

THERMODYNAMICS AND EQUILIBRIUM

Unit -1

CU-2016

3) a) show that, $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,N} = v_i$ where the terms have their usual significance.

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

Differentiating both side of (1) w.r.t.p at constant T and N (N=total no. Of moles of different constituents in the mixture), we get,

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,N} = \left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}\right] \text{-----(2)}$$

Since G is a state fanc. Hence it is a perfect differential and it can be written as,

$$\left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}} \right]_{T,N} = \left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i} \right)_{T,N} \right]_{T,P,n_{j \neq i}}$$

So, from (2) $\left(\frac{\partial \mu_i}{\partial p} \right)_{T,N} \left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i} \right)_{T,N} \right]_{T,P,n_{j \neq i}}$

For const composition and at const. Temp. T

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T,N} = \left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i} \right)_{T,N} \right]_{T,P,n_{j \neq i}}$$

$\left(\frac{\partial \mu_i}{\partial p} \right)_{T,N} = v_i$ where v_i = partial molar volume of i th constituent at pressure p and temp. T .

1) a) Derive an expression for the fugacity of a gas which obeys the eqnⁿ of state $PV_m = RT + AP + BP^2$ where V_m in the molar volume.

$$\begin{aligned} PV_m &= RT + AP + BP^2 \\ &= V_m = \frac{RT}{P} + A + BP \end{aligned}$$

Let at pressure p' and p , the fugacity of the gas be f' and f respectively

$$\therefore \Delta G = \int_{P'}^P dp = \int_{P'}^P \left(\frac{RT}{P} + A + BP \right) dp.$$

$$= \Delta G = RT \ln \frac{P}{P'} + A(P - P') + \frac{B}{2} (P^2 - P'^2)$$

Again, we have, $\Delta G = RT \ln \frac{f}{f'}$

$$\therefore RT \ln \frac{f}{f'} = RT \ln \frac{P}{P'} + A(P - P') + \frac{B}{2} (P^2 - P'^2)$$

$$= RT \ln \frac{f}{f'} - RT \ln \frac{P}{P'} = \frac{B}{2} (P^2 - P'^2) + A(P - P')$$

$$= RT \ln \frac{f}{f'} - RT \ln \frac{P}{P'} = \frac{B}{2} (P^2 - P'^2) + A(P - P')$$

$$= RT \ln \left(\frac{f}{f'} \cdot \frac{P'}{P} \right) = \frac{B}{2} (P^2 - P'^2) + A(P - P')$$

2) b) For the rea^n $2A(g) \rightleftharpoons 2B(g) + C(g)$, The K_p of the rea^n increases by 2% per degree Celsius rise in temp. Around 200°C . calculate ΔH° and ΔS° for the rea^n at this temperature.

$$\text{We know, } \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$= \frac{1}{K_p} \cdot \frac{dK_p}{dT} = \frac{\Delta H^\circ}{RT^2} = \frac{dK_p}{K_p} = \frac{\Delta H^\circ}{RT^2} dT$$

$$\text{Now, } \frac{dK_p}{K_p} = \frac{2}{100} = \frac{1}{50}, \quad dT=1\text{k}, \quad T=473\text{K}$$

$$\therefore \frac{1}{50} = \frac{\Delta H^\circ}{8.314\text{JK}^{-1}\text{mol}^{-1} \times (473)^2\text{k}^2} \times 1\text{k}$$

$$= \Delta H^\circ = 37.2 \text{ KJmol}^{-1}$$

ΔS° can not be calculated.

1)b) An exactly 1 molar aq sol^n of mannitol has a vapour pressure of 17.222 mm Hg at 20°C ; at the same temp. the vapour pressure of pure water is 17.535mm. calculate the activity of water in the given solution.

- Activity of water in the given sol^n , $a_{\text{H}_2\text{O}} = \frac{P}{P^\circ}$

Where p = vapour pressure of mannitol = 17.222 mm of Hg.

p° = vapour pressure of pure water = 17.535 mm of Hg .

$$\therefore a_{\text{H}_2\text{O}} = \frac{17.222}{17.535} = 0.982$$

3)b) An approximate equation of state for hydrogen gas at 25°C in $p(v-b)=RT$ for 1 mole of the gas. The value of b is $2.67 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$; when p is in Nm^{-2} use this information to evaluate the fugacity of hydrogen at 25°C and 50 atm pressure. (1 atm \equiv 1.013×10^5 pa)

$$p(V_m - b) = RT \quad \text{where } V_m = \text{molar volume}$$

$$= V_m = \frac{RT}{p} + b$$

$$\Delta G = \int_{P^\circ}^P V_m dp = \int_{P^\circ}^P \left(\frac{RT}{p} + b \right) dp$$

$$= RT \ln \frac{f}{f^\circ} = RT \ln \frac{P}{P^\circ} + b(P - P^\circ)$$

Now, let f be fugacity .when $p \rightarrow^\circ$

Where $p^\circ =$ pressure at standard state and

$f^\circ =$ fugacity at standard state.

