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**Chemistry**
**PAPER No. 6: Physical Chemistry -II (Statistical Thermodynamics, Chemical Dynamics, Electrochemistry and Macromolecules)**
**MODULE No. 25: Activity and Mean Activity Coefficient**

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**Chemistry**

**PAPER No. 6: Physical Chemistry -II (Statistical Thermodynamics, Chemical Dynamics, Electrochemistry and Macromolecules)**

**MODULE No. 25: Activity and Mean Activity Coefficient**

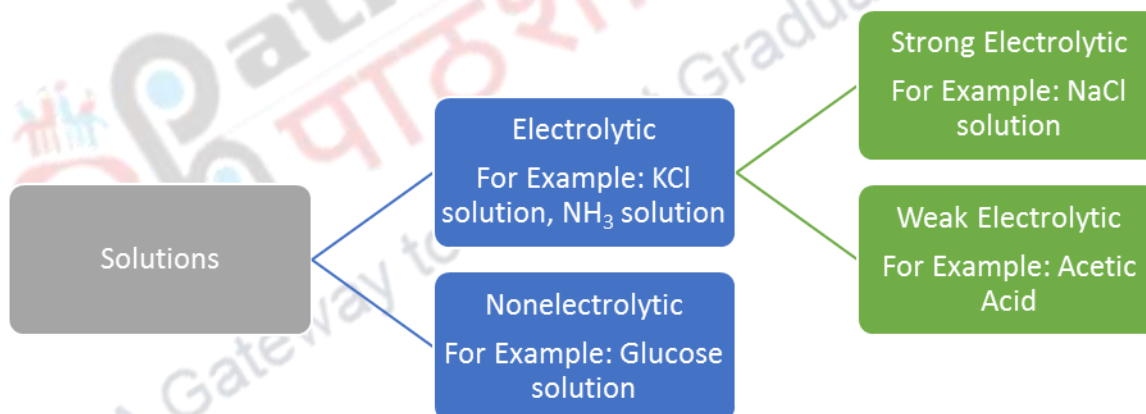
## 1. Learning Outcomes

After studying this module, you shall be able to :

- Know about “Ionic Strength” and “Activity”
- Understand Mean Activity Co efficient and its physical significance.
- Learn different ways to measure activity and mean activity coefficient

## 2. Introduction

We can broadly classify liquid solutions into following types on the basis of the degree of dissociation of the solute molecule.



In case of non-electrolytic solutions, the predominant intermolecular forces that exist between the components may be due to van der Waals interactions, dipolar interactions or of the hydrogen bond types. These solutions may be ideal obeying Raoult’s law or Henry’s law and can be nonideal if the interactions are somewhat stronger.

The solutions of electrolytes, especially of strong electrolytes deviate considerably from ideal behavior.

- ✓ In case of concentrated solution there exists strong ion-ion interactions & ion-solvent interactions while in the dilute case, the ion-ion interactions still persist but ion-solvent interaction play a predominant role. .

**Note: Irrespective of the concentration of the solution, ion-solvent interactions will always exist.**

In a solution of a strong electrolyte significant electrostatic interactions (which has a  $1/r^2$  dependence) both between ion-ion & ion-solvent exists, Therefore these type of solutions deviate from their ideal behavior and moreover properties of these electrolytic solutions usually deviates from the laws which are used to derive chemical potential of solutions.

### 3. Ionic Strength

Ionic Strength (I) of a solution is a measure of the electrical intensity due to the presence of ions in the solution. It is given as half of the sum of all the terms obtained by multiplying the molality of each ion by the square of its valency. In other words ionic strength is the cumulative measure of both charge on the ion as well as its concentration in the solution. Mathematically it is given as:

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (1)$$

where :

*$z_i$  is the charge on ion  $i$*

*$m_i$  is the molality of ion  $i$*

The concept of ionic strength is always applicable to strong electrolytes (i.e salts) and it cannot be applied to weak electrolytes

If we consider a solution which has more than one type of ions then ionic strength can be written as:

$$I = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + m_4 z_4^2 + \dots)$$

For a uni-univalent electrolyte (example : sodium chloride ,potassium chloride) the expression for ionic strength will contain only two terms i.e one for cation and other for anion. Hence,

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

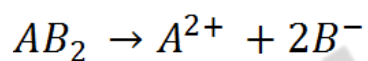
Where:

$m_+$  is the molality of cation

$m_-$  is the molality of anion

$z_+$  and  $z_-$  are the valencies of the cation and anion respectively .

