
$$\boxed{E_{ab} = 24.6\ KJ}$$



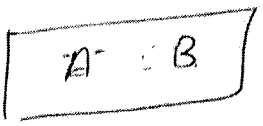
b) Derive the relationship for $\Delta G$ and $\Delta S$ mixing for gases in an ideal process. **[10]**

When gases are mixed their gibs energy and entropy changes.

Consider an example of two gases



Initial condition



Partition removed mixing of gases.

$G_{initial} = \underbrace{n_A}_{\text{no of moles of A}} \underbrace{\mu_A^\circ}_{\text{Standard Gibbs chemical potential of (A)}} + \underbrace{n_B}_{n_B} \mu_B^\circ$

$G_{final} = n_A \mu_A + n_B \mu_B$

$\mu_A = \mu_A^\circ + RT \ln\left(\frac{p_A}{p_0}\right)$ ($\alpha_A$ equal to the fraction)

using the relationship $\Rightarrow$

$G_{final} = n_A\left(\mu_A^\circ + RT \ln(\alpha_A)\right) + n_B\left(\mu_B^\circ + RT \ln \alpha_B\right)$

$G_{final} = n_A \mu_A^\circ + n_A RT \ln \alpha_A + n_B \mu_B^\circ + n_B RT \ln \alpha_B$

$G_{final} - G_{initial} = n_A RT \ln \alpha_A + n_B RT \ln \alpha_B$

$$\boxed{\Delta G = n_{RT} RT\left(n_A \ln \alpha_A + n_B \ln \alpha_B\right)}$$

$$\Delta G_{molar} = RT\left(\alpha_A \ln \alpha_A + \alpha_B \ln \alpha_B\right)$$

Now using generalization for (n) gases

$$\boxed{\Delta G_{mixing}^{molar} = RT \sum_{j=1}^{n} \alpha_j \ln \alpha_j}$$

Entropy of mixing

$dG = Vdp - SdT$.

at constant pressure

$dG = -SdT \Rightarrow S = -\left(\frac{dG}{dT}\right)_P$

$$\Delta S = -\left(\frac{d\left(RT \sum_{j=1}^{n} \alpha_j \ln \alpha_j\right)}{dt}\right)_P$$

$$\boxed{\Delta S = -R \sum_{j=1}^{n} \alpha_j \ln \alpha_j}$$

**c)** One mole of an ideal gas is expanded from 5 $dm^3$ to 10$dm^3$ in an evacuated container calculate entropy change for the process. **[10]**

Entropy is defined as heat supplied at constant pressure divided by temperature

$$ds = \frac{dq_{rev}}{T} \quad -(1)$$

The above given process is a Joule Thompson process

Using first law of thermodynamics

$$dq = dU + (-dw) \quad -(2)$$

using (2) in (1)

$$ds = \frac{dU}{T} - \frac{dw}{T} \qquad dw = -PdU$$

$$ds = \frac{nC_v dT}{T} + \frac{PdV}{T}$$

for gases

$C_v = 3/2\ R$

$C_p = 5/2\ R$

Integrating

$$\int ds = nC_v \int \frac{dT}{T} + \int \frac{nRT}{VT} dV$$

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad -2$$

Since the process is adiabatic irreversible process and gas is ideal (so) $T_2 = T_1$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \Rightarrow \frac{T_2}{T_1} = \left(\frac{1}{2}\right)^{1.4-1}$

$\frac{T_2}{T_1} = 0.66$

$\frac{T_2}{T_1} = 0.63$

$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$

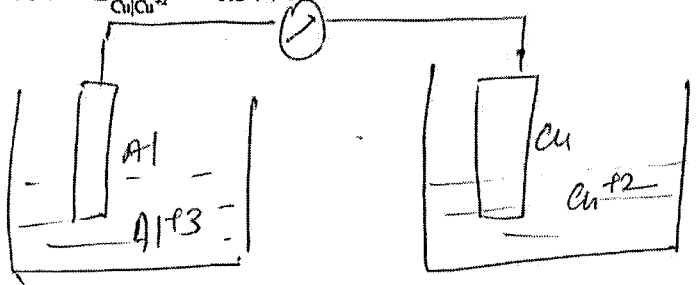
$\Delta S = 1R \ln\left(\frac{10}{5}\right)$

$\Delta S = R \ln 2$

**d)** Calculate EMF of a call given **[10]**

$Al\,|Al^{+3}\,(0.0005M)\,||\,Cu^{+2}\,(0.08M)\,|Cu$

$E^0_{Al^{+3}/Al} = -1.66V \quad E^0_{Cu|Cu^{+2}} = -0.34V$ At 25°C.




