Thermodynamics: Classical to Statistical

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Lecture - 10

Concept of activity and activity coefficients; Debye-Huckel limiting law

So far we have dealt with systems that are well behaved like ideal gases, ideal solutions, etc. As long as we are in the limits of dilute solutions or low concentration of solutes they behave ideally and no need to worry. But there are certain type of molecules for which we need to consider some special things. For example, if we consider electrolyte solutions, we know electrolyte solutions contain ions and they behave non-ideally in solutions, so we get non-ideal solutions. Even if the concentration of the solute is low, so usually we get non-ideal solution and we need to consider activity and activity coefficients.

Now, we will see that the activity is used to describe the correction to the chemical potential when a compound is not pure. So, we need to consider we know this equation, but in some different way like this.

$$\mu_i = \mu_i^0 + RT \ln a_i \text{ ---------------(1)}$$

Where, μ_i is the chemical potential, μ_i^0 is the chemical potential or standard chemical potential and a_i is the activity. So when solution is ideal one, for ideal solution activity of the solvent, if we say that is a_s, is just equal to its mole fraction that we know, but for dilute solute activity a_i you can write as mole fraction and we can consider the mole fraction of solvent x_s and mole fraction of solute is x_i.

So, for dilute solution $a_i = x_i$.

Now, we need to really consider activity coefficients for electrolyte solutions. We will now discuss activity coefficients of electrolyte solutions. So, we will start our discussion or we will begin with the discussion of non-ideality in electrolyte solutions and for that we define activity coefficients. Let us consider an electrolyte which when 1 mole of it is dissolved in water, consider ν_+ moles of positive ions with charge Z_+ and ν_- moles of negative ions with charge Z_- are produced. For example, if we dissolve Na_2SO_4 in water, we have $\nu_+ = 2$, we get 2 number of sodium ion and the charge of each sodium ion is +1 and we get 1 SO_4^{2-} ion so $\nu_- = 1$ and the charge of the anion is -2. So if n moles of this electrolyte is dissolved in water, then the contribution of the solute to Gibbs free energy of the entire solution is:

$$G = G_S = n\mu = n(\nu_+\mu_+ + \nu_-\mu_-) \text{ -------------}(2)$$

where, μ_+ and μ_- are the chemical potentials of the positive and negative ions respectively and G_S is the Gibbs free energy of the solvent. Because the effects of positive and negative ions are difficult to separate, so the mean ionic potential and we define this by $\mu_\pm$ is,

$$\mu = \nu\mu_\pm = \nu_+\mu_+ + \nu_-\mu_- \text{ --------------}(3)$$

where, ν = total number of ions produced = $\nu_+ + \nu_-$

So, we can write the chemical potential of the solutes (contribution from both positive and negative ions) is nothing but

$$\mu = \mu^0 + RT \ln a \text{ --------------}(4)$$

$$\mu = \nu\,(\mu^0_\pm + RT \ln a_\pm) \text{ --------------}(5)$$

where, $a_\pm$ is the main ionic activity of the solute and it is related to the activity by,

$$a = a_\pm^{\nu} \text{ -----------------}(6)$$

So, we can or we are able to write the chemical potential separately for the positive and the negative ions. So, we can write mu is nothing but,

$$\mu = \nu_+ (\mu^0_+ + RT\ \ln a_+) + \nu_- (\mu^0_- + RT\ \ln a_-) \text{ ---------------(7)}$$

In the above expression, a_+ and a_- are the activities of the positive and negative ions, respectively. Now, we see that mean ionic activity, we get like this,

$$a_\pm^{\nu} = a_+^{\nu_+} a_-^{\nu_-} \text{ --------------(8)}$$

So to quantify the concentration of electrolyte solutions it is convenient to use the molality rather than mole fraction.

Now, what we will do? We will discuss about Debye-Huckel limiting laws and then we learn how to calculate ionic strength. So Debye-Huckel limiting laws. What is this law says? The expression for this Debye-Huckel limiting law is,

$$\log_{10}\gamma_\pm = -\ |Z+Z-|\ A(I)^{1/2} \text{ ----------------(9)}$$

where A is a constant term and the value of A is 0.509 for water at 298 K temperature. And $\gamma_\pm$ is mean activity coefficient, I is ionic strength of the solution and Z_+ and Z_- are the charge of the cation and anion, respectively. So what Debye-Huckel theory does? Debye-Huckel theory or Debye-Huckel limiting law relates the total ionic strength, which is just a measure of how ionic the solution is and, the concentration of a particular ion pair of interest to the average or mean average activity coefficient for the ion pair.

