Lecture 28

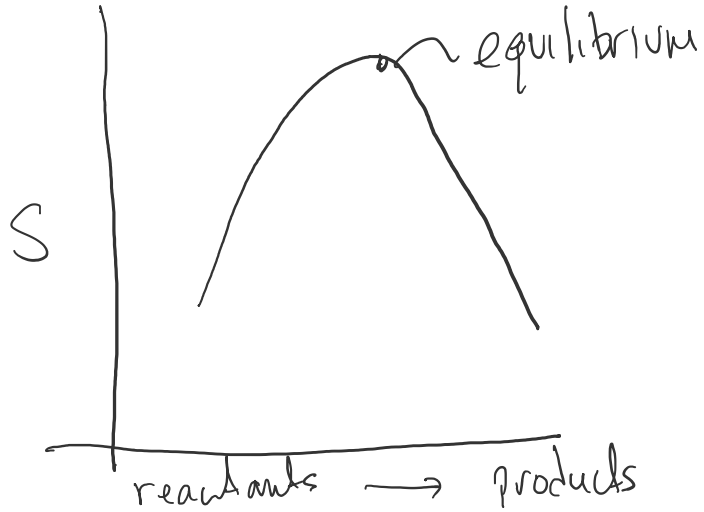
We now turn to the subject of central importance in thermodynamics, equilibrium. Since we are interested in equilibria under chemically interesting conditions and for chemical reactions, we will focus on the Gibbs Free Energy and the chemical potential. The starting point of our development of conditions for equilibrium is the qualitative interpretation of the meaning of ΔG that we developed in chapter five. This was expressed as three conditions:

If $\Delta G_{T,P} = 0$, we have equilibrium.

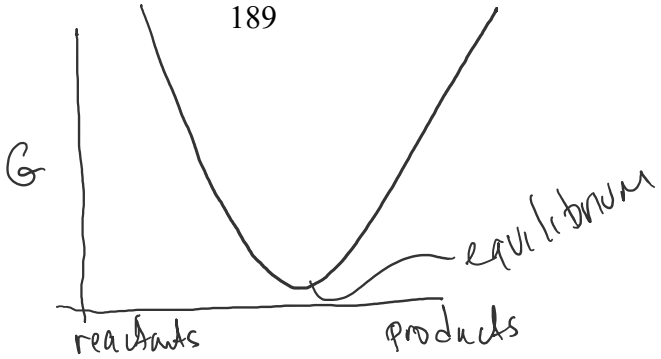
If $\Delta G_{T,P} < 0$, we have a spontaneous process.

If $\Delta G_{T,P} > 0$, the reverse process is spontaneous.

This can be partly understood if we remember that this interpretation of ΔG arises from the second law of thermodynamics, which states that the entropy of the universe rises in a spontaneous process. So if we draw a graph of the entropy of the universe of some spontaneous process, as it progresses we see that the entropy rises until we reach equilibrium and the process progresses no further.

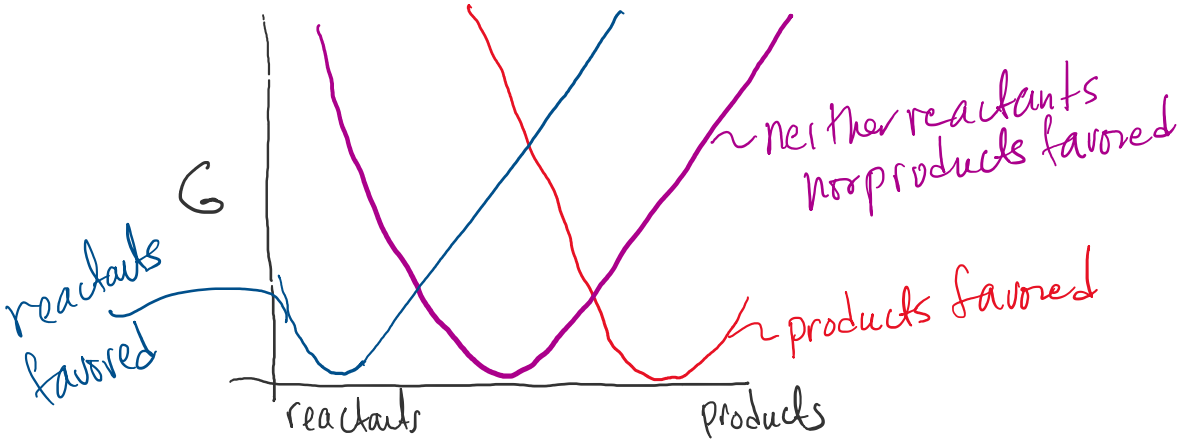


Since ΔG_{sys} decreases for processes in which ΔS_{tot} increases, it is logical that a graph of G_{sys} vs the progress of the process would display a minimum at equilibrium.



