M.Sc. I Sem.
CC-2, Unit-IV

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Concept of activity :-

According to Law of mass action, "The rate of reaction is proportional to the product of active masses of the reactants. In case of gases, partial pressures can be used in place of active masses as the two are proportional to each other. But when substances react in solution, it does not necessarily follow that their concentrations correspond entirely to their active masses. This would occur only if the solution are ideal i.e dilute solution, e.g. one component becomes hydrated or solvated and if only the non-solvated portion can react then it is only this portion that contributes to the active mass.

If the total concentration be c and that of the non solvated molecules be a then the ratio a/c is termed as activity coefficient usually repersented by f or γ, so

$$\frac{a}{c} = f \text{ or } \gamma \quad \text{——— (1)}$$

The same idea, has been applied to solution of strong electrolytes. In case of an ideal solution, the value of f is unity.

consider the following reaction to take place in solution.

$$A + B \rightleftharpoons C + D$$

At equilibrium.

$$K = \frac{a_C \times a_D}{a_A \times a_B}$$

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Where, a_A, a_B, a_C and a_D represent the ideal concentrations or activities of the respective constituents A, B, C and D. The concentration can be also expressed in terms of molality. (m) (no. of moles of solute in 1000 gm of solvent)

The ratio a/m is also known as activity cofficient (γ)

Consider a uni-univalent electrolyte of type BA. (eg. NaCl, KCl etc) whose ionisation as follows

$$BA \rightleftharpoons B^+ + A^-$$

Equilibrium constant

$$K = \frac{[B][A]}{[BA]} = \frac{a_+ a_-}{a_2} \quad \text{——— (2)}$$

where a_+ = activity of B^+
a^- = activity of A^-
a_2 = activity of undissociated electrolyte (BA)

The mean activity of the two ions ($a_\pm$) may be regarded as the geometric mean of the activities of the respective ions. from eq (2)

$$a_\pm = \sqrt{(a_+ \cdot a_-)} = (K a_2)^{1/2} \quad \text{——— (3)}$$

The seperate activity coefficient of the ions are.

$$\gamma_+ = \frac{a_+}{c_+} \quad \text{and} \quad \gamma_- = \frac{a_-}{c_-}$$

The mean activity ~~coef~~ coefficient $\gamma_\pm$ of the two ions. as so.

$$b = b_\pm = \sqrt{(b_+ b_-)}$$

$$= \sqrt{\left(\frac{a_+}{c_+} \cdot \frac{a_-}{c_-}\right)} = \frac{a_\pm}{c_\pm}$$

$$= \sqrt{\frac{K a_2}{c}} \quad \text{from eqn. (3)}$$

where $c_\pm = c$

In general, for an electrolyte which dissociates into ν_+ cation and ν_- anions we have:

$$B_{\nu_+} A_{\nu_-} \rightleftharpoons \nu_+ B^+ + \nu_- A^-$$

Let a_+, a_- and a_2 be the activity of the cations, anions and undissociated electrolyte respectively. Then

$$K a_2 = a_+^{\nu_+} \cdot a_-^{\nu_-}$$

The mean activity is then given by.

$$a_\pm = \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/(\nu_+ + \nu_-)}$$

$$= \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/\nu} = \left(K a_2\right)^{1/\nu} \quad \text{——— (4)}$$

where, ν = total no. of ions $= \nu_+ + \nu_-$

If the total concentration of the electrolyte is 'c' then the activity coefficients of the ions are-

$$b_+ = \frac{a_+}{\nu_+ c} \quad \text{and} \quad b_- = \frac{a_-}{\nu_- c} \qquad (5)$$

The mean activity coefficient of the electrolyte is given by,

$$b_\pm = \left(b_+^{\nu_+} \cdot b_-^{\nu_-}\right)^{1/\nu}$$

$$= \left[\left(\frac{a_+}{\nu_+ c}\right)^{\nu_+} \left(\frac{a_-}{\nu_- c}\right)^{\nu_-}\right]^{1/\nu} \quad \text{from eqn. (5)}$$

$$= \left(a_+^{\nu_+} \cdot a_-^{\nu_-}\right)^{1/\nu} \left[\frac{1}{(\nu_+ c)^{\nu_+} (\nu_- c)^{\nu_-}}\right]^{1/\nu}$$

$$b_\pm = \frac{a_\pm}{c_\pm} \qquad (6)$$

where $c_\pm = \left[(\nu_+ c)^{\nu_+} \cdot (\nu_- c)^{\nu_-}\right]^{1/\nu} = c\left(\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}\right)^{1/\nu} \qquad (7)$

The factor $\left[\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}\right]^{1/\nu}$ is known as valency factor

from eqn. (4), (6) and (7) we get,

$$b_\pm = \frac{(K a_2)^{1/\nu}}{c_\pm} \qquad (8)$$

If standard state chosen, then in all above calculation K put to be equal to unity.

$$BA \rightleftharpoons B^+ + A^-, \quad K = \frac{a_+ a_-}{a_2} = \frac{(b_+ c_+)(b_- c_-)}{b_2 c_2}.$$

$$K = \frac{b_+ b_-}{b_2} \cdot \frac{c_+ c_-}{c_2} = \frac{b_+ b_-}{b_2} \cdot K_1 \qquad [\because a = b \cdot c]$$

K is known as true or thermodynamic dissociation constant. where K_1 is known as classical dissociation constant.