While for uni-bivalent electrolytes, for example  $AB_2$  , ionic strength can be given as:



$$I = \frac{1}{2} (m_A z_A^2 + (2m_B) z_B^2)$$

While for a bivalent trivalent electrolyte , for example  $A_2B_3$ , ionic strength can be given as:



$$I = \frac{1}{2} \{2m(9) + 3m(4)\} = \frac{1}{2} \{30m\} = 15m;$$

$m$  is the molality of  $A_2B_3$  in the solution

The ionic strength lays stress on charges of ions because the charge numbers in the expression of ionic strength occur as their squares.

Note:

- Ionic strength includes contributions from both the number of ions in the solution and the charges on the individual ions
- Ionic Strength of a mixture of solutions can be exactly determined but total concentration of a mixture of solutions cannot be exactly determined

## 4. Non-ideality in Solutions

### 4.1 Activity

The deviation from ideality of a solute particle-(In this case solute behaves as a completely dissociated system, that is strong electrolyte) can be expressed in terms of solute activity, denoted by the letter 'a'.

The term "activity" was introduced by Lewis in 1920's, in order to describe deviation in behaviour of a gas, liquid or solid state from an idealized pressure state of fugacity.

Activity is defined as a measure of the effective concentration of a molecule or ionic species. Activity depends on the temperature, pressure and composition of the mixture of species.

Activity of a solute depends on its concentration, being proportional to concentration at sufficient dilution.

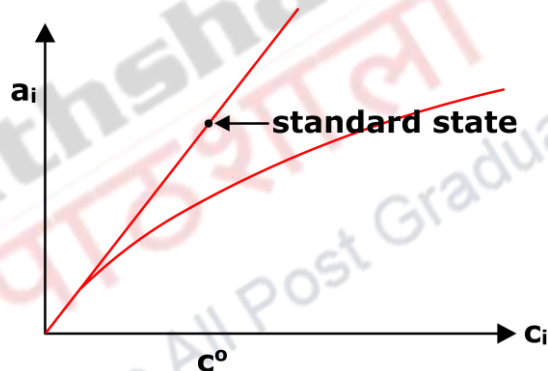


Fig. 1: Plot of activity with concentration

In the plot of  $a_i$  versus  $c_i$ , the region of linearity is rather limited, especially for ionic solutes. The standard state is chosen as a hypothetical state – which corresponds to the behaviour of solute at standard conditions  $c^0$ , in order to maintain the linear relationship upto that concentration.

Therefore, in an electrolytic solution, the activity of a solute 'a' is related to concentration, m as :-

$$a = \gamma m \quad (2)$$

Where:

- a = activity
- $\gamma$  = activity coefficient (concentration dependent)
- m = molality (mol/kg)

$\gamma$  (activity coefficient) is a correction factor (or we can also say proportionality constant) which take into account the departure from linearity (Fig. 1).

Here we have used molality as a unit of concentration because it is independent of temperature.

Concentration can be regarded as the number of ions present, while activity can be thought as the availability of the species to take part in chemical reactions and to determine the properties of a particular phase.

As concentration approaches zero, activity coefficient approaches to unity i.e

$$\gamma \rightarrow 1$$

Therefore:

$$a = m$$

► activity becomes equal to concentration.

In very dilute solutions, since the interactions become insignificant, therefore concentration and effective concentration are the same.

#### 4.1.1. Ionic activity

Ionic Activity has more importance in case of ionic solutions (electrolytic solutions) than in non-electrolytic solutions. This is due the presence of strong interactive forces among ions in eletrolytic solutions.