Suppose our process is a chemical reaction. I'm going to make a claim here. **If we know the position of the Gibbs function minimum we also know the extent to which the reaction will proceed**. Let's convince ourselves of this by plotting the free energy of some reaction mixture vs. its composition. As the reaction moves from reactants to products the composition of the mixture will change as well.

Say we have a reaction in which almost all of the reactants are converted to products. Then the Gibbs function minimum will be located at a composition on the product side.



If on the other hand, we have a reaction where the equilibrium composition heavily favors reactants, the Gibbs function minimum will be located on the reactant side. Finally, if we have a reaction in which the equilibrium composition is a mixture of reactants and products, the Gibbs function minimum will be located between reactants and products.It would be useful to quantify these ideas. To do this we first have to write a quantitative definition of the **extent of reaction**. To understand why we need to define such a quantity consider the following reaction:

$$N_2 + 3H_2 \leftrightarrow 2NH_3.$$

Suppose for this reaction that 0.5 mol of N_2 has reacted with 1.5 mol of H_2 to generate 1.0 mol of NH_3. Which quantity do we use to describe how far the reaction has progressed? Defining the extent of reaction allows us to solve this problem.

Here is the basic idea. The reason the amount produced or consumed for each of the reactants or products is different is because each has a different stoichiometric constant. So, if we divide the amount produced or consumed by its stoichiometric factor, remembering that the stoichiometric factor is positive for a product and negative for a reactant, we should get a single number that characterizes the reaction. In the case above the change in N_2 is -0.50 mol, and the stoichiometric factor is -1, so the ratio is 0.5. For H_2, the change is -1.50 mol, and the stoichiometric factor is -3, so the ratio is again 0.5. Finally, for NH_3, the change is 1.0 mol and the stoichiometric factor is 2, so the ratio is (sigh) yet again, 0.5. So our idea works. Dividing the change in mols of a substance in a reaction by its stoichiometric factor yields a number, with units of mols, which will be the same for every reactant and product. We call this ratio the extent of reaction, and we use it to describe how far a reaction has progressed.

We can formalize this definition as follows. Suppose we have our generic chemical reaction,

$$0 = \sum_i \nu_i S(i)$$

where S_i is the *i*th substance, and ν_i is positive for a product and negative for a reactant. During this chemical reaction, the change in the number of moles of a given substance, Δn_i, is proportional to its stoichiometric factor ν_i. The proportionality constant is called the extent of reaction, ξ (xi).

Therefore, the extent of reaction is defined as $\xi \equiv \frac{n_i - n_{i,0}}{\nu_i} = \frac{\Delta n_i}{\nu_i}$.

For example, in the reaction $PbI_2(s) \leftrightarrow Pb^{+2}(aq) + 2I^-(aq)$, suppose that 0.05 mol of $PbI_2(s)$ reacts. According to our definition, the extent of reaction here is 0.05 mol. Then 0.05 mol of $Pb^{+2}(aq)$ will have formed and 0.10 mol of $I^-(aq)$ will have formed. We have $\Delta n(PbI_2)$ = -0.05 mol = -1 (0.05 mol), $\Delta n(Pb^{+2})$ = 0.05 mol = 1 (0.05 mol) and $\Delta n(I^-)$ = 0.10 mol = 2 (0.05 mol), where the numbers -1, 1, and 2 are the stoichiometric coefficients.

ξ is a measure of how far the reaction has progressed. Since ν_i is dimensionless, and Δn_i has units of moles, ξ has units of moles as well. ξ is positive if the reaction proceeds toward products and is negative if the reaction proceeds toward reactants.

This is an important concept so let's look at an example.

Example:

Suppose 0.6 mol of O_2 reacts according to $3O_2 \rightarrow 2\ O_3$. Find ξ.

The change in number of moles of species i during a reaction is proportional to its stoichiometric coefficient ν_i, where the proportionality constant is the extent of reaction, ξ; $\Delta n_i = \nu_i \xi$. Since ν_{O2} = -3 and Δn_{O2} = -.6 mol, we have -.6 mol = -3ξ and ξ = 0.2 mol.

