$$m_- = 2 \times 0.2 = 0.4,\ Z_- = 1$$

$$\mu = \frac{1}{2}(0.2 \times 2^2 + 0.4 \times 1^2)$$

$$= 0.6$$

9.19. ACTIVITIES AND ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES:

The thermodynamic and other properties of the solutions of non-electrolytes can be adequately expressed in terms of their concentrations, even at moderate concentrations. But the solutions of electrolytes exhibit marked deviation even at relatively low concentrations. Dilute ionic solutions have concentration of 0.001 m or even less. According to Debye-Huckel theory of interionic attraction, the electrostatic attractions between the ions in the solution of an electrolyte have significant influence on the mobility of ions. The ionic concentrations in case of weak electrolytes, being low do not show appreciable deviation from the ideal behavior. But in solutions of strong electrolytes the ionic concentrations are large, so interionic forces cannot be neglected. Due to electrostatic attraction between fractions of cations and anions, the solution exhibits the properties of one in which the effective or apparent concentrations of the ions are less than the theoretical concentrations. Depending on the relative importance of factors, such as ion-ion attractions and ion-solvent interactions, the effective concentration of the solute dissolved in water may appear to be less than, equal to or greater than the molal concentration. This effect becomes more significant at higher concentrations and increasing valence of the ions.

G.N. Lewis suggested due to restricted, mobility of the ions in solutions of strong electrolytes the ions do not exert their *full effect* for showing their behavior. He proposed the term activity in place of concentration term (molarity, molality, formality, mole fraction), so as to explain the departure of electrolyte solution from ideal behavior. To distinguish between molar or molal or formal concentration of a substance and the effective concentration of a substance which accounts non-ideal behavior, the latter is called the activity of the species. So the effective concentration of an ion in a solution is called its *activity*. It is customary to relate the activity of a species to its concentration through the expression.

$$a_i = \gamma_i m_i \tag{9.63}$$

in which a_i is the activity of the substance i, γ_i, is the activity coefficient of the substance i and m_i is the molal concentration of the substance i. Activity coefficient (γ) is not a constant and its value varies with the concentration. For aqueous solutions, both activity and concentration are expressed in the same units, so that the activity coefficient is dimensionless. [For dilute solutions, the molarity is almost numerically equal to molality, which is preferred unit for colligative properties (because then the solution properties do not depend on the identity of the solute). Therefore, we can shift from molarity concentration units to molality concentration units].

For dilute solutions (< 0.001m), the electrostatic attractions can be neglected,

$$a_i = m_i$$

and value of γ_i becomes unity. For an electrolyte, such as NaCl, the activity of Na^+ and Cl^- ions can be written as

$$a_+ = \gamma_+ m_+$$

and $$a_- = \gamma_- m_-$$

Since it is not possible to get only positive or negative ions in the solution of an electrolyte, there is no experimental method available to determine the activity or activity coefficient of individual ionic species. The reasons is that the solutions are electrically neutral and we cannot increase the number of cations without an equal increase in the number of anions. Since we cannot study separately the effect of cations or anions in the presence of each other in a neutral solution, it is therefore, not possible to measure the individual ion activities. Fortunately for most purposes, it is sufficient to know the mean ionic activity ($a_\pm$) and mean activity coefficient ($\gamma_\pm$).

Since it is not possible to substitute concentrations for activities in ionic solutions, it is essential to consider how the ionic concentrations may be converted to the activities and how such activities can be evaluated. In order to introduce some definitions commonly employed in dealing with the activities of strong electrolytes. Consider an electrolyte A_xB_y which ionizes in the solution according to

$$A_xB_y = xA^{z+} + yB^{z-}$$

When Z_+ and Z_- are the charges on the cation and anion respectively. The activity of the electrolyte as a whole, a_2, is defined in terms of the activities of the two ions, a_+ and a_- as

$$a_2 = a_+^x a_-^y \tag{9.64}$$

If V is the total number of the ions furnished by one molecule of the electrolyte, i.e., $V = x + y$, then mean activity is defined as

$$a_\pm = (a_2)^{1/v} = (a_+^x a_-^y)^{1/v} \tag{9.65}$$

The activities of the ions are related to their concentrations through the relation.

