VIVEKANANDA COLLEGE
THAKURPUKUR
KOLKATA-700063

NAAC ACCREDITED ‘A’ GRADE

Topic: Non Ideal Solutions

Course Title: General Physical Chemistry

Paper: BCMA CC3

Unit: Non Ideal Solutions and Thermodynamics of EMF of cells

Semester: 2

Name of the Teacher: **Dr. Subharthi Banerjee**

Name of the Department: Biochemistry

[redacted]

⇒ Concept of activity :

We know, $\mu_i = \mu_i^\circ + RT\ln\left(\frac{p_i}{p^\circ}\right)$ for an ideal gas system,

where, $\mu_i \rightarrow$ chemical potential of the i-th species

$p^\circ \rightarrow$ Standard pressure (1 bar)

⇒ To have the same type of dependence of any substance (s/l/g), G.N. Lewis modified the equation to give

$$\mu_i = \mu_i^\circ + RT\ln a_i ,$$

where $a_i \rightarrow$ a dimensionless quantity called 'activity' of the i-th species

⇒ For a substance in solid/liquid phase :

$$\mu_i = \mu_i^\circ + V_{m,i}(p - p^\circ)$$

[Variation of μ with p]

Thus, $RT\ln a_i = V_{m,i}(p - p^\circ)$

$$\Rightarrow a_i = \exp\{V_{m_i}(p - p^\circ)/RT\}$$

Small variations of pressure do not have any significant effect on the activity.

→ For components in an ideal liquid solution:

We know, $\mu_i(l) = \mu_i(g)$ at $l \rightleftharpoons v$

$$\Rightarrow \mu_i^\circ(l) + RT\ln a_i = \mu_i^\circ(g) + RT\ln\left(\frac{p_i}{p^\circ}\right) \ldots \text{①}$$

For a pure liquid, $a_i = 1$ and $p_i = p_i^*$ (V.P. of pure liquid

$$\therefore \mu_i^\circ(l) + RT\ln a_i = \mu_i^\circ(g) + RT\ln\left(\frac{p_i^*}{p^\circ}\right)$$

$$\Rightarrow \mu_i^\circ(l) + \cancel{RT\ln} = \mu_i^\circ(g) + RT\ln\left(\frac{p_i^*}{p^\circ}\right)$$

Substituting in ①,

$$\mu_i^\circ(g) + RT\ln\left(\frac{p_i^*}{p^\circ}\right) + RT\ln a_i = \mu_i^\circ(g) + RT\ln\left(\frac{p_i}{p^\circ}\right)$$

$$\Rightarrow RT\ln a_i = RT\ln\left(\frac{p_i}{p^\circ}\right) - RT\ln\left(\frac{p_i^*}{p^\circ}\right)$$

$$= RT\left[\ln \frac{p_i}{p^\circ} \times \frac{p^\circ}{p_i^*}\right]$$

$$\Rightarrow RT\ln a_i = RT\ln\left(\frac{p_i}{p_i^*}\right)$$

Thus, $\boxed{a_i = \frac{p_i}{p_i^*}}$

Ideal behaviour follows Raoult's law. $[\, p_i = x_i p_i^* \,]$

$$\therefore a_i = \frac{x_i p_i^*}{p_i^*}$$

$$\Rightarrow \boxed{a_i = x_i}$$

⇒ For components in a non-ideal liquid <u>solution</u>:

Non-ideal liquid solutions show deviations from Raoult's law. To account for the non-ideality, the activity (a_i) is defined as:

$$a_i = x_i \gamma_i ,$$

where $\gamma_i \rightarrow$ activity coeff. [a measure of deviation from Raoult's law]

$\because \gamma_i \rightarrow 1$ as $x_i \rightarrow 1$

For ⊕ve deviations, $\gamma_i > 1$
⊖ve " , $\gamma_i < 1$

$$\because \quad a_i = \frac{p_i}{p_i^*}$$

$$\Rightarrow \quad x_i \gamma_i = \frac{p_i}{p_i^*}$$

$$\Rightarrow \boxed{\gamma_i = \frac{p_i}{x_i p_i^*}}$$

⇒ For electrolytes in solution:

$$\mu(M_x X_y) = x\mu(M^{y+}) + y\mu(X^{x-})$$

and $\mu = \mu^\circ + RT \ln a$

$$\therefore \mu(M_x X_y) = x\left[\mu^\circ(M^{y+}) + RT \ln a_{M^{y+}}\right] + y\left[\mu^\circ(X^{x-}) + RT \ln a_{X^{x-}}\right]$$

$$= x\mu^\circ(M^{y+}) + y\mu^\circ(X^{x-}) + RT \ln\left[(a_{M^{y+}})^x (a_{X^{x-}})^y\right]$$

$$\Rightarrow \boxed{\mu(M_x X_y) = \mu^\circ(M_x X_y) + RT \ln a_{M_x X_y}}$$

where, $a_{M_x X_y} = (a_{M^{y+}})^x (a_{X^{x-}})^y$

or, simply, $\boxed{a = (a_+)^x (a_-)^y}$

$\boxed{a_i = x_i \gamma_i}$

$$\Rightarrow a_+ = \left(\frac{m_+}{m^\circ}\right)\gamma_+$$

$m^\circ \rightarrow$ Standard state molality $[1 \text{ mol kg}^{-1}]$

$$a_- = \left(\frac{m_-}{m^\circ}\right)\gamma_-$$

$$\therefore a_+ = m_+' \gamma_+ \quad \& \quad a_- = m_-' \gamma_-$$

$$m_+' = \frac{m_+}{m^\circ} \Big/ m_-' = \frac{m_-}{m^\circ}$$

Since individual activities cannot be determined, it is more appropriate to express activity of an ion in terms of mean activity of the electrolyte.

