# Thermodynamics: Classical to Statistical

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## Lecture - 09

## Partial molar quantities; excess thermodynamic quantities

In this lecture we will discuss partial molar quantities. We consider a simple non-reactive binary mixtures of two liquids suppose ‘A’ and ‘B’, and ‘A’ and ‘B’ are nonelectrolytes. So in our system there are no ions. So we can write,

$$x_A + x_B = 1$$

where, $x_A$ is the mole fraction of A and $x_B$ is the mole fraction of B. So to understand the concept of partial molar quantities, the easiest property one can visualize is this volume, ‘V’. So, if we mix ‘A’ and ‘B’ we will have three possibilities. What are those possibilities?

i) No volume change. Suppose we are mixing 10 ml of A and 10 ml of B and if the total volume is 20 ml then effectively there is no volume change in that sense. We are getting the expected volume. We get no total volume change.

ii) Then we can have also volume contraction.

iii) The third possibility is volume dilution. So these are the three possibilities one can have.

So, in the first case suppose as I discussed in the first case, means there is no volume change if we mix 10 ml of A and 10 ml of liquid B and if we get a total volume of 20 ml then we can say that there is no effective volume change. In that case the interaction between A and B are equal to A---A and B---B interactions.

But, this does not happen always. So you get either volume contraction or you get volume dilution. For example, the molar volume of water is 18 cc and the molar volume of ethanol is 58 cc. Now if we add one mole of water in large volume of ethanol then what we expect? We expect, volume should increase by 18 cc. But, what we get? We add one mole of water to large volume of ethanol we get an increase in volume of 14 cc. So it says that the partial molar volume of water for that composition mixture is 14 cc. Now we will discuss **partial molar volume**. The partial molar volume changes with composition because molecular environment also changes. So the partial molar volume of a substance is defined by,

$$V_i = (\delta V/\delta n_i)_{P,T,ni =/ nj}$$

So once we know the partial molar volume of both the components in the mixture, we can calculate the total volume.

$$V = n_A V_A + n_B V_B$$

Where, $n_A$ is the numbers of moles of component A or liquid A and $n_B$ is number of moles of liquid B. Now how you can calculate partial molar volume. We have,

$$V = n_A V_A + n_B V_B$$

$$n_A + n_B = n$$

$$V/n = (n_A/n)VA + (n_B/n)VB$$

$$V_m = x_A V_A + x_B V_B$$

Where, $x_A$ an $x_B$ are mole fractions of component A and component B, respectively and $V_m$ is the total molar volume. Now on differentiating we get,

$$dV_m = V_A dx_A + V_B dx_B$$

$$dV_m/dx_B = V_B - V_A$$

$$V_B = V_A + dV_m/dx_B$$

$$V_m = x_A V_A + x_B(V_A + dV_m/dx_B)$$

$$V_m = x_A V_A + V_A(1 - x_A) + x_B(dV_m/dx_B) \text{ (as, } x_B = 1 - x_A)$$

So what we get? Finally we get,

$$\mathbf{V_m = V_A + x_B(dV_m/dx_B)}$$

Now if we plot molar volume, $V_m$ versus mole fraction of component B or $x_B$, xB goes from 0 to 1, this type of plot (Figure 1) you can expect,

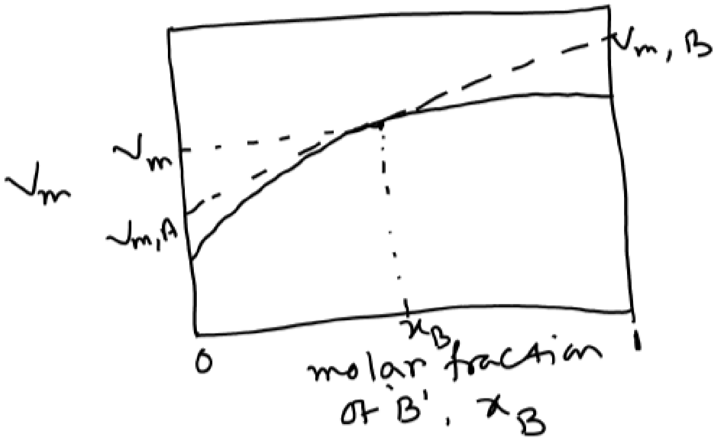

**Figure 1**

Then we calculate partial molar Gibbs function. So we know,

$$\mu_i = (\delta G/\delta n_i)_{P,T,ni=/nj}$$

We have used here binary mixture of A and B. So the total Gibbs function of the mixture,

$$G = n_A\mu_A + n_B\mu_B$$

If you differentiate, on differentiating we get,

$$dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B$$

We know,

$$dG = \mu_A dn_A + \mu_B dn_B$$

Since G is a state function, we can write,

$$n_A d\mu_A + n_B d\mu_B = 0$$

In general,

$$\mathbf{\Sigma_i n_i d\mu_i = 0}$$

This is known as **Gibbs-Duhem** equation. Next we will consider chemical potential of liquids. For a pure liquid in equilibrium with vapour we can write,