For our generalized reaction,

$$0 = \sum_j \nu_j S_j$$

the amount of the *j*th substance produced or consumed is given by

$$dn_j = \nu_j d\xi$$

We want to know the **effect of a reaction on the free energy**. To simplify things lets limit our initial discussion to the simplest possible reaction,

$$A \leftrightarrow B$$

We already know that at constant temperature and pressure,

$$dG_{T,p} = \mu_A dn_A + \mu_B dn_B$$

$$= -\mu_A d\xi + \mu_B d\xi$$

If we divide both sides by dξ we get

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \mu_B - \mu_A$$

We can see the significance of this expression if we use this to calculate dG, the change in the Gibbs free energy for the reaction. The equation is

$$dG_{T,p} = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} d\xi = (\mu_B - \mu_A) d\xi.$$

Let's see if we can interpret this equation. Remember that as the reaction proceeds from reactants to products, $d\xi > 0$. This means that if $\mu_A > \mu_B$, then $dG_{T,p} < 0$ and the reaction A → B will be spontaneous. If $\mu_A < \mu_B$, then $dG_{T,p} > 0$ and it will be the reverse reaction, B → A, which will be spontaneous. Finally, if $\mu_A = \mu_B$, then $dG_{T,p} = 0$ and the reaction will be in equilibrium.

This is very important. Note that in this equation we are using μ not μ° to determine the dG. Since μ changes as the composition of a system changes, this means that as the reaction proceeds the value of μ changes, and therefore the value of dG changes. Remember the difference. μ° is a constant for any substance at a given T. μ depends on composition and pressure.

We now introduce the **reaction Gibbs Function**, $\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,p}$. For our two component system this is the same as $\Delta_r G = \mu_B - \mu_A$. For a more general reaction,

$$aA + bB \leftrightarrow cC + dD$$

$$\Delta_r G = c\mu_C + d\mu_D - a\mu_A - b\mu_B.$$

Finally, for our most general form of a chemical reaction,

$$0 = \sum \nu_j S_j$$

We have

$$\Delta_r G = \sum_j \nu_j \mu_j$$

If we compare this with our result for the two component case we just studied, we see that the **condition for equilibrium** is $\Delta_r G = 0$. If $\Delta_r G < 0$ the reaction has a tendency to proceed from reactants to products, and is called **exergonic**. If $\Delta_r G > 0$ the reaction has a tendency to proceed from products to reactants and is called **endergonic**.

In addition to calculating the reaction Gibbs function this way, we can calculate it from free energies of formation. In general, $\Delta_r G = \sum_{j=1}^{n} \nu_j \Delta G_f(S_j)$. In addition, if we define **standard Gibbs free energies of formation,** we can use these to calculate standard Gibbs reaction functions. ΔG_f^0 is the standard Gibbs free energy change for the formation of a compound from its elements in their reference states at a pressure of one bar. Q: WHAT WOULD ΔG_f^0 FOR AN ELEMENT IN ITS REFERENCE STATE BE? [0, $\Delta H = 0$, $\Delta S = 0$ so $\Delta G = 0$] Using our earlier notation for a generalized reaction we can therefore write the standard Gibbs free energy change for a reaction as

$$\Delta_r G^0 = \sum_j \nu_j \Delta G_f^0(j)$$

Note that $\Delta_r G^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0$ and is also given by

$\Delta_r G^0 = c\Delta G_f^0(C) + d\Delta G_f^0(D) - a\Delta G_f^0(A) - b\Delta G_f^0(B)$. We conclude from this that in calculating free energies of reaction we can substitute standard free energies of formation for standard chemical potentials. Note that this does not mean that the standard chemical potential and the standard free energy of formation are the same, but rather that the difference between two standard free energies of formation will be the same as the difference between two standard chemical potentials.

Once again, I want to emphasize the difference between $\Delta_r G$ and $\Delta_r G^0$.

$$\Delta_r G \neq \Delta_r G^0.$$

$$\Delta_r G = \mu_B - \mu_A. \qquad \Delta_r G^0 = \mu_B° - \mu_A°$$

$\Delta_r G$ changes as the reaction proceeds. $\Delta_r G^0$ is a constant.