Cell Assembly

Anode $Al_{(s)} \rightleftharpoons Al^{+3}_{(aq)} + 3e^{\ominus}$

Cathode $Cu^{+2}_{(aq)} + 2e^{\ominus} \rightleftharpoons Cu_{(s)}$

Net Cell reaction $= 2Al_{(s)} + 3Cu^{+2}_{(aq)} \rightleftharpoons 2Al^{+3}_{(aq)} + 3Cu_{(s)}$

total exchange of $6e^{\ominus}$ in this reaction

$E^0_{cell} = E^0_{Anode} + E^0_{Cathode}$

$= E^0_{Al/Al^{+3}} + E^0_{Cu^{+2}/Cu}$

$E^0_{cell} = 1.66 + 0.34 \Rightarrow 2.0\,V$ at 25°C

**e)** Draw the conductometric Titration curve of [10]

(i) HCl Vs. NaOH

(ii) $NH_4OH$ Vs. $CH_3COOH$

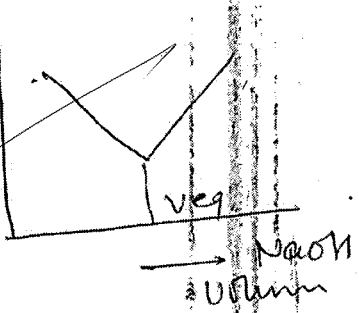
Conductometric Titration is used to measure the concentration of a electrolyte in a solution. It is done through the measurement of ($\Lambda_m$) molar conductance.

(i) HCl vs NaOH.

Before HCl $\rightleftharpoons$ $H^+ + Cl^-$ (aq).

During Titration HCl $\xrightarrow{NaOH}$ NaCl + $H_2O$

After titration 0 HCl $\xrightarrow{NaOH}$ $Na^+ + OH^-$



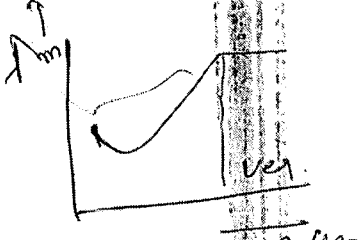

The molar conductance will decrease due to consumption of fast moving $H^+$ and formation of slow moving NaCl. After titration the ($\Lambda_m$) will start increasing due to $OH^-$ ion

(ii) $NH_4OH$ vs $CH_3COOH$.

Before $NH_4OH$ $\rightleftharpoons$ $NH_4^+ + OH^-$

During titration $NH_4OH \xrightleftharpoons{CH_3COOH}$ or $NH_4^+ CH_3COO^- + H_2O$

After 0 $NH_4OH \xrightleftharpoons{CH_3COOH}$ $CH_3COO^- + H^+$.




Initially ($\Lambda_m$) will decrease due to common ion effect of $NH_4^+$ and then it will increase due to formation of $NH_4^+ CH_3COO^-$ salt. After titration ($\Lambda_m$) will become constant due to dissociation of $CH_3COOH$

4. (a) Radii of two reactants A and B participating in a bimolecular reaction are 3 and 4 A respectively. If the partial pressure of A and B at 500k are 0.2 and 0.4 bar respectively, then what is the rate of the reaction at 25°C if steric factor is equal to 0.02 and the activation energy of the reaction is 83.1 KJ/mol, the reduced molar mass of A and B is 78. $\left[12\frac{1}{2}\right]$

The rate of reaction is provided by the collision Theory. According to which molecules collision lead to the formation of product

$$-\frac{dN_A}{dt} = Z_{AB} \times p \times e^{-E_0/RT}$$

$Z_{AB}$: Bimolecular frequency. $p$: Probability factor. $e^{-E_0/RT}$: fraction of molecules above threshold energy. $E_0$ – activation energy.

$$-\frac{d(N_A)}{dt} = \pi \sigma_{AB}^2 \left(p_A\right) \left(\sqrt{\frac{8RT}{\mu\pi}}\right) \exp\left(-E_0/RT\right) \times N_A'' \times N_B''$$

$\frac{dN_A}{dt}$: Rate of reaction. $\sigma_{AB}$: radii of A+B (in m). $\mu$: Reduced Mass (in kg). $N_A''$, $N_B''$: No. of molecules of A & B per unit volume.