$$\mu_A^*(l) = \mu_A^0 + RT\ln P_A^*$$

For solution,

$$\mu_A(l) = \mu_A^0 + RT\ln P_A$$

If you combine these two equation, we can write,

$$\mu_A(l) = \mu_A^*(l) + RT\ln(P_A/P_A^*)$$

The ratio, $P_A/P_A^* = x_A$

So, $P_A = x_A P_A^*$

This is known as Raoult's law. We have already studied Raoult's law. Thus, the chemical potential of liquid, we can write,

$$\mu_A(l) = \mu_A^*(l) + RT\ln x_A$$

This important equation is the definition of ideal solutions. Alternatively, we can say that an ideal solution is the one in which all the components obey the Raoult's laws. We already studied these things. So, if we plot mole fraction of A versus pressure, we can get a plot like this (Figure 2). So when $x_A$ is 0 this is nothing but $P_B^*$ and $x_A$ equals to 1 this is nothing but $P_A$*. Now if we join these two lines this represent partial pressure of component A, this is nothing but partial pressure of component of A, and if we join these two points (it is not drawn in proper manner but you get a straight line kind of thing) this is partial pressure of B, and total

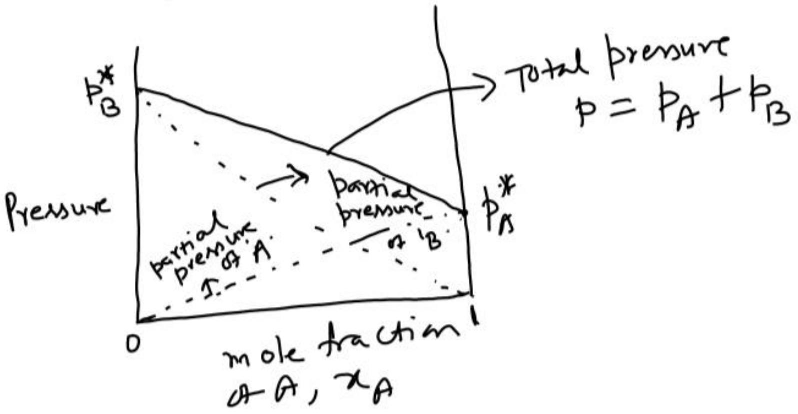

**Figure 2**

pressure is this one this is nothing but total pressure P = $P_A$ + $P_B$. How total pressure is changing as we change the composition of the mixture. In ideal solutions, the solute as well as the solvent, obeys Raoult's law. But in some cases, in ideal solution the partial pressure of solute is proportional to the mole fraction but the constant of proportionality is not the pure component vapour pressure, but constant, known as Henrey's constant, we already studied the Henrey's constant $k_h$, we can write it $k_B$ also.

$$P_B = k_B x_B$$

This is known as Henrey's law.

Next we consider, we can plot actually, we can plot Henrey's law (Figure 3),

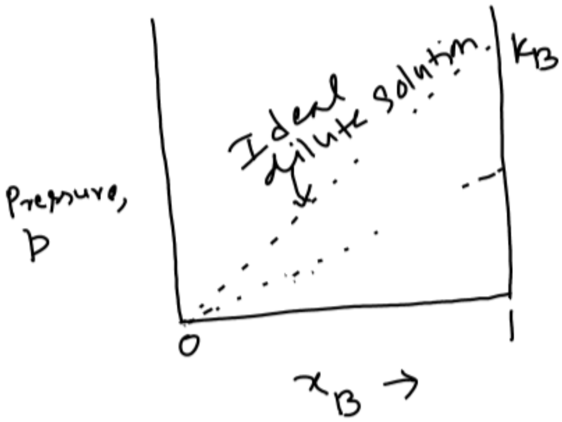

**Figure 3**

we are changing mole fraction of B here and this is pressure P and then we can draw like this. When $x_B$ equals to 1 the pressure is nothing but Henrey's constant $k_B$ and we get like this one so this is for ideal dilute solution and we get like this. This is how we can plot Henrey's law. Next we discusses excess functions. In real solution, real solution means the solutions which do not obey Raoult's law. Real solutions have different molecular interactions between A---A, A---B and B---B particles. As a result, ΔH =/ 0, ΔV =/ 0. Suppose, ΔH is positive and ΔS is negative, in that case, since, $\Delta G = \Delta H - T\Delta S$. So we get, ΔG is positive. The liquids are immiscible. The thermodynamic properties of real solutions can be expressed in terms of excess functions. So the thermodynamic properties of real solutions are in generally expressed in terms of excess functions. For example, for entropy, we can write excess entropy is,

$$S^E = \Delta S_{mix}(\text{real}) - \Delta S_{mix}(\text{ideal})$$

$$S^E = \Delta S_{mix}(\text{real}) + nR(x_A \ln x_A + x_B \ln x_B)$$

In this context or in this regard the concept of regular solutions is very important. In these solutions,

$$H^E \neq 0 \text{ but } S^E = 0$$

So, for this solutions excess enthalpy is not equals to 0 but excess entropy is equal to 0.