

Reading

K&K chapter 9 and start on chapter 10. Also, some of the material we'll be discussing this week is taken from Mandl, chapter 11.

Gibbs Free Energy

As we discussed last time, the Gibbs free energy is obtained from the energy via two Legendre transformations to change the independent variables from entropy to temperature and from volume to pressure,

$$\begin{array}{ccc}
 & dU(\sigma, V, N) = +\tau d\sigma - p dV + \mu dN & \\
 & \swarrow & \searrow \\
 F = U - \tau\sigma & & H = U + pV \\
 dF(\tau, V, N) = -\sigma d\tau - p dV + \mu dN & & dH(\sigma, p, N) = +\tau d\sigma + V dp + \mu dN \\
 \downarrow & & \downarrow \\
 G = F + pV & & G = H - \tau\sigma \\
 & G = U - \tau\sigma + pV & \\
 & dG(\tau, p, N) = -\sigma d\tau + V dp + \mu dN. &
 \end{array}$$

There are a couple of general points to make here. First of all, if the system has other ways of storing energy, those ways should be included in all these thermodynamic functions. For example, if the system is magnetic and is in a magnetic field, then there will have to be an integral of the magnetization (magnetic dipole moment per unit volume) times the magnetic field times the volume element to account for the magnetic energy. The second point is that if the system contains several different kinds of particles, then μdN is replaced by $\sum_i \mu_i dN_i$, where the index i runs over the particle types. (We will be doing this shortly!) The above way of writing the energy, the Helmholtz free energy, F , the enthalpy, H , and the Gibbs free energy, G are really just shorthand for what might actually have to be included.

As remarked earlier, the Gibbs free energy is particularly useful for situations in which the system is in contact with a thermal reservoir which keeps the temperature constant, $d\tau = 0$, and a pressure reservoir which keeps the pressure constant, $dp = 0$. Then if the number of particles doesn't change, the Gibbs free energy is an extremum $dG = 0$, and in fact, it must be a minimum (because the entropy enters with a minus sign!).

Another thing to note is that τ , p , and μ are intensive parameters while σ , V , N , and G itself are extensive parameters. This means that for fixed temperature and pressure, G must be proportional to the number of particles. Or, $G = Nf(\tau, p)$ where f is some function of the temperature and pressure. If we differentiate with respect to N , we have

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

If we compare this with the earlier expression for dG , we see that $f(\tau, p) = \mu(\tau, p)$. In other words, the chemical potential of a single component system depends only on the temperature and pressure. Furthermore,

$$G(\tau, p, N) = N\mu(\tau, p).$$

What happens when there is more than one kind of particle in the system? In this case, we can show that

$$G(\tau, p, N_1, N_2, \dots) = \sum_i N_i \mu_i,$$

We must have for any λ ,

$$G(\tau, p, \lambda N_1, \lambda N_2, \dots) = \lambda G(\tau, p, N_1, N_2, \dots),$$

as this just expresses the fact that G and the N_i are extensive parameters. Now, set $x_i = \lambda N_i$ and differentiate with respect to λ ,

$$\sum_i \frac{\partial G}{\partial x_i} \frac{\partial x_i}{\partial \lambda} = G(\tau, p, N_1, N_2, \dots).$$

Note that $\partial x_i / \partial \lambda = N_i$ and when $\lambda \rightarrow 1$, then $x_i \rightarrow N_i$, and $\partial G / \partial N_i = \mu_i$, so

$$G(\tau, p, N_1, N_2, \dots) = \sum_i N_i \mu_i,$$

but it is not necessarily true that μ_i depends only on τ and p .

As an example, We can write down the Gibbs free energy for a classical ideal gas. We worked out the Helmholtz free energy in lecture 14. For a single component ideal gas, it is

$$F = N\tau \left(\log \frac{n}{n_Q Z_{\text{int}}} - 1 \right),$$

so

$$\begin{aligned} G &= N\tau \left(\log \frac{n}{n_Q Z_{\text{int}}} - 1 \right) + pV, \\ &= N\tau \left(\log \frac{N/V}{n_Q Z_{\text{int}}} - 1 \right) + N\tau, \\ &= N\tau \log \frac{p}{\tau n_Q Z_{\text{int}}}, \end{aligned}$$

where we used the ideal gas law to replace $N\tau$ with pV and N/V with p/τ . Of course, we could also have obtained this result with our expression for μ that we worked out in lecture 14! Note that, as advertised, μ is a function only of p and τ .