$$(a_\pm)^\nu = (a_+)^x . (a_-)^y$$, where $\nu = x + y$ = total no. of ions produced by 1 molecule of an electrolyte $M_x X_y$

Again, $a = (a_+)^x (a_-)^y$

i.e. $(a_\pm)^\nu = a$

$$(a_\pm)^\nu = (m_+' \gamma_+)^x (m_-' \gamma_-)^y = m_\pm'^{\nu} \gamma_\pm^{\nu}$$

$$\Rightarrow \boxed{a_\pm = m_\pm' \gamma_\pm}$$

$$m_\pm'^{\nu} = m_\pm'^{x+y} = m_+'^{x} m_-'^{y} = x^x y^y m'^{x+y}$$

$$\Rightarrow m_\pm' = (x^x y^y)^{\frac{1}{x+y}} m'$$

$$\underline{a(MX)} = a_\pm^2 = (m_\pm' \gamma_\pm)^2 = m'^2 \gamma_\pm^2$$

$$\underline{a(MX_2)} = a_\pm^3 = (m_\pm' \gamma_\pm)^3 = (m_+' m_-'^2) \gamma_\pm^3 = (m')(2m')^2 \gamma_\pm^3$$

$$\underline{a(MX_3)} = a_\pm^4 = (m')(3m')^3 \gamma_\pm^4$$

$$\underline{a(M_2X_3)} = a_\pm^5 = (2m')^2 (3m')^3 \gamma_\pm^5$$

⇒ Debye-Huckel law:

Because of ionic interactions, many bulk properties of an electrolyte are not related directly to the actual concentration, but with the activity of the electrolyte.

Concentration and activity are related according to:

$$a = \left(\frac{c}{c^{\circ}}\right)\gamma_c \text{ or } \left(\frac{m}{m^{\circ}}\right)\gamma_m \text{ or } x\,\gamma_x$$

$\gamma \rightarrow$ activity coeff.

$$\left.\begin{aligned}(a_{\pm})^{\nu} &= (a_{+})^{\nu_+}(a_{-})^{\nu_-}\\ (\gamma_{\pm})^{\nu} &= (\gamma_{+})^{\nu_+}(\gamma_{-})^{\nu_-}\end{aligned}\right\} \quad \nu = \nu_+ + \nu_-$$

= total no. of ions derived from 1 molecule of an electrolyte

$$\boxed{\mu_i = \mu_i^{\circ} + RT\ln x_i + RT\ln\gamma_i} \text{ for non-ideal solutions}$$

The activity coeff. can be theoritically predicted on the basis of Debye-Huckel theory.

Each ion is surrounded by a spherically symmetrical ionic atmosphere consisting of other ions whose net charge is opposite to that of the central ion. The activity coeff. may be considered as the contribution of this ionic atmosphere.

⇒ Limiting form of D-H equation:

$$\log\gamma_{\pm} = -|z_+ z_-|A\sqrt{\mu} \boxed{= -0.514|z_+ z_-|\sqrt{I}}$$

where $A \rightarrow$ constant

$z_+/z_- \rightarrow$ cationic/anionic charges

$$I = \frac{1}{2}\sum_i c_i z_i^2$$

$c_i \rightarrow$ molality

A for water at 298 K = $0.514\ mol^{-1/2}\ dm^{3/2}$

Accd. to the equation, $\log f_{\pm}$ decreases with increase in ionic strength of the solution. For the D-H Theory, electrolytes must completely dissociate and their solutions are very dilute (assumptions)

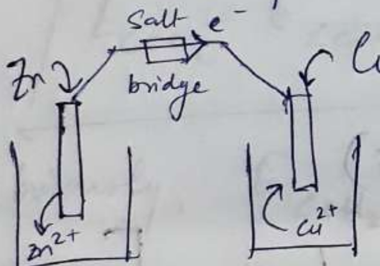
- Electrochemical cells:

→ Electrolytic → electrical energy to chemical energy

→ Galvanic → chemical " " electrical "

eg Daniel cell

$Zn|Zn^{2+}||Cu^{2+}|Cu$



$E_{cell} = E_R - E_L$

= Higher reduction potential

− Lower reduction potential

$Zn \rightarrow Zn^{2+} + 2e$ | $Cu^{2+} + 2e \rightarrow Cu$

Left hand $\frac{1}{2}$ cell | Right hand $\frac{1}{2}$ cell

Oxidation | Reduction

Anode | Cathode

⊖ | ⊕