$E_0 = E_a - \frac{RT}{2} \Rightarrow$ 81.021 KJ.

$PV = nRT$

$P = \frac{N''}{N} KT \Rightarrow PN = N''KT$

$N_A'' \cdot P_A N = N_A'' RT \Rightarrow$ [illegible]

$\Rightarrow N_A' = \cdot 28.47 \times 10^{23} \cdot 17.20 \times 10^{23} (28.9 \times 10^{23})$

$N_B' = 57.9 \times 10^{23} \cdot 34.52 \times 10^{23} \quad 57.9 \times 10^{23}$

Putting all the values

$$-\frac{d(N_A)}{dt} = 6.51 \times 10^{23} \cdot 9.23 \times 10^{17} \text{ molecules per sec}$$

$9.23 \times 10^{17}$ molecules/sec

b) (i) Discuss the concept of over potential?

(ii) Pt| $H_2$ |HX (pH =?)|| $Cu^{+2}$ (1M)|Cu at 25° if cell potential is 0.80 V then calculate pH of solution. $E^0_{Cu|Cu^{+2}} = -0.34V$ $\left[6\frac{1}{2}+6\right]$

(i) Overpotential is the potential required over and above the standard electrode potential for the bubbling of gas.

$\eta$ = $E_{actual} - E_{theoritical}$

Eg with zinc overpotential is 0.78 V for the bubbling of ($H_2$) gas

(ii)

Pt | $H_2$ | HX | pH = 2 || $Cu^{+2}$ (1M) | Cu

at anode $H_2 + 2X^- \rightleftharpoons 2HX + 2e^-$

~~$H_2 + 2e^- \rightleftharpoons 2H^+ + 2X^-$~~

~~$2HX \rightleftharpoons H_2 + 2e^- + 2X^-$~~

at Cathode $Cu^{+2} + 2e^- \rightleftharpoons Cu(s)$

Overall reaction $H_2 + 2X^-(aq) + Cu^{+2}(aq) \rightleftharpoons 2HX + Cu(s)$

or $H_2 + Cu^{+2}(aq) \rightleftharpoons 2H^+ + Cu(s)$

$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln\left(\frac{[H^+]^2}{[Cu^{+2}]\, P_{H_2}^{1/2}}\right)$

$E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln[H^+]$

$0.80 = E^\circ_{cell} - \frac{RT}{F} \ln[H^+]$

$E^\circ_{cell} = 0.34 + 0$

$E^\circ_{cell} = 0.34$ volt

$0.80 = 0.34 + \frac{RT}{F} \log[H^+]$

$0.46 = +0.059\, pH$

$\therefore pH = 7.78$

c) (i) What are first and second order phase transitions.

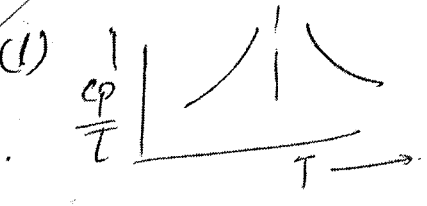
(ii) Calculate B.pt. of water at 10 atm pressure if Normal b.pt. Of water is 100°C and $\Delta H_f = 80$ Kcal mol$^{-1}$. $\left[6\frac{1}{2}+6\right]$

(i) First Order phase transition is that in which free energy remains continuous but first derivative of free energy becomes discontinuous

Second Order phase transition in which free energy and its first derivative remain continuous but the second derivative becomes discontinuous.

eg He-I(l) ⟹ He-II(l)

Sudden change in CP.




(ii) Using Clausius-Clayperon Equation

$H_2O(l) \rightleftharpoons H_2O(g)$ 100°C

$$\ln\left(P_2/P_1\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(10/1\right) = \frac{80 \times 4.2}{8.314}\left(\frac{1}{373} - \frac{1}{T_2}\right)$$

$T_2 = 381K$

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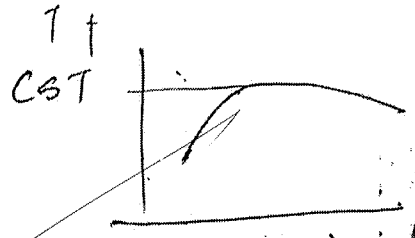
d) (i) What is critical solution temperature? Discuss effect of impurity on CST?

