

**CU-2015**

1)a) Derive the relationship  $\frac{dmk_p}{dT} = \frac{\Delta H^\circ}{RT^2}$

- we know, the Gibbs Helmholtz equation is,

$$\Delta G^\circ = \Delta H^\circ + T \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right]_P \text{ ----- (1)}$$

Dividing both side of equation (1) by  $T^2$ ,

$$\frac{\Delta G^\circ}{T^2} = \frac{\Delta H^\circ}{T^2} + \frac{1}{T} \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right]_P$$

$$= \frac{1}{T} \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right]_P - \frac{\Delta G^\circ}{T^2} = -\frac{\Delta H^\circ}{T^2}$$

$$= \left[ \frac{\partial}{\partial T} \left( \frac{\Delta G^\circ}{T} \right) \right]_P = -\frac{\Delta H^\circ}{T^2} \quad \left[ \because \frac{\partial}{\partial T} \left( \frac{\Delta G^\circ}{T} \right) = \frac{1}{T} \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right] - \frac{\Delta G^\circ}{T^2} \right] \text{ --- (2)}$$

Again, we know,  $\Delta G^\circ = -RT \ln K_P = \frac{\Delta G^\circ}{T} = -R \ln K_P$  ----- (3) So, from (2)

and (3) we can write.

$$\left[ \frac{\partial}{\partial T} (-RmK_p) \right] = -\frac{\Delta H^\circ}{T^2}$$

$$= R \frac{\partial mK_p}{\partial T} = \frac{\Delta H^\circ}{T^2}$$

$$=$$

$\frac{\partial mK_p}{\partial T} = \frac{\Delta H^\circ}{RT^2}$
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(PROVED)

B) In the above relationship,  $\Delta H^\circ$  is assumed to be a constant. If this is not so and  $\Delta H^\circ$  can be expressed as a power series in T, such as

$$\Delta H^\circ = \Delta H^\circ + A'T + B'T^2 + C'T^3 + \dots$$

Obtain an expression for  $mK_p$  using this value of  $\Delta H^\circ$ .

$$\frac{\partial mK_p}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

$$= \partial mK_p = \frac{\Delta H^\circ}{RT^2} dT$$

$$= \partial mK_p = \frac{1}{RT^2} (\Delta H^\circ + A'T + B'T^2 + C'T^3 + \dots) dT$$

$$= \partial mK_p = \frac{1}{R} \left( \frac{\Delta H^\circ}{T^2} + \frac{A'}{T} + B' + C'T + \dots \right) dT$$

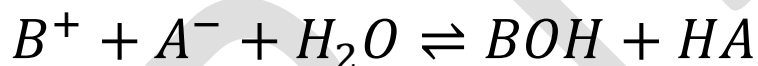
Integrating.

$$\int \partial m K_p = \frac{1}{R} \int \left( \frac{\Delta H^\circ}{T^2} + \frac{A'}{T} + B' + C'T + \dots \right) dT$$

$$= m K_p = \frac{1}{R} \left( -\frac{1}{T} + A'mT + B'T + \frac{C'T^2}{2} + \dots \right)$$

5) b) show that the degree of concentration of a salt of weak acid and weak base is independent of concentration of the solution.

-let BA be the salt of weak acid (HA and weak base, BOH The salt undergoes deionisation in the following way-



$$\therefore \text{degree of hydrolysis of the salt, } k_n = \frac{a_{BOH} a_{HA}}{a_{B^+} \cdot a_{A^-} \cdot a_{H_2O}}$$

$$= k_n = \frac{a_{BOH} a_{HA}}{a_{B^+} \cdot a_{A^-}} \left[ \because a_{H_2O} \approx 1 \right]$$

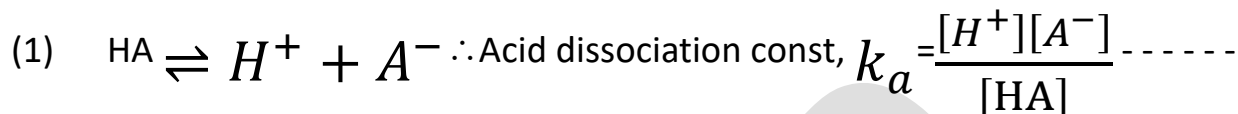
Replacing activities by conc.,

$$k_n = \frac{[BOH][HA]}{[B^+][A^-]} \cdot \frac{\gamma_{BOH} \gamma_{HA}}{\gamma_{B^+} \cdot \gamma_{A^-}}$$