For an ionic solute ( $A_xB_y$ ), that dissociates completely, according to the equation:



Where:

x is the number of cations with charge  $z^+$

y is the number of anions with charge  $z^-$

Let  $v$  denote the total number of ions:

$$v = x + y$$

We also define stoichiometric molalities of each ion, based on the analytic molality of the solid electrolyte,  $m_i$

$$\left. \begin{array}{l} m_+ = x \cdot m \\ m_- = y \cdot m \end{array} \right\} \quad (3)$$

Absolute activities of cations & anions cannot be determined because activity of a single ion depends on the nature of counter-ion to preserve the overall electroneutrality of the solution. For eg: In a solution of NaCl or Na<sub>2</sub>SO<sub>4</sub>, the activity of Na<sup>+</sup> will depend on the nature of the anion, such as Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>. Therefore, we define activity of an electrolyte in terms of the ions into which it dissociates. Since, positive and negative ions coexist we define mean ionic quantities.

If the activity of the cation and anion is  $a_+$  and  $a_-$  respectively then the mean activity is given as:

$$a_{\pm} = a_+^x a_-^y \quad (4)$$

The symbol  $\pm$  refers to a mean ionic variable and is defined in terms of number of ions.

We also define mean ionic molality  $m_{\pm}$ :

$$m_{\pm} = (m_+^x m_-^y)^{\frac{1}{x+y}} \quad (5)$$



The individual activities of cation  $a_+$  can be written as:

$$\begin{aligned} a_+ &= m_+ \gamma_+ \\ &= xm \gamma_+ \end{aligned}$$

Similarly for anion

$$\begin{aligned} a_- &= m_- \gamma_- \\ &= ym \gamma_- \end{aligned}$$

(6)

Substituting equation 6 in equation 4, we get:

$$\begin{aligned} a_{\pm} &= (xm\gamma_+)^x (ym\gamma_-)^y \\ a_{\pm} &= (x)^x (y)^y m^{(x+y)} \gamma_+^x \gamma_-^y \end{aligned} \quad (7)$$

Where :-

$m$  = Molality

$\gamma_+$  = activity coefficient for positive ion

$\gamma_-$  = activity coefficient for negative ion

#### 4.2 Mean activity coefficient

Activity coefficient of individual ions can never be determined because in a strong electrolytic solution only cations and only anions can never exist, cations are always accompanied by anions and vice-versa. Therefore  $\gamma_+$  and  $\gamma_-$  cannot be determined individually so, we define a new term mean activity coefficient which is represented as:

$\gamma_{\pm}$

Mean activity coefficient ( $\gamma_{\pm}$ ) is a measure of ion-ion interactions in solution.

Mathematically it is given as:

$$\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{\frac{1}{x+y}} \quad (8)$$

Taking log on both sides of equation (8) we have;

$$(x + y) \log \gamma_{\pm} = (x \log \gamma_{+} + y \log \gamma_{-})$$

$$\log \gamma_{\pm} = \frac{1}{x + y} (x \log \gamma_{+} + y \log \gamma_{-})$$

$$\gamma_{\pm}^{x+y} = \gamma_{+}^x \gamma_{-}^y \quad (9)$$

In this equation the value of x & y depends on the nature of electrolyte.

Using equation (9) in equation (7):

$$a = x^x y^y m^{x+y} \gamma_{\pm}^{x+y}$$

$$a = x^x y^y (m \gamma_{\pm})^{x+y} \quad (10)$$

Debye and Huckel suggested a theory to find out the mean activity coefficient ( $\gamma_{\pm}$ ) in order to measure the ion-ion interactions present in the solution. This theory is applicable only to strong electrolytes (like salts). These types of solutions are electrically neutral & they dissociate completely (eg: NaCl)

- For ideal solutions

Mean activity coefficient ( $\gamma_{\pm}$ )  $\rightarrow$  1 as m approaches 0

- For even low concentration solutions  $\gamma_{\pm}$  value deviates from 1.