If we have a multicomponent ideal gas, the situation is slightly more complicated. Starting from the Helmholtz free energy again, we have

$$\begin{aligned}
 G &= \sum_i \left[N_i \tau \left(\log \frac{n_i}{n_{i,Q} Z_{i,\text{int}}} - 1 \right) \right] + pV , \\
 &= \sum_i \left[N_i \tau \log \frac{N_i/V}{n_{i,Q} Z_{i,\text{int}}} \right] - \sum_i N_i \tau + pV , \\
 &= \sum_i \left[N_i \tau \log \frac{(N_i/N)(N/V)}{n_{i,Q} Z_{i,\text{int}}} \right] - \sum_i N_i \tau + pV , \\
 &= \sum_i \left[N_i \tau \log \frac{x_i p}{\tau n_{i,Q} Z_{i,\text{int}}} \right] - N \tau + pV , \\
 &= \sum_i N_i \tau \log \frac{x_i p}{\tau n_{i,Q} Z_{i,\text{int}}} ,
 \end{aligned}$$

where x_i is the fractional concentration of molecules of type i , $x_i = N_i/N = n_i/n$. Also, $x_i p = p_i$, the partial pressure of molecules of type i . The quantum concentrations are given a molecular subscript since they depend on the masses of the molecules as well as the temperature. The Gibbs free energy is of the form, $\sum_i N_i \mu_i$, and the chemical potentials depend on pressure, temperature, and the intensive parameters x_i .

The derivation of G in the above paragraph hides an important issue in the internal partition functions, $Z_{i,\text{int}}$. This is the fact that all energies in the system must be measured from the same zero point. In particular, if we have molecules that can undergo chemical reactions (which is where we're headed), then we might have a reaction like



If C is stable, then the reaction of A and B to produce C gives up some binding energy ϵ_b , so the ground state energy for $Z_{C,\text{int}}$ is lower than zero by ϵ_b . In other words, the internal energy states of the molecules are

$$\begin{array}{llll}
 A : & 0, & \epsilon_{A,1}, & \epsilon_{A,2}, & \epsilon_{A,3}, & \dots , \\
 B : & 0, & \epsilon_{B,1}, & \epsilon_{B,2}, & \epsilon_{B,3}, & \dots , \\
 C : & -\epsilon_b, & -\epsilon_b + \epsilon_{C,1}, & -\epsilon_b + \epsilon_{C,2}, & -\epsilon_b + \epsilon_{C,3}, & \dots .
 \end{array}$$

When we compute the internal partition function for molecule C we need to include $-\epsilon_b$ as part of the energy in every term in the sum. This extra energy will factor out and we will have

$$Z_{C,\text{int}} = e^{+\epsilon_b/\tau} Z_{0,C,\text{int}} ,$$

where $Z_{0,C,\text{int}}$ is the usual partition function with the ground state at 0. Since the logarithm of the partition function occurs in the chemical potential, the net effect is to add $-\epsilon_b$ to μ_C

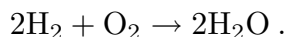
and $-N_C \epsilon_b$ to the Gibbs free energy. The message is that energies must be measured on a common scale. We will sometimes assume the internal partition functions are calculated with the internal ground state energy set to 0 and explicitly add any binding energies to the chemical potentials. Other times, we will assume that all binding energies are incorporated into the internal partition functions!