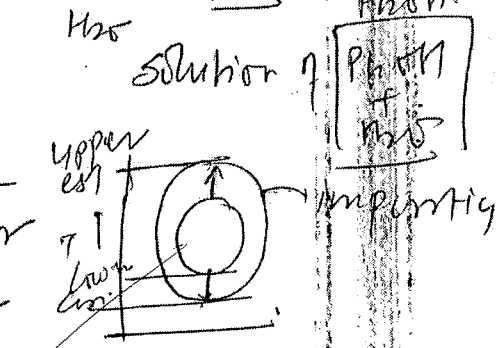
(ii) Calculate final temperature of a monoatomic ideal gas undergoes adiabatic expansion reversibly from 10L to100 L at temperature 300 K. $\left(7+5\frac{1}{2}\right)$

(i) The temperature at which two partially soluble liquids becomes soluble in all proportions is called as critical solution temperature




Impact of impurity

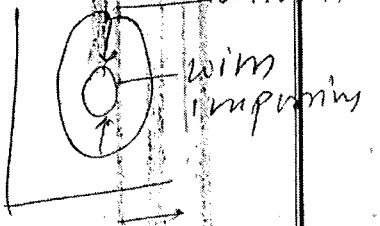
1. If impurity is soluble in only one component then it decreases mutual solubility of that component for the upper CST increase and the lower CST also decreases




2. If impurity is soluble with both the components then it acts as a Bridge to bring two components closer. So each other so that their mutual solubility increases.

upper CST decreases

lower CST increases



Ideal gas undergoing adiabatic expansion follows $TV^{\gamma-1} = \text{constant}$

Monoatomic gas $C_v = \frac{3}{2}R$ | $C_p = C_v + R = \frac{5}{2}R$

$\gamma = \frac{5}{3} \Rightarrow 1.67$

$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$

$T_2 \times (100)^{0.66} = 300 \times (100)^{0.66}$

$T_2 = 65.6\ K$ ∴

5. (a) Derive Gibb's Helmholtz equation and give its one application. $\left[12\frac{1}{2}\right]$

Gibbs free energy is defined as

$$G = H - TS \quad \text{— (1)}$$

Differentiating

$$dG = dH - TdS - SdT$$

$$dG = VdP - SdT$$

at constant pressure.

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

Using this in equation - (1)

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

$$\boxed{G = H + T\left(\frac{\partial G}{\partial T}\right)_P}$$

Gibbs-Helmholtz Equation.

Dividing by $-1/T^2$

$$-G/T^2 = -H/T^2 - \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P$$

$$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - G/T^2 = -H/T^2$$

derivative of $(G/T)$ wrt $T$

$$\boxed{\frac{\partial (G/T)}{\partial T} = -H/T^2} \quad \text{(2)}$$

Application of Gibb's Helmholtz Equation in Vant Hoff Isochore

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

$$\Delta G^\circ/T = -R \ln K_{eq}$$

Differentiate wrt $T$

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

from (2)

$$-\frac{\Delta H}{T^2} = -R \frac{\partial \ln K_{eq}}{\partial T}$$

OR

$$\boxed{\ln K_{eq} = \frac{\Delta H}{RT^2}}$$

Relation between equilibrium constant and enthalpy.

b) Discuss basic principle of amperometry? Draw amperometric titration curve of $K_2SO_4$ Vs $Pb^{+2}$ at $E_{1/2}$ of $Pb^{+2}$. $\left[12\frac{1}{2}\right]$

Amperometry is done to find out the conc of ions in the solution. By measuring the diffusion current upon passing A potential is applied to the solution and residual diffusion current is measured.