There are some limitations of Debye-Huckel limiting law.

i) It is applicable for ions, so it is applicable for electrolytes solutions.

ii) Molecules that are not charged, have an activity coefficient of 1.

This is applicable for dilute solutions. So there is deviation of Debye-Huckel limiting law when the concentration is high.

Now, what is ionic strength? And how do we calculate it? Calculation of ionic strength. Ionic strength we define by I and it is a measure of the amount of ions present and the formula for ionic strength is,

$$I = 1/2 \Sigma_i m_i Z_i^2 \text{ ----------------(10)}$$

In some books you will find that the unit of ion strength is in molar unit and in few other books you will find that ionic strength is unitless. So here we consider, ionic strength is calculated from concentrations relative to the standard state or we consider 1 molal. We consider that 'I' is unitless. There is no unit of ionic strength. Now, how do we calculate ionic strength? Suppose, we have an aqueous solution of NaCl (sodium chloride) and for that we consider that concentration is 100 mili molar, this is the concentration of the solution. Now, how do we calculate the ionic strength of this 100 mM solution?

$$\text{Concentration} = 100 \text{ mM} = 0.1 \text{ M}$$

$$I = 1/2 \Sigma_i m_i Z_i^2$$

$$I = (1/2)\times[Na^+]\times(+1)^2 + (1/2)\times[Cl^-]\times(-1)^2$$

$$I = (1/2) \times (0.1) \times 1 + (1/2) \times (0.1) \times 1$$

$$I = 0.1$$

This gives you 0.1. So this is the ionic strength of 100 mm sodium chloride solution.

Now, we will consider 1 more complicated little complicated example. We consider 100 mM aqueous $MgCl_2$ solution aqueous (magnesium chloride solution). So, when you dissolve $MgCl_2$ in water it gives,

$$MgCl_2 = Mg^{2+} + 2Cl^-$$

Consider 100 mM $MgCl_2$ solution = 0.1 M.

So, $[Mg^{2+}] = 0.1$ M, $[Cl^-] = 0.2$ M, $Z_{Mg^{2+}} = +2$, $Z_{Cl^-} = -1$

$$\text{So, } I = I = (1/2)\times[Mg^{2+}]\times(Z_{Mg^{2+}})^2 + (1/2)\times[Cl^-]\times(Z_{Cl^-})^2$$

$$I = (1/2) \times 0.1 \times(+2)^2 + (1/2) \times 0.2 \times (-1)^2$$

$$I = 0.3$$

So the ionic strength of 100 mM aqueous $MgCl_2$ solution is 0.3.

From the Debye-Huckel theory or Debye-Huckel limiting law we know,

$$\log_{10}\gamma_\pm = - |Z+Z-|\ A(I)^{1/2}$$

So, if we plot $\log_{10}\gamma_\pm$ versus $\sqrt{I}$, what we get? We should get a straight line up to certain concentration (Figure 1).

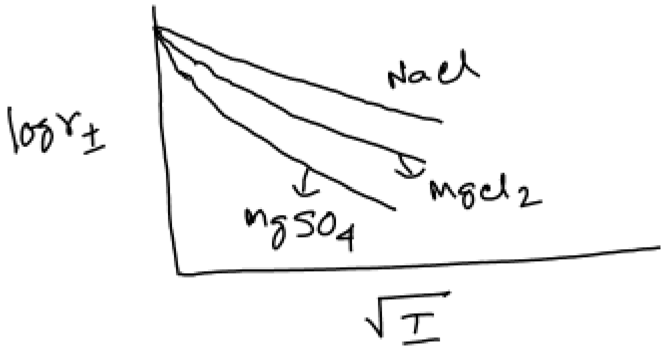

Figure 1

Suppose, this is for NaCl, for $MgCl_2$, you get something like this, and you get this kind of plot for $MgSO_4$. So for a particular ionic strength, the slope of this curve depends on this factor |Z+Z-| × A. 'A' is a constant term. For $MgSO_4$, Z_+ times Z_- gives you 4 and you have the minus signs, so you get much the decrease of

$\log_{10}\gamma_{\pm}$ as you increase the concentration, as you increase the ionic strength this is much faster compared to $MgCl_2$ for which the $|Z_+Z_-|$ is 2 and for NaCl it is only 1. So that is how you get different slope for different ionic solutions.