Phys 112 : Lecture 28

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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December 5, 2017

1 Mixing

Suppose that we had a pure solvent. Then we would have a Gibbs free energy of:

$$G_A = N_A \mu_0(\tau, p)$$

where μ_0 is the chemical potential of the solvent. In the case of an ideal gas, we would have for example:

$$\mu = \tau \ln\left(\frac{n}{n_Q}\right) = \tau \ln\left(\frac{p}{\tau n_Q}\right)$$

Now, suppose we add some particles, we get:

$$G_A = N_A\left[M_0 + \frac{d\mu}{dn_A}\partial n_A\right]$$

$$\frac{d\mu}{dn_A} = \tau\frac{1/n_Q}{n_A/n_Q} = \frac{\tau}{n_A}$$

Now, assuming the particles A and B take up the same volume in a sense, then we have:

$$\partial n_A = -\partial n_B$$

$$\frac{\partial\mu}{\partial n_A}\partial n_A = \frac{\tau}{n_A}(-\partial n_B) = -\tau\frac{N_B}{N_A}$$

$$M_A = M_0 - \tau\frac{N_B}{N_A} = M_0 - \tau X$$

Where

$$X = \frac{N_B}{N_A}$$

So

$$G_A = N_A M_0 - \tau N_B$$

So the total gibbs free energy is:

$$G = N_A\tau\ln\left(\frac{n_A}{n_Q}\right) + N_B\tau\ln\left(\frac{n_B}{n_Q}\right) - \tau N_B$$

This is in the limit that we have a very low amount of impurity, i.e. a low amount of B compared to A.

Now, let's consider a situation where we can control the pressure; and we want to reach equilibrium. We have that:

$$\mu = \mu_0 - \frac{N_B}{N_A}\tau$$

$$\mu_0(\tau, P_1) = \mu_0(\tau, P_2) - \frac{N_B}{N_A}\tau$$

$$\mu_0(\tau, P_2) = \mu_0(\tau, P_1) + (P_2 - P_1)\frac{\partial \mu_0}{\partial P}$$

So

$$(P_2 - P_1)\frac{\partial \mu_0}{\partial P} = \frac{N_B}{N_A}\tau$$

Now,

$$\left(\frac{\partial G}{\partial P}\right)_\tau = V; \qquad \frac{\partial \mu}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N} = \frac{1}{n}$$

Substituting this back in, we find that:

$$P_2 - P_1 = n_B\tau = \Delta P$$

This is osmotic pressure. The situation is that we have pure water and impure water; and we are applying pressure to fight against the osmotic pressure to reach equilibrium.

Now, let's consider a liquid gas interface. For equilibrium:

$$\mu_{liq}(\tau, P) = \mu_{gas}(\tau, P)$$

$$\mu_l(\tau, P) = \mu_0(\tau, P) - \frac{N_B}{N_A}\tau$$

$$\mu_0(\tau, p) = \mu_0(\tau_0, P) + (\tau - \tau_0)\frac{\partial \mu_0}{\partial \tau}$$

$$\frac{\partial \mu_0}{\partial \tau} = \frac{1}{N}\left(\frac{\partial G}{\partial \tau}\right) = -\frac{\sigma}{N} = -S\left(\frac{\text{entropy}}{\text{particle}}\right)$$

$$\mu_0(\tau, P) = \mu_0(\tau_0, P) - (\tau - \tau_0)S$$

Now, plugging this into our equilibrium condition,

$$(\tau - \tau_0)(S_g - S_l) = \frac{N_B}{N_A}\tau_0 = X\tau_0$$

$$(\tau - \tau_0) = \frac{X\tau_0}{S_g - S_l}$$

Now we can define:

$$l_v = \tau(S_g - S_l) = \tau\Delta S; \qquad L_V = N_{Avo}\tau(S_g - S_l)$$

$$\tau - \tau_0 = \frac{X N_{Avo} \tau_0^2}{L_V} = \frac{X R \tau_0^2 k_B}{L_V}$$

$$T - T_0 = \frac{X R T_0^2}{L_V}$$

Now, consider a vapor in contact with a liquid, and we are polluting the liquid. (i.e. water vapor, over salty sea) We have:

$$\frac{\Delta P}{P} = -X$$