Thermodynamics: Classical to Statistical
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Lecture - 08
Calculation of fugacity; free energy of mixing

In the last class we were discussing Fugacity. We know that Fugacity is a measure of non-ideality. Today will start with how we can calculate Fugacity. Fugacity, we define by f is function of pressure and temperature. So will consider the following scheme (Figure 1).

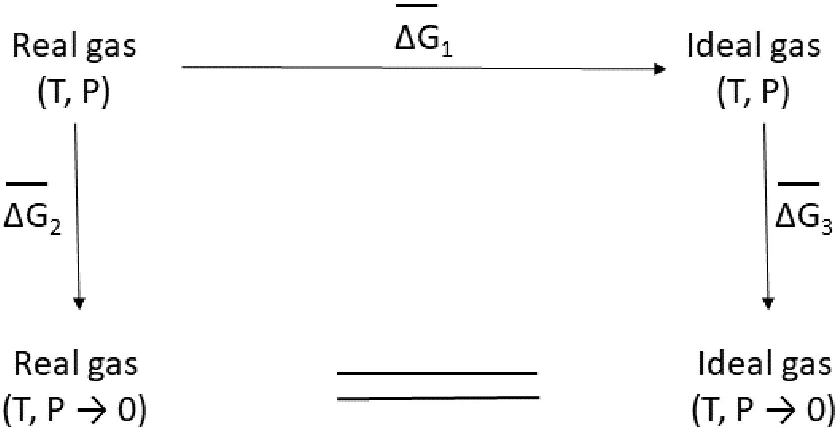

Figure 1

From this above scheme, we can write,

$$\Delta\bar{G}_1 = \Delta\bar{G}_2 + \Delta\bar{G}_3$$

What is $\Delta\bar{G}_1$?

$$\Delta\bar{G}_1 = \bar{G}^{id}(T,P) - \bar{G}\,(T,P)$$

$$\Delta\bar{G}_1 = RT\ln(P/P^0) - RT\ln(f/f^0) \text{ ---------------(1)}$$

But the standard state of the real gas has chosen such that, $f^0 = P^0 = 1$ bar. Thus, we can write like this,

$$\Delta\bar{G}_1 = RT\ln(P/f) \text{ -----------------(2)}$$

Now, lets see what is $\Delta\bar{G}_2$ and $\Delta\bar{G}_3$?

$$\Delta\bar{G}_2 = \int_{P}^{P\to 0} \bar{V}\, dP'$$

$$\Delta\bar{G}_3 = \int_{P\to 0}^{P} \bar{V}^{id}\, dP' = \int_{P\to 0}^{P} \frac{RT}{P'}\, dP'$$

Again, we know,

$$\Delta\bar{G}_1 = \Delta\bar{G}_2 + \Delta\bar{G}_3$$

So,

$$RT\ln\frac{P}{f} = \int_{P}^{P\to 0} \bar{V}\, dP' + \int_{P\to 0}^{P} \frac{RT}{P'}\, dP'$$

We can further simplified this as,

$$\Rightarrow RT\ln\frac{P}{f} = \int_{P\to 0}^{P} \left(\frac{RT}{P'} - \bar{V}\right) dP'$$

$$\Rightarrow \ln\frac{P}{f} = \int_{0}^{P} \left(\frac{1}{P'} - \frac{\bar{V}}{RT}\right) dP'$$

$$\Rightarrow \ln\frac{f}{P} = \int_{0}^{P} \left(\frac{\bar{V}}{RT} - \frac{1}{P'}\right) dP' \quad - ③$$

Now, if P, V and T (or the equation of state for a real gas) are known, we can calculate f/P for the gas at any Pressure and Temperature. We will see one example here. Here it is to be noted that if the gas behaves ideally under the conditions of interest (i.e., $\bar{V} = \bar{V}^{id}$ in equation 3. Then,

f/P = 1 (or, ln(f/P) = 0), so, **f = P**

It says that the extent of the deviation of f/P from unity is a direct indication of the extent of the deviation of the gas from ideal behaviour.