At dil sol<sup>n</sup>.  $\gamma_{B^+} = \gamma_{A^-} = 1$  and also,  $\gamma_{BOH} = \gamma_{HA} = 1$

$$\therefore k_n = \frac{[BOH][HA]}{[B^+][A^-]} \text{-----(1)}$$

The other equilibrium in the  $sol^n$  are,



(2)



-(3)



---(4)

From(1), multiplying  $[H^+][OH^-]$  on numerator and denominator ,

$$k_n = \frac{[BOH][HA][H^+][OH^-]}{[B^+][A^-][H^+][OH^-]} = \frac{[BOH]}{[B^+][OH^-]} \frac{[HA]}{[H^+][A^-]} [H^+][OH^-]$$

$$= k_n = \frac{k_w}{k_a k_n} \text{-----(5)}$$

If  $\alpha$  be the degree of hydrolysis of the salt having initial conc. Of c mol  $L^{-1}$

Then from (1),  $k_h = \frac{c\alpha \cdot c\alpha}{c(1-\alpha) \cdot c(1-\alpha)}$

$$=k_h = \left(\frac{\alpha}{1-\alpha}\right)^2 \text{-----(6)}$$

comparing (5) and (6),  $\left(\frac{\alpha}{1-\alpha}\right)^2 = \frac{k_w}{k_a k_b}$

Now,  $\alpha \ll 1 \therefore 1-\alpha \approx 1 \qquad \therefore \alpha^2 = \frac{k_w}{k_a k_b}$

$$= \alpha = \left(\frac{k_w}{k_a k_b}\right)^{1/2}$$

This shows that the degree of hydrolysis of salt of weak acid and weak base is independent of the conc. Of the  $sol^n$ .

(a) The ionic strength of 0.1 N  $CH_3COOH$  solution is 0.001 at  $20^\circ C$  calculate the  $p^H$  of the  $sol^n$ .

-  $CH_3COOH$  dissociates in the following way.



Initial conc.                    c                    0                    0

At equilibrium                 $c(1-\alpha)$                  $c\alpha$                  $c\alpha$                      $\alpha =$  degree of hydrolysis

$\therefore k_a = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)}$                     since,  $\alpha \ll 1 \therefore 1-\alpha \approx 1$

$$\therefore k_a = c \alpha^2 \Rightarrow \alpha = \sqrt{\frac{k_a}{c}} \quad \therefore C_{H^+} = c \alpha = \sqrt{k_a c}$$

A.c.t., Debye-huckel limiting law,  
 activity coefficient .

$\gamma_{\pm}$  = mean ionic

$$\log \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{\mu}$$

$\mu$  = ionic strength.

From question,  $\mu = 0.001$ ,  $c = 0.1$ (N)

$$\therefore \log \gamma_{\pm} = -0.509 \sqrt{0.001} \times 1 = -0.016$$

$$\gamma_{\pm} = 0.963.$$

$$\text{Now, } p^H = -\log a_{H^+} = -\log (\gamma_{\pm} C_{H^+}) = -\log (\gamma_{\pm} \cdot \sqrt{k_a c})$$

$$\therefore p^H = -\log \gamma_{\pm} - \log (\sqrt{k_a c})$$

$$= -\log \gamma_{\pm} - \frac{1}{2} \log k_a - \frac{1}{2} \log c.$$

$$\therefore p^H = -(-0.016) - \frac{1}{2} \log(1.8 \times 10^{-5}) - \frac{1}{2} \log 0.1$$

$$= 0.016 + 2.37 + 0.5$$

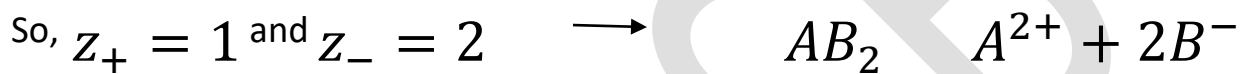
$$p^H = 2.886.$$

- (2) b) The mean ionic activity coefficient of a 1-2 type electrolyte in 0.005 M solution is 0.75. Calculate Debye-Huckel constant using the limiting law.