$\Delta_r G$ predicts spontaneity……. $\Delta_r G^0$ predicts equilibrium composition

Now let's use the reaction Gibbs function to calculate the **composition of reaction mixtures at equilibrium**. Let's begin with an ideal gas and the reaction A $\rightarrow$ B. For this reaction

$$\Delta_r G^0 = \mu_B - \mu_A.$$

Since for an ideal gas, $\mu = \mu^o + RT\ln\frac{p}{p^o}$, we can write this as

$$\Delta_r G = \mu_B^o + RT\ln\frac{p_B}{p^o} - \mu_A^o - RT\ln\frac{p_A}{p^o}.$$

Since $\Delta_r G^0 = \mu_B° - \mu_A°$, and since ln a - ln b = ln a/b, we can rewrite this as

$$\Delta_r G = \Delta_r G^0 + RT\ln\frac{p_B}{p_A}.$$

We call the quotient $\frac{p_B}{p_A}$, Q_p, the reaction quotient. This is the same reaction quotient that you all saw in General Chemistry. Thus in general we can write:

$$\Delta_r G = \Delta_r G^0 + RT \ln Q_p$$

At equilibrium $\Delta_r G = 0$ and we define the equilibrium constant K_p as $K_p \equiv Q_p$ (equilibrium) $= (p_B/p_A)_{eq}$. It is important to note here that $Q_p = K_p$ only at equilibrium. We can combine this definition of K_p with our previous result and obtain

$$\Delta_r G^0 = -RT \ln K_p.$$

This equation allows us to directly link equilibrium with the standard reaction free energy. It is especially useful when we realize that $\Delta_r G^0 = \mu_B° - \mu_A° = \Delta G_f^0(B) - \Delta G_f^0(A)$. This means that for any reaction where we know ΔG_f^0 of the starting materials and products we can calculate the equilibrium constant.

We can simply extend these results to real gases by turning to the fugacity. We begin with

$$\Delta_r G = \mu_B - \mu_A = \mu_B° - \mu_A° + RT \ln f_B/p° - RT \ln f_A/p°$$

$$= \Delta_r G^0 + RT \ln f_B/f_A$$

which means for real gases, $Q_p = f_B/f_A$ and $K_p = (f_B/f_A)_{eq}$.

Typically we do our chemistry in solution phase as well as in the gas phase, so it would be nice to have a form of this relation that refers to solutions, solids and all real solutions. Once again, it was G.N. Lewis of Berkeley who came up with an appropriate form by introducing the use of the activity. As we noted earlier, the activity is an effective concentration for real solutions, whether solid, liquid or gas. The way that the activity is used to figure out chemical equilibria is

through the equation

$$\mu_i = \mu_i° + RT \ln a_i.$$

For a real gas the activity $a_i = f_i/p°$. In general, the chemical potential of any substance in its pure form is $\mu_i°$. This means that the activity of any substance pure form is 1.

We can use the activity to generalize our definition of the equilibrium constant. For our reaction $A \rightarrow B$, the equation for $\Delta_r G$ becomes

$$\Delta_r G = \mu_B - \mu_A = \mu_B° - \mu_A° + RT \ln a_B - RT \ln a_A$$

$$= \Delta_r G^0 - RT \ln a_B/a_A.$$

This leads to new, more general, definitions of Q and K, $Q = a_B/a_A$ and $K = (a_B/a_A)eq$.

Now all that remains is to generalize this result to reactions with more reactants and products. Let's begin with the reaction

$$aA + bB \rightarrow cC + dD.$$

For this reaction

$$\Delta_r G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

$$= c(\mu_C° + RT \ln a_C) + d(\mu_D° + RT \ln a_D) - a(\mu_A° + RT \ln a_A) - b(\mu_B° + RT \ln a_B)$$

$$= \Delta_r G^0 + RT(c \ln a_C + d \ln a_D - a \ln a_A - b \ln a_B)$$

Which yields

$$\Delta_r G = \Delta_r G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Our reaction quotient is

$$Q_R = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

and our equilibrium constant is

$$K = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)_{eq}$$

Finally we can further generalize to our most general representation of a reaction, $0 = \sum_j \nu_j S_j$. For this case

$$\Delta_r G = \sum_j \nu_j \mu_j$$

$$= \sum \nu_j (\mu_j^0 + RT \ln a_j)$$

$$= \Delta_r G^0 + RT\left(\sum_j \nu_j \ln a_j\right)$$

$$= \Delta_r G^0 + RT \ln\left(\prod_j a_j^{\nu_j}\right)$$

where

$$\prod_j x = x_1 \cdot x_2 \cdot x_3 \cdots x_n$$

and therefore

$$Q = \prod_j a_j^{\nu_j} \text{ and } K = \left(\prod_j a_j^{\nu_j}\right)_{eq}$$

Since at equilibrium, $\Delta_r G = 0$, we have for any reaction $\Delta_r G^0$ = -RT ln K.