$$a_+ = \gamma_+ m_+ \tag{9.66}$$

$$a_- = \gamma_- m_- \tag{9.67}$$

Where m_+ and m_- are the molalities of the cation and anions and γ_+ and γ_- are the corresponding activity coefficients. These activity coefficients are appropriate factors which when multiplied by the molalities of the respective ions yield their activities. Introducing Eq (9.66) and (9.67) into Eq (9.64), we obtain for a_2

$$a_2 = (m_+\gamma_+)^x (m_-\gamma_-)^y$$

$$a_2 = (m_+^x m_-^y)\ (\gamma_+^x \gamma_-^y) \tag{9.68}$$

and for mean activity from Eq. (9.65)

$$a_\pm = (a_2)^{1/v} = (m_+^x m_-^y)^{1/v} \gamma_+^x \gamma_-^y)^{1/v} \tag{9.69}$$

The factor $(m_+^x m_-^y)^{1/v}$ is defined as the mean molality of the electrolyte.

$$m_\pm = (m_+^x m_-^y)^{1/v}$$

Similarly $(\gamma_+^x \gamma_-^y)^{1/v}$ is known as mean activity coefficient

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/v}$$

In terms of mean molality and mean activity coefficient, Eq (9.68) and (9.69) may be written as

$$a_2 = a_\pm^v = m_\pm \gamma_\pm \tag{9.70}$$

$$a_\pm = a_2^{1/v} = (m_\pm \gamma_\pm)^v \tag{9.71}$$

Finally since for any electrolyte of molality m, we have

$$m_+ = xm$$

$$m_- = ym$$

Eqs. (9.70) and (9.71) then take the form

$$a_\pm = (m_+^x m_-^y)^{1/v} \gamma_\pm$$

$$= \left[(xm)^x (ym)^y\right]^{1/v} \gamma_\pm$$

$$= \left[\left(x^x m^x\right)\left(y^y m^y\right)\right]^{1/v} \gamma_\pm$$

$$= \left[\left(x^x y^y\right)^{1/v} \left(m^{x+y}\right)\right]^{1/v} \gamma_\pm$$

$$= \left(x^x y^y\right)^{1/v} m\ \gamma_\pm \tag{9.72}$$

and $$a_2 = (a_\pm)^v = \left[(x^x y^y)^{1/v} m\ \gamma_\pm\right]^v$$

$$= \left(x^x y^y\right) m^v \gamma_\pm^v \tag{9.73}$$

Equation (9.72) and (9.73) are the expressions needed for converting activities to molalities, or vice versa. Thus for 1:1 electrolyte such as KCl, of molality m, we have x = 1, y = 1, V = 2 and therefore.

$$a_{\pm} = (1\times 1)^{1/2} m\, \gamma_{\pm}$$

$$a_2 = a_{\pm}^2 = m^2 \gamma_{\pm}^2$$

Again for an electrolyte of the 2:1 type, such as $BaCl_2$, we have x = 1, y = 2 and V = 3.

$$a_{\pm} = \left(1\times 2^2\right)^{1/3} m\, \gamma_{\pm}$$

$$= (4)^{1/3} m\, \gamma_{\pm}$$

$$a_2 = a_{\pm}^3 = 4m^3 \gamma_{\pm}^3$$

Example 9.5.

Calculate the mean and total activity of the following electrolytes: (i) $CuSO_4$ (ii) $Na_3\,PO_4$ (iii) $Ca_3\,(PO_4)_2$

Solution:

(i) $CuSO_4$ x = 1, y = 1, and V = 1 + 1 = 2

$$a_{\pm} = (1\times 1)^{1/2} m\, \gamma_{\pm}$$

$$= m\gamma_{\pm}$$

$$a_2 = (a_{\pm})^2 = m^2 \gamma_{\pm}^2$$

(ii) Na_3PO_4 x = 3, y = 1, V = x + y = 4

$$a_{\pm} = (3^3\times 1^1)^{1/4} m\, \gamma_{\pm} = (27)^{1/4} m\gamma_{\pm}$$

$$a_2 = (a_{\pm})^4 = 27m^4 \gamma_{\pm}^4$$

(iii) $Ca_3(PO_4)_2$ x = 3, y = 2, V = x + y = 3 + 2 = 5

$$a_{\pm} = (3^3 2^2)^{1/5} m\, \gamma_{\pm} = (108)^{1/5} m\, \gamma_{\pm}$$

$$a_2 = 108 m^5 \gamma_{\pm}^5$$

Example 9.6. Calculate the mean activity of the ions and activity of the electrolyte in 0.1m NaCl solution. The $\gamma_{\pm}$ is 0.778.

Solution:

$$m = 0.1 \text{ and } \gamma_{\pm} = 0.778$$

$$a_{\pm} = m\gamma_{\pm} = 0.1\times 0.778 = 0.0778$$

$$a_2 = (a_{\pm})^2 = (0.0778)^2 = 6.05\times 10^{-3}$$