# Activity coefficients of electrolytes

## Activity coefficients:-

$$MA \rightleftharpoons M^+ + A^-$$

Applying the law of chemical equilibrium we have,

$$K = \frac{(a_{M^+})(a_{A^-})}{a_{MA}} \quad\quad - ①$$

The activity is related concentration expressed in term of molality i.e. in terms of moles per kg of solvent by the expression.

$$a = \gamma m \quad\quad - ②$$

$$\gamma \rightarrow activity\ coefficient$$

Thus

$$K = \frac{(\gamma_{M^+} m_{M^+})(\gamma_{A^-} m_{A^-})}{\gamma_{MA}\, m_{MA}} = \left(\frac{\gamma_{M^+}\, \gamma_{A^-}}{\gamma_{MA}}\right)\left(\frac{m_{M^+}\, m_{A^-}}{m_{MA}}\right) - ③$$

## Mean Ionic Activity coefficient:-

Consider ionization of uni-univalent electrolyte MA

$$MA \rightleftharpoons M^+ + A^-$$
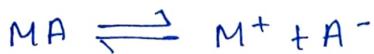
$a_+ \rightarrow$ activity of cation

$a_- \rightarrow$ activity of anion

Both the quantities are indeterminable since it is not possible to have ions exclusively of one charge present in a solution.

Mean-ionic activity and ionic activity can be related as:-

$$a = (a_+)(a_-) = (a_\pm)^2 \quad — \text{①}$$

For electrolytes with formula $M_x A_y$ which ionizes as

$$M_x A_y \rightleftharpoons x M^+ + y A^-$$

The mean ionic activity is given by,

$$a = (a_+)^x (a_-)^y = (a_\pm)^{x+y} \quad — \text{②}$$

If $m$ is the initial concentration of the electrolyte $M_x A_y$ in terms of moles per $1000\ g$ of solvent

The concentration of $M^+$ and $A^-$ can be given as $xm$ and $ym$ respectively. Knowing the activity related to molal concentration by expression

$$a = \gamma m \quad — \text{③}$$

equation ② may be rewritten as

$$a = (\text{☓}) (x + m)^x (y\gamma_- m)^y — \text{④}$$

$$a = x^x y^y \gamma_+^x\ m^{x+y}\ \gamma_-^y — \text{⑤}$$

$$= x^x y^y (\gamma_\pm m)^{x+y} — \text{⑥}$$

Here $\gamma_\pm$ is mean molal ionic coefficient

Defined as

$$(\gamma_\pm)^{x+y} = (\gamma_+)^x (\gamma_-)^y — \text{⑦}$$

The value of $a$ can be calculated experimentally. The value of mean activity coefficient can be calculated eq ⑦.

$x$ and $y$ depend upon the electrolyte being used.

For uni-univalent    $x = 1$, $y = 1$

for uni-bivalent    $x = 2$ $y = 1$,    like $K_2 SO_4$

for bi-univalent    $x = 1$, $y = 2$    like $BaCl_2$.

For uni-univalent
$$a = (\gamma_{\pm} m)^2$$
For uni bivalent or bi-univalent
$$a = 2^2 \times 1 \, (\gamma_{\pm} m)^{2+1}$$
$$= 4\gamma_{\pm}^3 \, m^3$$
The activity coefficient of each electrolyte at infinite dilution is taken as unity.

* At lower concentration the mean ionic ~~concentration~~ activity coefficient is close to unity ie. the departure from ideal behaviour is small. As the concentration increases, the activity coefficients falls much below unity and approaches a certain minimum value indicating much larger departures from ideal behaviour.
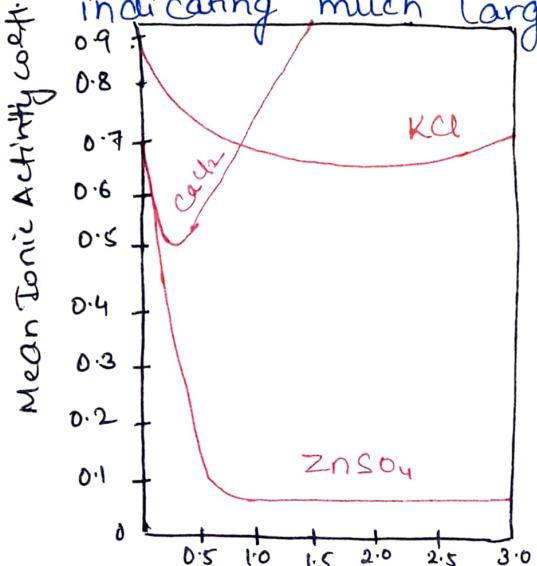


* From graph it is clear that mean ionic activity coefficient keeps falling as the concentration is increased for $ZnSO_4$ but for $CaCl_2$ it decrease and then jumps up.

* The electrolytes with same values like $KCl$ and $NaCl$ showed equivalent values of mean ionic activity coefficient. at same concentration particularly. when the concentration is not too high.