The ratio, f/P = γ. This γ is known as fugacity coefficient. So we just discussed γ = 1 for ideal gas. Now from equation 3, we can write,

$$\ln \gamma = \int_0^P \frac{Z-1}{P'} \, dP' \quad — ④$$

$$\text{where, } Z = \frac{P\bar{V}}{RT} \Rightarrow \text{compressibility factor}$$

Now, we will consider one example. We will derive an expression for the fugacity of a gas that obeys the equation of state

$$P(\bar{V} - b) = RT, \text{ b is a constant}$$

$$\bar{V} = (RT/P) + b$$

We know,

$$\ln \gamma = \int_0^P \left(\frac{\bar{V}}{RT} - \frac{1}{P'} \right) dP'$$

$$\ln \gamma = \int_0^P \left\{ \frac{1}{RT} \left(\frac{RT}{P'} + b \right) - \frac{1}{P'} \right\} dP'$$

So what we get? We get,

$$\Rightarrow \ln \gamma = \int_0^P \frac{dP'}{P'} + \frac{b}{RT}\int_0^P dP' - \int_0^P \frac{dP'}{P'}$$

$$\Rightarrow \ln \gamma = \frac{b}{RT}\int_0^P dP'$$

$$\Rightarrow \ln \gamma = \frac{bP}{RT}$$

$$\Rightarrow \boxed{\gamma = e^{\frac{bP}{RT}}}$$

Now, we will come back again and will consider thermodynamics of mixing for perfect gas or ideal gas. Previously we have calculated the entropy of mixing for ideal gas. Today will calculated basically free energy of mixing and then we will also calculate ΔH mixing, ΔV mixing for ideal gas. So we will consider the following experiment (Figure 1).

Figure 1

We have gas A here in this left hand side container and gas B there in right hand side container and there is a stopcock and then pressure of this different side container is P and T. This is our initial state, and if you remove the stop cock we will get like this. The gas molecules will makes each other. So we guess gas A here, A gas plus B gas both are here. So what is the Gibbs free energy of the initial state?

$$G_i = n_A(\mu_A^0 + RT\ln P) + n_B(\mu_B^0 + RT\ln P)$$

Where, n_A is the number of moles of gas 'A' and n_B number of moles of gas 'B' and μ_A^0 and μ_B^0 are the chemical potential or standard chemical potential of gas 'A' and gas 'B' respectively. And we are getting this equation from like this,

$$G_i = (G_A)_{initial} + (G_B)_{initial}$$

$$\text{Where, } G = n\mu = n(\mu^0 + RT\ln P)$$

So what is the free energy of the final state?

So after mixing, if we say free energy change of the final state G_f, we can write,

$$G_f = n_A(\mu_A^0 + RT\ln P_A) + n_B(\mu_B^0 + RT\ln P_B)$$

So what is P_A and what is P_B? P_A and P_B are partial pressures of gas A and gas B, respectively. If we now calculate ΔG_{mix} this is nothing but,

$$\Delta G_{mix} = G_f - G_i$$

$$\Rightarrow \Delta G_{mix} = n_A RT \ln P_A + n_B RT \ln P_B - n_A RT \ln P - n_B RT \ln P$$

$$\Rightarrow \Delta G_{mix} = n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}$$

$$\Rightarrow \Delta G_{mix} = nRT\, x_A \ln x_A + nRT\, x_B \ln x_B$$

Where, 'x_A' and 'x_B'are the mole fraction of gas 'A' and Gas 'B' respectively. So, what we got? We got,

$$\Delta G_{mix} = nRT\textstyle\sum_i x_i \ln x_i$$

Since, $x_i < 1$, it is a fraction,

So, ΔG_{mix} is a negative tetrm.

So from there we can also write ΔS_{mix} is,

$$\Delta S_{mix} = -\,(\delta(\Delta G_{mix})/\delta T)_{P,nA,nB}$$

$$\Delta S_{mix} = -\,nR\textstyle\sum_i x_i \ln x_i$$

So, ΔS_{mix} is a positive term. So, what about ΔH mixing?

