

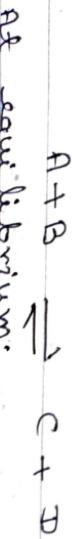
### concept of activity:-

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 similarly to their active masses. This would occur only if the solution are ideal i.e dilute solution, w.r.t one component. Because 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 represented by  $\gamma$  or  $\alpha$ , so

$$\frac{a}{c} = \gamma \quad (1)$$

The same idea has been applied to solution of strong electrolytes. In case of an ideal solution, the value of  $\gamma$  is unity, consider the following reaction to take place in solution.



At equilibrium:

$$K = \frac{ac \times ad}{a_A \times a_B}$$

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 also be expressed in terms of molality (m) (no. of moles of solute in 1000 gm of solution)

The ratio  $a/m$  is also known as

activity coefficient (f)

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



Equilibrium constant

$$K = \frac{[B^+][A^-]}{[BA]} = f_+ f_- \quad (2)$$

where  $f_+$  = activity of  $B^+$

$f_-$  = activity of  $A^-$

$a_2$  = activity of undissociated electrolyte (BA)

The mean activity of the two ions ( $f_{\pm}$ ) may be regarded as the geometric mean of the activities of the respective ions. from  $\text{eqn } (2)$

$$a_{\pm} = \sqrt{a_+ a_-} = (Ka_2)^{1/2} \quad (3)$$

The separate activity coefficient of the ions are

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

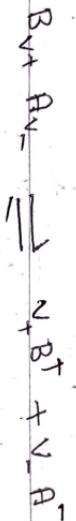
The mean activity coefficient  $f_{\pm}$  at the two ions, as so,

$$b = b^+ = \sqrt{b + b^-}$$

$$= \sqrt{\left(\frac{a^+}{c^+} \cdot \frac{a^-}{c^-}\right)} = \frac{a^+}{c^+}$$

$$= \frac{K_{a^+}}{c} \quad \text{from law. (3)}$$

In general, for an electrolyte which dissociates into  $v_+$  cation and  $v_-$  anions we have.



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

$$K_{a_2} = a_+^{v_+} \cdot a_-^{v_-}$$

The mean activity is then given by

$$a_+ = (a_+^{v_+} a_-^{v_-})^{1/(v_+ + v_-)}$$

$$= (a_+^{v_+} a_-^{v_-})^{1/v} = (K_{a_2})^{1/v} \quad (4)$$

where,  $v = \text{total no. of ions} = v_+ + v_-$

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

$$b^+ = \frac{a^+}{\sqrt{c}} \quad \text{and} \quad b^- = \frac{a^-}{\sqrt{c}} \quad (5)$$

The mean activity coefficient of the electrolyte is given by,

$$b^\pm = (b_+^{v+} \cdot b_-^{v-})^{1/v}$$

$$= \left[ \left( \frac{a^+}{\sqrt{c}} \right)^{v+} \left( \frac{a^-}{\sqrt{c}} \right)^{v-} \right]^{1/v} \quad \text{from eqn (5)}$$

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

$$b^\pm = \frac{a^\pm}{c^\pm} \quad (6)$$

$$\text{where } c^\pm = [(v+ c)^{v+} \cdot (v- c)^{v-}]^{1/v} = c (v_+^{v+} \cdot v_-^{v-})^{1/v}$$

The factor  $[v_+^{v+} \cdot v_-^{v-}]^{1/v}$  is known as valency factor

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

$$b^\pm = (K a_2)^{1/v} \quad (8)$$

If standard state  $c^\pm$  chosen, then in all above calculation  $K$  put to be equal to unity.

$$B A \rightleftharpoons B^+ + A^- , \quad K = \frac{a^+ a^-}{a_2} = \frac{(b^+ c^+)(b^- c^-)}{b^2 c^2} .$$

$$K = \frac{b^+ b^-}{b^2} \cdot \frac{c^+ c^-}{c^2} = \frac{b^+ b^-}{b^2} \cdot K_1 \quad [ \because a = b \cdot c ]$$

$K_1$  is known as true or thermodynamic dissociation constant. Where  $K_1$  is known as classical dissociation constant.