Y-axis: Mean Ionic Activity coeff.
X-axis: √molality

Graph labels: $CaCl_2$, $KCl$, $ZnSO_4$

Ionic Strength:- The Ionic strength I of a solution is a measure of electrical intensity due to the presence of ions in the solution. It is given by half of the sum of all the terms obtained by multiplying the molality of each

ion by square of its valency.

$$I = \frac{1}{2}\left(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \cdots\right) - \text{①}$$

where $m_1$, $m_2$ and $m_3$ ..... are the ~~molalities~~
molalities and $z_1$, $z_2$, $z_3$ .... are valencies of
various ions present in the solution.

For a single electrolyte $KCl$ and $ZnSO_4$ have
two ions [ one cation one anion). Hence

$$I = \frac{1}{2}\left(m_+ z_+^2 + m_- z_-^2\right) - \text{②}$$

Question: Find the ionic strength of $NaCl$ (0.1) molal
and $CaCl_2$ (0.01) under complete state of
ionization in a solution.

$NaCl$: for $Na^+$ $m_1 = 0.1\ M$ , for $CaCl_2$ $m_2 = 0.01\ M$

Total molality of ~~Co~~ $Cl^-$, $m_3 = 0.1 + 0.02$
$$= 0.12$$

Therefore $I = \frac{1}{2}\left(0.1 \times 1^2 + 0.01 \times 2^2 + 0.12 \times 1^2\right)$

$$= \frac{1}{2}\left(0.1 + 0.04 + 0.12\right)$$

$$= \frac{1}{2} \times (0.26) = 0.13$$

* calculate ionic strength of following —
  a) 0.15 molal $KCl$ solution
  b) 0.25 molal $K_2SO_4$ solution
  c) 0.25 molal $BaCl_2$ solution.

# Debye Huckel Theory of mean ionic Activity coefficient:

→ Consider uni-univalent electrolyte.

According to electrostatics there exists as an average potential $\psi$ at a distance $r$ from a given ion. The potential energy of ion under this potential is $e\psi$ where $e$ is the electronic charge.

→ According to Boltzmann distribution law, the probability that a given positive charge is in region of potential $\psi$ around a particular ion having the same charge is given by

$$n_+ = ne^{-\bar{e}\psi/kT} \qquad ——①$$
$$n_- = ne^{\bar{e}\psi/kT} \qquad ——②$$

→ Net charge density $\rho$ is given by

$$\rho = (n_+ - n_-)\bar{e} = n\bar{e}(e^{-\bar{e}\psi/kT} - e^{\bar{e}\psi/kT}) \qquad ——③$$

$\bar{e}$ for charge symbol.

If the dielectric constant of medium is $\epsilon_r$, The Poissan equation

$$\bar{\nabla}^2\psi = -4\pi\rho/\epsilon_r \qquad ——④$$

$\bar{\nabla}$ → Laplacian operator.

In terms of spherical polar coordinates the poissan eqn is

$$\bar{\nabla}^2\psi = \frac{1}{r^2} \times \frac{d}{dr}\left[r^2\frac{d\psi}{dr}\right] = -4\pi\rho/\epsilon_r \qquad ——⑤$$

Substituting equation ⑤ in equation ③ we get

$$\nabla^2\psi = -\frac{4\pi n\bar{e}}{\varepsilon_r}\left(e^{-\bar{e}\psi/kT} - e^{\bar{e}\psi/kT}\right)$$

— ⑥

This equation is known as <u>Poisson- Boltzmann</u> <u>equation</u>.

\* For $\psi$ not high the equation can be expanded linearly as

$$e^{\bar{e}\psi/kT} = 1 + \frac{\bar{e}\psi}{kT} + \text{high powers of} \left(\frac{\bar{e}\psi}{kT}\right) \text{— ⑦}$$

$$e^{-\bar{e}\psi/kT} = 1 - \frac{\bar{e}\psi}{kT} + \text{high powers of} \left(\frac{\bar{e}\psi}{kT}\right) \text{— ⑧}$$

Therefore

$$\nabla^2\psi = \left[\frac{8\pi n\bar{e}^2}{\varepsilon_r kT}\right]\psi \quad\text{— ⑨}$$

Also $K \Rightarrow$ can be defined as

$$K^2 = \frac{4\pi \bar{e}^2}{\varepsilon_r kT}\sum n_i z_i^2 \quad\text{— ⑩}$$

$z_i$ is the charge on the ion, we have for uni-univalent electrolyte

$$K^2 = \frac{8\pi n\bar{e}^2}{\varepsilon_r kT} \quad\text{— ⑪}$$

eq ⑨ can be rewritten as

$$\nabla^2\psi = K^2\psi \quad\text{— ⑫}$$

and thus, $\boxed{\psi(r) = \dfrac{z\bar{e}}{\varepsilon_r r} - \dfrac{z\bar{e}K}{\varepsilon_r}}$ — ⑬

In the eq ③

$$\frac{ze}{\varepsilon_r r} \rightarrow$$ Potential due to the charge on the ion itself while the second term can be thought as the potential due to charge $-ze$ at a distance $1/\kappa$, ~~which~~ ~~has~~.

$1/\kappa$ has the dimension of length called <u>effective radius of ionic atmosphere</u> or <u>Debye length</u>

\* Please mail on ankitaojha26@gmail.com to join for online classes.

\* Send your details as name, Roll no. and scanned ID.