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} \text{ (because, } \Delta H = \Delta G - T\Delta S\text{)}$$

So,

$$\Delta H_{mix} = nRT\sum_i x_i \ln x_i + T(- nR\sum_i x_i \ln x_i)$$

$$\Delta H_{mix} = 0$$

So, the enthalpy change of mixing for ideal gas is 0, as should be expected for a system in which there are no interactions between the particles. Therefore, the whole of the driving force for mixing of two ideal gases (in this case we consider gas A and gas B) comes from the increase of entropy of the system. In other words, we can write ideal gases mix slowly on account of their tendency to spread into the total volume made available by opening the partition between the two containers. Next question is what is ΔV mixing for ideal gases? This is our next question. We can very easily calculate ΔV mixing like (because we have already derived this expression) like this,

$$V = (\delta G/\delta P)_{T,n}$$

$$V_{mix} = (\delta(\Delta G_{mix})/\delta P)_{T,n}$$

And what is ΔG_{mix}? we will go back and check it, we find that since, ΔG_{mix} is independent of pressure, so, $\boldsymbol{\Delta V_{mix} = 0}$ for ideal gases. Next question is what is ΔU_{mix} for ideal gas? So we know,

$$\Delta H_{mix} = \Delta U_{mix} + P\Delta V_{mix}$$

$$\Delta U_{mix} = \Delta H_{mix} - P\Delta V_{mix}$$

$$\boldsymbol{\Delta U_{mix} = 0} \text{ (as, } \Delta H_{mix} = 0, \Delta V_{mix} = 0\text{)}$$

So, what we find? We find that there is no change of internal energy on mixing of ideal gases. In case of real gas, there are interaction between the particles, so in case of real gas usually ΔH_{mix} is non-zero quantity (is not 0). As, ΔS_{mix} is positive, but not by the amount of $-\Delta G_{mix}/T$. In case of real gases, ΔG_{mix} depends on the pressure because it is affected by intermolecular forces. Next, we will consider why some liquids mix? Ideal solution is nothing but very similar to that of perfect gas. Remember one thing in ideal solution particle they interact, but in case of perfect gas or ideal gas there is no forces of interaction between the particles. Now,

$$\Delta G_{mix} = nRT\sum_i x_i \ln x_i$$

Now, if we plot these mixing quantities with mole fraction of gas A (x_A), we get the plot as of Figure 2,

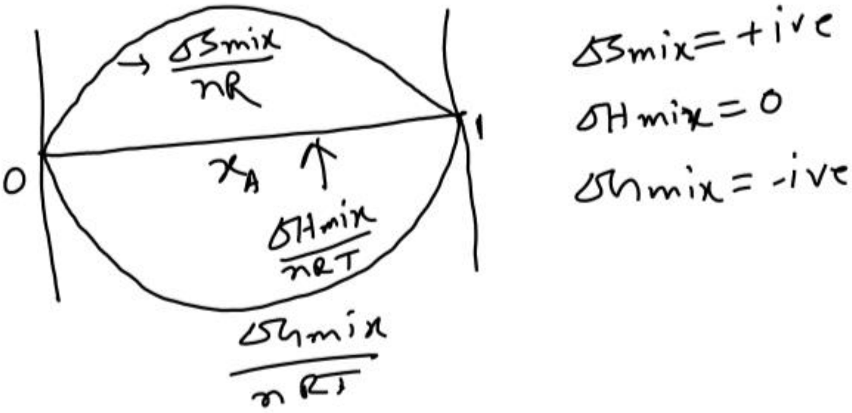

Figure 2

this is mole fraction suppose this is xA, we have A and B particles ideal gas or ideal solution we have like this. So ΔS_{mix} and ΔG_{mix}, they cancel each other and that gives you ΔH_{mix} is 0. Now, if is ΔH positive and large than it may overcome the entropy change and as a consequence, ΔG may be positive for the mixing process. So for this kind of mixing process ΔG is a positive, so in that case unmixing, we say unmixing is then spontaneous. If A and B are liquids, then the liquids are immiscible. So then those liquids they will not mix with each other. So there must be some balance between ΔH and $T\Delta S$, in order to say the mixing process is spontaneous one or not.