Chemical Equilibrium

Suppose we have a chemical reaction which takes place at constant temperature and pressure. Then, we know that the Gibbs free energy is a minimum. But in addition to this condition, we also have the constraint imposed by the reaction. In particular, we can write any chemical reaction as

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \cdots + \nu_l A_l = 0 ,$$

where A_i stands for a particular compound and ν_i denotes the relative amount of that compound which occurs in the reaction. For example, the formation of water from hydrogen and oxygen is typically written,



This becomes

$$2\text{H}_2 + \text{O}_2 - 2\text{H}_2\text{O} = 0 ,$$

with

$$\begin{array}{lll} A_1 = \text{H}_2 , & A_2 = \text{O}_2 , & A_3 = \text{H}_2\text{O} , \\ \nu_1 = 2 , & \nu_2 = 1 , & \nu_3 = -2 . \end{array}$$

If the reaction occurs, the change in numbers of molecules is described by ν_i ,

$$dN_i = \nu_i dR ,$$

where dR is the number of times the reaction occurs in the direction that makes the left hand side. Then the change in the Gibbs free energy is

$$dG = \sum_i \mu_i dN_i = \sum_i \mu_i \nu_i dR = \left(\sum_i \mu_i \nu_i \right) dR .$$

This must be an extremum which means that there is no change in G if the reaction or the inverse reaction occurs ($dR = \pm 1$), so

$$\sum_i \mu_i \nu_i = 0 ,$$

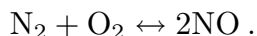
when a reaction occurs at constant temperature and pressure.

Note 1: the expression we've just derived also holds if the temperature and volume are held fixed. This is most easily seen by noting that when the temperature and pressure are held fixed, the reaction proceeds until $\sum_i \mu_i \nu_i = 0$ at which point the system has some particular volume determined by the total amount of reactants, the pressure and temperature. If we start with the temperature fixed and some particular volume, the reaction proceeds to equilibrium at which point the system has some pressure. Now imagine that one had started with this pressure, and allowed the reaction to proceed at constant pressure. Assuming there are not multiple minima in G , the reaction will wind up at the same place and have the same volume!

Note 2: the expression we've just derived holds for a single chemical reaction. If there are several reactions going on but the net reaction can be reduced to a single reaction, the above holds. For example, if the reaction is catalyzed by another molecule via an intermediate step, the reaction rate might differ with and without the catalyst, but the equilibrium will be the same.

Note 3: the ν_i are fixed. It is the chemical potentials which adjust to satisfy the equilibrium condition. Other constraints may need to be satisfied as well. For example, in the water reaction above, the equilibrium condition provides one equation for the three unknown chemical potentials. Two other conditions might be the total amount of hydrogen and the total amount of oxygen.

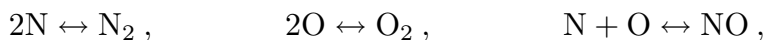
Note 4: if there is more than one reaction, there may be several equations similar to $\sum_i \mu_i \nu_i = 0$ which must be satisfied at equilibrium. As an example, consider



The equilibrium condition, $\sum_i \mu_i \nu_i$, can be written

$$\mu_{\text{N}_2} + \mu_{\text{O}_2} = 2\mu_{\text{NO}} .$$

In other words, we just substitute the appropriate chemical potentials for the chemicals in the reaction equation. If we also have



then we also have the additional relations among the chemical potentials (at equilibrium),

$$2\mu_{\text{N}} = \mu_{\text{N}_2} , \quad 2\mu_{\text{O}} = \mu_{\text{O}_2} , \quad \mu_{\text{N}} + \mu_{\text{O}} = \mu_{\text{NO}} .$$

Note that there are five kinds of molecules. There must be a total amount of nitrogen and a total amount of oxygen (two conditions), and there are four conditions of chemical equilibrium. There are six conditions for five chemical potentials. However, the four

equilibrium conditions are not all independent. For example, the last one can be derived from the previous three.

