

Phys 112 : Lecture 16

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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1 Gibbs Free Energy Relations

Recall that from last lecture we defined a quantity, the Gibbs Free Energy G , that depends on the number of particles, the pressure, and the temperature. Note that for any system of N particles (that exist in some symmetrical state), we could arbitrarily partition the entire system into two subsystems with $N/2$ particles each, and since the system will still be in equilibrium, we have:

$$G(N/2, p, \tau) + G(N/2, p, \tau) = G(N, p, \tau)$$

In general, it can be shown that G is completely linear in N , that is that G is N times some function that only depends on pressure and temperature. Note that:

$$\left(\frac{\partial G}{\partial N} \right)_{p, \tau} = M$$

the chemical potential! So we have altogether that:

$$G(N, p, \tau) = NM(p, \tau)$$

Recall that from last lecture we found that $dG = MdN$, so this shouldn't be too surprising. Note that in real life systems, we will often have several independent components that contribute to the Gibbs free energy, so we will really have a sum of some kind:

$$G = \sum_j G_j = \sum_j N_j M_j$$

As a final note, note that we have two similar but not the same formulas:

$$M(N, \tau, V) = \left(\frac{\partial F}{\partial N} \right)_{\tau, V}; \quad M(\tau, p) = \left(\frac{\partial G}{\partial N} \right)_{\tau, p}$$

2 Ideal Gas free energies

Recall that for an ideal gas:

$$Z = \frac{(n_Q V)^N}{N!}; \quad F = -\tau \ln Z = N\tau \left[\ln \left(\frac{N}{V n_Q} \right) - 1 \right]$$

so the free energy is not linear in N for the Helmholtz free energy, but we didn't really expect that to hold. In the other case, we have for the Gibbs free energy:

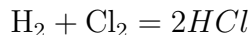
$$G = F + pV = F + N\tau = N\tau \ln \left(\frac{N}{n_Q V} \right) = N\tau \ln \left(\frac{p}{\tau n_Q} \right)$$

where we use many times the ideal gas law $PV = N\tau$, we find that the Gibbs free energy is linear in N when p and τ are held constant. So, in the case of an ideal gas, we find that the chemical potential is given by:

$$M = \left(\frac{\partial G}{\partial N} \right)_{\tau, p} = \tau \ln \left(\frac{p}{\tau n_Q} \right)$$

3 Chemical Reactions

Chemists care a lot about chemical reactions, and occasionally phisists do too. As an example of a chemical reaction, we might consider:



We can always rearrange such chemical reactions into the form:

$$\sum_j V_j A_j = 0$$

where V_j are coefficients, and A_j is the species (reactant). Now, for a fixed τ, p , we have that in equilibrium:

$$dG = \sum_j M_j dN_j = \hat{N} \left(\sum_j V_j M_j \right) = 0$$

where \hat{N} is the number of reactions that occur, so we have $dN_j = V_j \hat{N}$. Now, this equation implies that for the chemical reaction above, we have:

$$M_{\text{H}_2} + M_{\text{Cl}_2} + 2M_{\text{HCl}}$$

4 Internal degrees of freedom

In general, we have internal degrees of freedom. In some cases, these don't matter, as they just introduce more degeneracy (for instance a cloud of noninteracting electrons, their spins

constitute an internal degree of freedom, but if there isn't a magnetic field/some other field, then there is no energy split between spin up and spin down, so it doesn't affect any of our subsequent calculations). In some cases, it does matter though, so that we have:

$$M = \tau \ln \left(\frac{n}{n'_Q} \right) = \tau \ln \left(\frac{N}{Z'_1} \right); \quad Z'_1 = Z_1 + Z_{\text{int}}$$

so for the A_j species, we have that:

$$M_j = \tau \left[\ln(n_j) - \ln(n_{Q_j} Z_{j(\text{int})}) \right]$$

So, when we have a chemical reaction in equilibrium, we can substitute our new chemical potential into our old formula:

$$\sum M_j V_j = 0$$

Then, using the fact that a sum of logs gives the log of the products, and we end with:

$$\prod_j n_j^{V_j} = \prod_j (n_{Q_j} Z_{j(\text{int})})^{V_j} = k(\tau)$$

where $k(\tau)$ is just an observation that the right hand side is just a function of τ . From this, we have derived the "Law of mass action:

$$\prod_j n_j^{V_j} = \prod_j n_{Q_j}^{V_j} e^{-V_j F_{j(\text{int})}/\tau}$$

where we use the relation:

$$Z_{\text{int}} = e^{-F_{\text{int}}/\tau}$$

Note that we have:

$$Z_{\text{int}} = \sum_i g_{ij} e^{-\epsilon_{ij}/\tau} = g_j e^{-\epsilon_j/\tau}$$

where the sum over i is the sum over the internal degrees of freedom of the molecule, and the right hand side equation holds if all the energy levels are the same, and we are essentially just dealing with extra degeneracy. (Recall that the g are the multiplicity for each of the energy levels). In this case, the "Law of mass action" simplifies:

$$\prod_j n_j^{V_j} = \prod_j (n_{Q_j} g_j)^{V_j} e^{-V_j \epsilon_j/\tau}$$

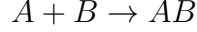
So, considering a simple chemical reaction $H_2 \rightarrow 2H$, we have:

$$\frac{n_{H_2}}{(n_H)^2} = \frac{n_Q(H_2)}{(n_Q(H))^2} e^{-\epsilon_{H_2}/\tau}$$

where we are setting the zero of the energy level to be the internal energy of the Hydrogen atom. Substituting in the quantum concentration, and solving for n_H , we find that:

$$n_H = \sqrt{n_{H_2}} \left[\frac{m_H^2}{m_{H_2}} \frac{\tau}{2\pi\hbar^2} \right]^{3/4} e^{-I/2\tau}$$

where $I = -\epsilon_{H_2}$ is the binding energy of the Hydrogen molecule. In this simple case, we haven't observed any degeneracy in the internal degrees of freedom. We can derive a more general formula for a more difficult reaction, including degeneracy:



we have:

$$\frac{n_A n_B}{n_{AB}} = \left[\frac{m_A m_B}{m_{AB}} \frac{g_A g_B}{g_{AB}} \frac{\tau}{2\pi\hbar^2} \right]^{3/2} e^{-I_{AB}/\tau}$$

where I_{AB} is the binding energy for going from $A + B$ to AB . In many cases, the degeneracies just cancel each other out though. For instance, if we have an electron and a proton going into a Hydrogen atom, the electron has degeneracy two (spin), proton has degeneracy two (spin), and the proton has degeneracy four (also from spin, up up, up down, down up, down down), so in this case the term involving degeneracies just cancels out.¹ If we plug in everything for the proton electron to hydrogen equation, we find:

$$X = \frac{n_p}{n_H} = \frac{1}{\sqrt{n_H}} \left[\frac{m_e \tau}{2\pi\hbar^2} \right]^{3/4} e^{-I_H/2\tau}$$

where we are using an electrically neutral plasma, i.e. $n_e = n_p$.

¹As a side, if you are confused about the sign in front of the binding energy, just use physical intuition to figure it out; i.e. as binding energy increases we expect more of the bound state, since it is much less likely for thermal fluctuations to break apart any of the bound states