A.c.t, Debye-Huckel limiting law,

$$\log \gamma_{\pm} = -A z_+ z_- \sqrt{\mu} \text{ ----- (1)}$$

1-2 type electrolyte means  $AB_2$  type electrolyte



Given,  $\gamma_{\pm} = 0.75$

Now, ionic strength,  $\mu = \frac{1}{2} \sum m_i z_i^2$

Here,  $m_{A^{2+}} = 0.005$  M and  $z_{A^{2+}} = 2$  and,  $m_{B^{-}} = (2 \times 0.005)$  M = 0.01 M

$$z_{B^{-}} = 1$$

$$\therefore \mu = \frac{1}{2} [0.005 \times 2^2 + 0.01 \times 1^2] = 0.015$$

$$\therefore \text{From (1), } \log 0.75 = -A \times 1 \times 2 \times \sqrt{0.015}$$

$$= A = - \frac{\text{Log } 0.75}{1 \times 2 \times \sqrt{0.015}} = 0.510$$

$\therefore$  Debye-Huckel constant = 0.510

4) b) show that  $\mu_i = \left( \frac{\partial H}{\partial n_i} \right)_{s,p,n_{j \neq i}}$

- The change of free energy of a system of variable composition can be expressed as,

$$dG = vdp - sdT + \sum_i \mu_i dn_i \text{ ----- (1)}$$

Again, we have,  $G = H - Ts = H - G + Ts$

Differentiating both sides,  $dh = dG + Tds + sdT$

Expressing  $dG$  in terms of (1), we can write,

$$\begin{aligned} dH &= vdp - sdT + \sum_i \mu_i dn_i + Tds + sdT \\ = dH &= vdp + Tds + \sum_i \mu_i dn_i \text{ ----- (2)} \end{aligned}$$

This is the expression for change of  $H$  of a system with variable composition again for a system with variable composition, we have,

$H = f(p, s, n_1, n_2, n_3 \text{ --- })$  where  $n_1, n_2, n_3 \text{ ---}$  are the no. Of moles of constituent 1,2,3 respectively.



$$\begin{aligned} \therefore dH &= \left(\frac{\partial H}{\partial S}\right)_{S,N} dp + \left(\frac{\partial H}{\partial S}\right)_{P,N} ds \\ &+ \left(\frac{\partial H}{\partial n_1}\right)_{P,S,n_2,n_3} dn_1 \quad \text{and total no. Of moles no} \\ &= n_1 + n_2 + n_3 + \\ &+ \left(\frac{\partial H}{\partial n_2}\right)_{P,S,n_1,n_3} dn_2 \\ = dH &= \left(\frac{\partial H}{\partial S}\right)_{S,N} dp + \left(\frac{\partial H}{\partial S}\right)_{P,N} ds + \\ &\sum_i \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_{j \neq i}} dn_i \quad \text{--- (3)} \end{aligned}$$

At constant composition,

$$\left(\frac{\partial H}{\partial P}\right)_{S,N} = V \quad \text{and} \quad \left(\frac{\partial H}{\partial S}\right)_{P,N} = T$$

So, equ<sup>n</sup> (3) becomes,

$$dH = vdp + Tds + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_{j \neq i}} dn_i \quad \text{--- (4)}$$

comparing (2) and (4) we can write,

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

- a) The relation  $K_P = K_C(RT)$  for the equilibrium  
 $N_2O_2(g) \rightleftharpoons 2NO_2(g)$  implies that  $K_P/K_C$  has the S.I.  
unit joule  $mol^{-1}$

Justify or criticize the statement.

From relation,  $K_P = K_C(RT) = \frac{K_P}{K_C} = RT$

$\therefore$  unit of  $\frac{K_P}{K_C} = J k^{-1} mol^{-1} \times k = J mol^{-1}$

From this relation it is seen that the unit of  $\frac{K_P}{K_C}$  is  $J mol^{-1}$