The Law of Mass Action

We've seen that for chemical equilibrium, the chemical potentials adjust to satisfy the equilibrium condition, $\sum_i \mu_i \nu_i = 0$. Among other things, the chemical potentials depend on the concentrations of the molecules. To bring this out, we'll consider the case that all molecules participating in a reaction can be treated as an ideal classical gas. (This, of course, works for low density gases, but also for low concentration solutes.) Then

$$\mu_i = \tau \log \frac{n_i}{n_{i,Q} Z_{i,\text{int}}} = \tau \log n_i - \tau \log n_{i,Q} Z_{i,\text{int}} = \tau \log n_i - \tau \log c_i ,$$

where

$$c_i = n_{i,Q} Z_{i,\text{int}} ,$$

and c_i depends on the characteristics of molecule i through its mass in the quantum concentration and its internal states in the partition function, but otherwise c_i depends only on the temperature. Note that in this expression, we're assuming that any binding energies are included in the internal partition function.

The equilibrium condition can be written

$$\begin{aligned} \sum_i \nu_i \log n_i &= \sum_i \nu_i \log c_i , \\ \sum_i \log n_i^{\nu_i} &= \sum_i \log c_i^{\nu_i} , \\ \log \prod_i n_i^{\nu_i} &= \log \prod_i c_i^{\nu_i} , \\ \prod_i n_i^{\nu_i} &= \prod_i c_i^{\nu_i} , \\ \prod_i n_i^{\nu_i} &= K(\tau) . \end{aligned}$$

The last line is known as the *law of mass action*. The quantity $K(\tau)$ is known as the *equilibrium constant* and is not a constant but depends on temperature. In terms of molecular properties, it's given by

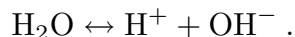
$$K(\tau) = \prod_i c_i^{\nu_i} = \prod_i (n_{i,Q} Z_{i,\text{int}})^{\nu_i} .$$

Note that at a given temperature, measurement of all the concentrations allows one to determine the equilibrium constant at that temperature. For complicated situations it is

easier to determine the constant experimentally than to calculate it from the molecular properties!

Application: pH

Water can undergo the reaction



In water at room temperature a very small fraction of the water molecules are dissociated into hydrogen and hydroxyl ions. The equilibrium concentrations satisfy

$$[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ l}^{-2} .$$

The notation [whatever] denotes the concentration of whatever. This is almost in the form of the law of mass action. We need to divide by the concentration of H_2O to place it in the proper form. However, the concentration of water in water is about 56 mol/l and it doesn't change very much, so we can treat it as a constant, and then the law of mass action takes the form of the above equation. Note that in pure water, the concentrations must be equal, so

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol l}^{-1} .$$

The pH of a solution is defined as

$$\text{pH} = -\log_{10}[\text{H}^+] .$$

The pH of pure water is 7. If an acid, such as HCl is dissolved in water, the increased availability of H^+ shifts the equilibrium to increase $[\text{H}^+]$ and decrease $[\text{OH}^-]$, but the product stays constant. When H^+ goes up, the pH goes down. Similarly, adding a base, such as NaOH, increases the concentration of $[\text{OH}^-]$ and increases the pH.

Other Ways of Expressing the Law of Mass Action

We have written the law of mass action in terms of the particle concentrations, $n_i = N_i/V$. The partial pressure of component i is $p_i = N_i\tau/V$, or $n_i = p_i/\tau$. If we substitute these forms in the law of mass action and rearrange slightly, we have

$$\prod_i p_i^{\nu_i} = \left(\prod_i \tau^{\nu_i} \right) K(\tau) = \tau^{\sum \nu_i} K(\tau) = K_p(\tau),$$

where the equilibrium constant is now called $K_p(\tau)$, depends only on temperature, and is the product of $K(\tau)$ and the appropriate power of the temperature.

We can also write the law of mass action in terms of the fractional particle concentrations, $x_i = N_i/N = p_i/p$, introduced earlier. We simply divide each partial pressure above by p (or each concentration by the overall concentration $n = N/V$ and we have

$$\prod_i x_i^{\nu_i} = \left(\frac{\tau}{p} \right)^{\sum \nu_i} K(\tau) = K_x(\tau, p),$$

where the equilibrium constant is the product of $K(\tau)$ and the appropriate power of τ/p . In this case, the equilibrium constant is a function of pressure as well as temperature.