Experimental plot for variation of  $\gamma_{\pm}$  with  $\sqrt{I}$  (square root of ionic strength) is shown in Fig 2. The variation depends on the nature of electrolytes

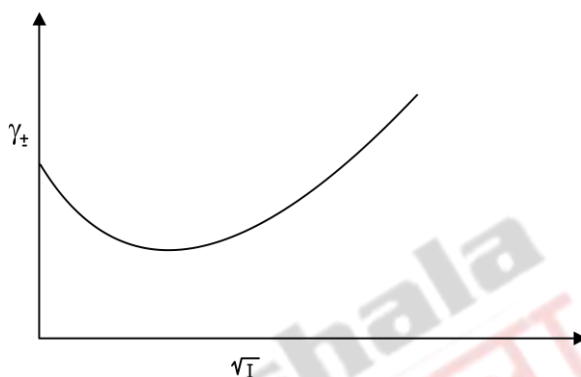


Fig. 2: Graph showing variation of  $\gamma_{\pm}$  with  $\sqrt{I}$  (square root of ionic strength)

Debye Huckel theory ultimately accounted for variation of mean activity coefficient with  $\sqrt{I}$  (square root of ionic strength)

Therefore using Debye – Huckel theory, we find  $\gamma_{+}$  &  $\gamma_{-}$  theoretically.

For different types of electrolytes, the activity can be calculated as :

For example :

1. Uni-univalent electrolyte :AB



$$x = 1$$

$$y = 1$$

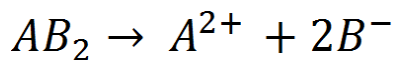
$$a = (x)^x (y)^y (m\gamma_{\pm})^{x+y}$$

$$a = (1)^1 (1)^1 (m\gamma_{\pm})^2$$

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

eg. – NaCl, CuSO<sub>4</sub>

2. Uni-bivalent electrolyte:  $AB_2$



$$x = 1$$

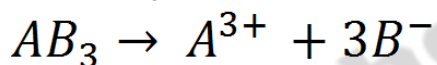
$$y = 2$$

$$a = (1)^1 (2)^2 (m\gamma_{\pm})^3$$

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

e.g.  $BaCl_2$

3.  $AB_3$



$$x = 1$$

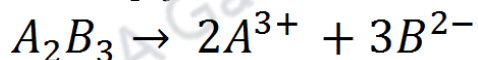
$$y = 3$$

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

$$= 27m^4\gamma_{\pm}^4$$

e.g. –  $FeCl_3$

4.  $A_2B_3$



$$x = 2$$

$$y = 3$$

$$a = (2)^2 (3)^3 (m\gamma_{\pm})^5$$

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

eg:  $Fe_2Cl_3$

### 4.3 Measurement of Activity

For volatile species, activity can be measured from its equilibrium partial vapour pressure. For non-volatile components such as NaCl, BaCl<sub>2</sub> we do not measure activity from the partial vapour pressure because they do not have measurable vapour pressure at most of the temperatures. We, therefore use a different approach that is the vapour pressure of the solvent is measured and using Gibb's Duhem relation the change in solvent vapour pressures is translated with concentration into activities for solute in the solution. The activity ('a') of an electrolyte is a property that can be measured by experiment e.g.: by measuring colligative properties such as osmotic pressure or freezing point depression of the solution.

We can determine the mean ionic activity coefficient ( $\gamma_{\pm}$ ) of ions in solutions using either Debye-Hückel equation or from the solubility product or from electrochemical methods (using Nernst Equation).

## 5. Summary

In this module we have learnt:

- Electrolytic solutions deviate from ideality due to the presence of significant electrostatic interactions.
- In order to account for deviation from ideality of solutes Lewis introduced the term activity which is represented as :

$$a = \gamma m$$

- Due to the interactions between the component ions in solutions, they deviate from their ideal state. The factor which influences this interaction is the charge on a particular ion and therefore useful function in this context is Ionic strength (I)

$$I = \frac{1}{2} \sum m_i z_i^2$$

- In order to maintain electroneutrality in solution cations and anions exist simultaneously that is positive and negative ions co-exist therefore we define mean ionic quantities for such solutions:

✓ Mean Ionic Activity:

$$a_{\pm} = a_+^x a_-^y$$

✓ Mean Ionic Molality:

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

✓ Mean Ionic Activity Coefficient:

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

- We measure activity through experiments such as by measuring colligative properties which include osmotic pressure, depression in freezing point etc.