Since, the pressure term does not involve any force of attraction term,

So, at standard state, $f^\circ = p^\circ = 1 \text{ atm}$.

$$\therefore 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (m f) \times 298 \text{ K} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \frac{m^{50} + 2.67 \times 10^{-5} m^3 \text{ mol}^{-1} \times (50 - 1) \times 1.013 \times 10^{-5}}{1}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times m f \times 298 \text{ K} = 9692.31 \text{ J mol}^{-1} + 132.53 \text{ J mol}^{-1}$$

$$= m f = 3.965 = f = 52.72.$$

4)a) write down the Debye-Huckel limiting law, and explain all the terms. The value of A depends on a number of factors – mention them.

- According to Debye-Huckel limiting law, for dilute sol^n , the activity coefficient (γ_i) of any ion having charge z_i is given by

$$\log \gamma_i = -A z_i^2 \sqrt{\mu}$$

Where μ is the ionic strength of the sol^n and A is a constant.

- The value of A depends on – 1) dielectric constant of the medium .

2) Temperature

B) calculate the p^H of a weak monoacidic base which has been neutralized by a strong monobasic acid to the extent of 65%. The solvent is water and the temperature is 25°C . (Given, $K_w = 1.0 \times 10^{-14}$, $K_b = 2.0 \times 10^{-5}$).

- when a strong monobasic acid is added to a solution of weak monoacidic base, a basic buffer sol^n is formed.

For the basic buffer, $p^{OH} = p_{K_b} + \log \frac{[salt]}{[base]}$

let the initial conc. Of the base = a moles L^{-1} 65% of the base is neutralised .

$$\therefore [salt] = \frac{65a}{100} \quad \therefore [base]_{\text{remaining unneutralised}} = a - \frac{65a}{100} = \frac{35a}{100}$$

$$\therefore p^{OH} = -\log (2.0 \times 10^{-5}) + \log \frac{\frac{65a}{100}}{\frac{35a}{100}} = 4.96$$

$$\therefore p^H = 14 - p^{OH} = 14 - 4.96 = 9.04$$

$\therefore p^H$ of the sol^n is 9.04.

5)a) Define the term buffer capacity .show that the buffer capacity of acetic

acid –acetate buffer is maximum under the condition $\frac{[salt]}{[Acid]} = 1$.

- The buffer capacity is defined as the amount (no. Of moles) of the acid or base which when added to 1 litre of the given buffer sol^n ,changes its p^H by unity.

Buffer capacity, $\beta = \frac{\text{no.of moles of acid or alkali added/litre}}{\text{change in } p^H}$

$$\therefore \beta = \frac{d[B]}{dp^H} = - \frac{d[A]}{dp^H}$$

$d[B]$ = change in conc. Of base.

$d[A]$ = change in conc. Of acid .

- Let 'a' moles of acetic acid is taken and 'b' moles of strong base is added to it (b < a).

$$\therefore [salt] = b \text{ mol } L^{-1} \quad [Acid] \text{ remaining unneutralised} = (a - b) \text{ mol } L^{-1}$$

$\therefore p^H$ of the sol^n is given by handerson's equ^n ,

$$p^H = p^{Ka} + \log \frac{b}{a - b}$$

$$= p^H = p^{Ka} + \log b - \log(a - b)$$

$$= p^H = p^{Ka} + \frac{1}{2.303} (\log b - \log(a - b))$$

\therefore change of p^H of the sol^n w.r.t. the no. Of moles of base added .

$$\frac{dp^H}{db} = \left[\frac{1}{b} + \frac{1}{a - b} \right] \frac{1}{2.303} = \frac{a}{b(a - b)} \cdot \frac{1}{2.303}$$

$$\therefore \text{buffer capacity, } \beta = \frac{db}{dp^H} = \frac{b(a - b) \times 2.303}{a} = \left(b - \frac{b^2}{a} \right) 2.303$$

$$\beta \text{ is maximum, } \gamma \frac{d\beta}{db} = 0$$

$$= \frac{d}{db} \left[\left(b - \frac{b^2}{a} \right) 2.303 \right] = 0$$

$$= 2.303 \left(1 - \frac{2b}{a} \right) = 0$$

$$= \frac{2b}{a} = 1$$

$$= b = \frac{a}{2}$$

Hence, β is maximum. When the no. of moles of added base is exactly half of the total no. of moles of acid. At this stage,

$$[\text{salt}] \propto b \text{ and } [\text{acid}] \propto (a - b)$$

$$= \frac{[\text{salt}]}{[\text{Acid}]} = \frac{b}{a-b} = \frac{a/2}{a-a/2} = 1$$

Hence, buffer capacity is maximum under the condition $\frac{[\text{salt}]}{[\text{base}]} = 1$

b) The volume (in ml) of NaCl *solⁿ*, per 1000gm of water at 25°C is given by.

$$V = 1002.9 + 16.40m + 2.5m^2 \text{ where } m \text{ is conc. In molality. derive general}$$

expression for partial molar volume of NaCl in aq. sol^n .

– partial molar volume of NaCl in aq. sol^n is,

$$\left(\frac{\partial v}{\partial m}\right)_{T,P} = 16,40 + 5.0m$$

This is the required general expression.

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