

It is important to emphasize that the influence of high frequency currents and high voltages provides strong arguments in favor of the view that under normal conditions ionic velocities, and hence conductances are below those for infinite dilution because of the effect of the ionic atmosphere which increases with increasing concentration.

9.18 IONIC STRENGTH

When we dissolve an electrolyte into aqueous solution, it dissociates into positive and negative ions. When the concentration of the electrolyte increases in the solution, there occurs an interaction between positive and negative ions. Because of this interaction the ions behave differently from those in dilute solutions. The behavior of ions in solution is influenced by a number of factors, chief among which are the natural attraction of ions of unlike charge and repulsion of ions of like charge (Coulomb's law) and the influence of thermal agitation (Boltzmann distribution law) to counteract the electrical attraction and repulsion. The effects are dependent upon the total ionic composition of the solution, which is expressed by G.N. Lewis in a concept called *ionic strength* of the solution. Ionic strength is a useful concept because it allows us to consider some general expressions that depend only on ionic strength and not on the identities of the ions themselves. This quantity is a measure of electrical environment in the solution.

Ionic strength is given the symbol μ and is defined as half the sum of the terms obtained by multiplying the molality (or concentration) of each ionic species present in the solution by the square of its valence; thus

$$\mu = \frac{1}{2} \sum m_i Z_i^2 \quad (9.60)$$

Where m_i is the molality of the ion and Z_i is its ionic charge. The product $m_i Z_i^2$ is summed for all the ions in the solution then divided by two to give the ionic strength.

If a solution contains a number of ionic species indicated by the subscripts 1, 2, 3, etc. so that their respective molalities are m_1, m_2, m_3 , etc. in gram ions per 1000 gram of solvent, and Z_1, Z_2 and Z_3 etc. are the corresponding valencies, then the ionic strength is given by

$$\mu = \frac{1}{2} (m_1 Z_1^2 + m_2 Z_2^2 + m_3 Z_3^2 + \dots) \quad (9.61)$$

For a single electrolyte such as sodium chloride or potassium sulfate, the above equation reduces to two terms, one for positive and one for negative ion, viz.

$$\mu = \frac{1}{2} (m_+ Z_+^2 + m_- Z_-^2) \quad (9.62)$$

When m_+ and m_- are the molalities and Z_+ and Z_- are the valences of positive and negative ions. Ionic strength is an empirical relationship and is expressed in terms of molal concentration of the ions rather than in SI unit of ions per cubic meter.

For uni-univalent electrolyte such as NaCl or KCl of molality m , the ionic strength is equal to its molality.

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

$$\mu = \frac{2m}{2} = m$$

Thus for 1:1 electrolyte μ is equal to its m . One should remember that ionic strength is a property of the solution and not of any particular ion.

Example 9.4

Calculate the ionic strength of (i) 0.1 molal NaCl (ii) 0.2 molal K_2SO_4 (iii) a solution containing 0.1 m KCl and 0.2 m K_2SO_4 (iv) 0.2 m $BaCl_2$ solution.

Solution:

- (i) $m_+ = m_- = 0.1$, $Z_+ = Z_- = 1$, so

$$\mu = \frac{1}{2} (0.1 \times 1^2 + 0.1 \times 1^2)$$

$$\mu = 0.1$$

- (ii) K_2SO_4 produces two K^+ ions and one SO_4^{2-} ion

$$m_+ = 2 \times 0.2 = 0.4, \quad Z_+ = 1$$

$$m_- = 0.2 \quad Z_- = 2$$

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

$$= 0.6$$

- (iii) In a mixture of solution containing 0.1m KCl and 0.2m K_2SO_4 ,
Total molality of K^+ ion = $m_1 = 0.1 + 0.4 = 0.5$

$$\text{molality of } Cl^- \text{ ion} = m_2 = 0.1$$

$$\text{molality of } SO_4^{2-} \text{ ion} = m_3 = 0.2$$

$$\mu = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2)$$

$$= \frac{1}{2} (0.5 \times 1^2 + 0.1 \times 1^2 + 0.2 \times 2^2)$$

$$= 0.7$$

- (iv) $BaCl_2$ produces one Ba^{2+} ion and two Cl^- ions

$$m_+ = 0.2, \quad Z_+ = 2$$