**Principle** – Amperometry is done at $E_{1/2}$ of the ion. At $E_{1/2}$ all the current passing through the solution is only due to diffusion. and the current is directly proportional to the bulk concentration According to Ilkavic Equation $i_d \propto c_B$

Titration curve of $K_2SO_4$ vs $Pb^{+2}$ at $E_{1/2}$ of $Pb^{+2}$

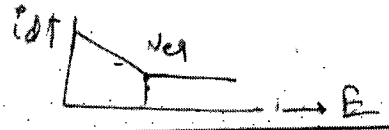
Before Titration. $0\ K_2SO_4 \xrightarrow{\bullet Pb^{+2}}$ ~~No current~~ only residual diffusion current

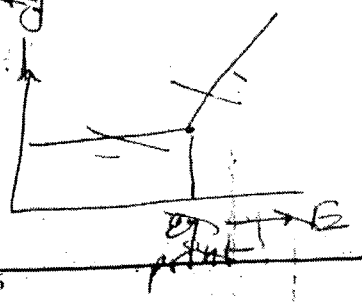
at titration $K_2SO_4 + Pb^{+2} \longrightarrow PbSO_4 \downarrow + 2K^+$ ppt

~~after titration~~ $0\ Pb^{+2}$ ~~$0\ K_2SO_4$~~ $Pb^{+2}$ $Pb^{+2}$ ~~will conduct electricity~~

after titration $0\ Pb^{+2} \xrightarrow{K_2SO_4} K_2SO_4^{2-}$ (No current)

**Curve**

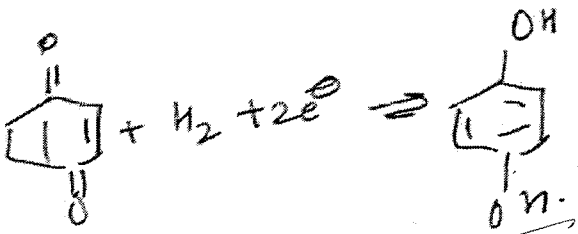


c) Discuss the principle and working of quinhydrone electrode. Why its fails miserably above pH = 10. $\left[12\frac{1}{2}\right]$

Quinhydrone electrode is made up of quinone and hydroquinone at equal quantities. It is generally used to measure pH of the solution

$$Q + H_2 + 2e^{\ominus} \rightleftharpoons QH_2$$



1 : 1 } Equal amount

$$E_{el} = E^{\circ}_{Q/QH_2} - \frac{RT}{2F} \ln\left(\frac{[QH_2]}{[Q][H^+]^2}\right)$$

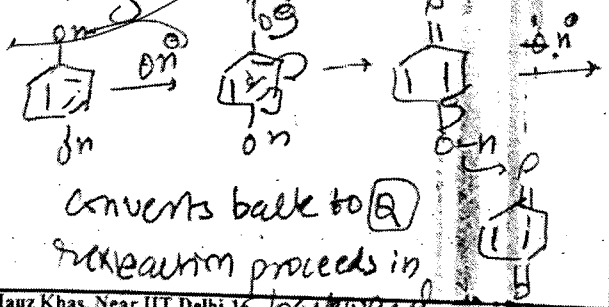
$(QH_2 = Q)$ initially; practically the concentration change is not much

$$E_{el} = E^{\circ}_{Q/QH_2} - \frac{RT}{2F} \ln\left(\frac{(1+x)}{(1-x)\cdot[H^+]^2}\right)$$

$$E_{el} = E^{\circ}_{Q/QH_2} + \frac{RT}{F} \ln[H^+]$$

$$E_{el} = E^{\circ}_{Q/QH_2} + 0.0591\ pH$$

It fails measurably due to ionization of phenol



converts back to Q

Reaction proceeds in backward direction

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d) Derive general expression for $C_p - C_v$ and hence calculate $C_p - C_v$ an ideal gas. $[12\frac{1}{2}]$

$C_p - C_v$ can be calculated by using the Enthalpy equation $[H = U + PV]$

$dH = dU + d(PV)$

$dH = dU + PdV + VdP$

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

$\left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV + VdP$

$C_p$ $C_v$

using the condition constant $T = P$

$C_p dT + 0 = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV + 0$

Using Thermodynamic Equation of state-1

$C_p dT - C_v dT = \left[T\left(\frac{\partial P}{\partial T}\right)_V - R\right] dV + PdV$

$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right) dV$

$\boxed{(C_p - C_v) = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$

For ideal gas

$PV = nRT$

$P = \frac{nRT}{V}$ | $V = \frac{nRT}{P}$

$\frac{\partial P}{\partial T} = \frac{nR}{V}$ | $\frac{\partial V}{\partial T} = \left(\frac{nR}{P}\right)$

$C_p - C_v = T\left(\frac{nR}{V}\right)\left(\frac{nR}{R}\right)$

$PV = nRT$

$\boxed{C_p - C_v = nR}$

$\boxed{C_{p,m} - C_{v,m} = R}$