The equilibrium constant, K, is a function of the temperature only. However, because it contains stoichiometric coefficients, the number we calculate for an equilibrium constant depends on how we write the chemical equation. For example, the equilibrium constant for the reaction

$$H_2 + 1/2\ O_2 \rightarrow H_2O$$

will be different than the equilibrium constant for the reaction

$$2H_2 + O_2 \rightarrow 2H_2O.$$

For this reason, you should always write a balanced chemical reaction along with your equilibrium constant to indicate exactly what reaction the equilibrium constant refers to. Note that **although the equilibrium constant changes when you change the way the reaction is written, the equilibrium compositions calculated from the equilibrium constants are the same**.

Let's look at our equilibrium expression for the specific case of gases. For a real gas, $a_j = f_j/p°$. So

$$K = \left(\prod_j \left(\frac{f_j}{p°} \right)^{\nu_j} \right)_{eq}$$

This form is rarely used, because although fugacities can be calculated as we showed earlier, they are extremely hard to calculate for mixtures of gases. This form of the equilibrium constant is exact and will depend only on the temperature of the system.

For ideal gases, the form of the equilibrium constant is

$$K = (\prod_j (\frac{p_j}{p°})^{\nu_j})_{eq}$$

Since the equilibrium constant based on the ideal gas law is not the true equilibrium constant, but only an approximation, if we use this equation to calculate the equilibrium constant for real gases, it will depend on both temperature and pressure. This is because under most conditions, the ideal gas pressure will not equal the fugacity. To see this note that we can rewrite the equilibrium constant based on fugacities as

$$K = \prod_j \left(\frac{p_j}{p^0} \right)^{\nu_j} \gamma_j^{\nu_j}.$$

Since K is independent of pressure, and γ depends on pressure and temperature, the *approximate* equilibrium constant calculated using pressures will also change with pressure.

The p° in this equation has important ramifications. Remember that ΔG_r^0 = -RT ln K. In this equation, K is the argument of a natural logarithm. Functions like ln and exp must have dimensionless quantities for their arguments. Suppose we have a reaction like

$$2NO_2(g) \rightarrow N_2O_4(g).$$

For this reaction K is given by

$$K = \left(\left(\frac{p_{N_2O_4}}{p^0}\right) / \left(\frac{p_{NO_2}}{p^0}\right)^2\right)$$

If we weren't dividing by p°, 1 atm, then K would have units of either atm^{-1} or $torr^{-1}$. A second point is that it is easy to see that unless we divide by p°, K would have a different value if we measure pressure in torr.

For example, if at equilibrium, $p_{eq}(N_2O_4)$ = 0.75 atm and $p_{eq}(NO_2)$ = 0.5 atm then if we don't divide by p°, $K = .75/.5^2 = 3\ atm^{-1}$. However, if we measure p in torr, then K = 570 torr/(380 torr)^2 = 3.95 x 10^{-3} $torr^{-1}$. This is all resolved if we divide by p°. In the first case K remains the same:

$$K = \left(\frac{(.75atm / 1atm)}{(.5atm / 1atm)^2}\right) = 3$$

For the calculation in torr,

$$K = \left(\frac{(570torr / 760torr)}{(380torr / 760torr)^2}\right) = 3$$

Let's look at a couple of examples.

Example 1: What is K for the reaction $3H_2 + N_2 \rightarrow 2NH_3$ at 298K? To answer this we first need

to calculate ΔG_r^0. ΔG_f^0 (H_2) = ΔG_f^0 (N_2) = 0. ΔG_f^0 (NH_3) = -16.45 kJ/mol. Therefore ΔG_r^0 = -32.9 kJ/mol. ΔG_r^0 = -RT ln K and therefore

$$K = \exp(-\Delta G_r^0/RT) = \exp\left(\frac{32900\ J\ mol^{-1}}{8.314\ J\ mol^{-1}K^{-1} \cdot 298K}\right) = \exp(13.3) = 5.84 \times 10^5.$$

So this reaction is highly favored.

We can use this example to show the danger of using ΔG_r^0 to calculate equilibrium constants. Suppose we had mistakenly measured ΔG_r^0 = -31.9 kJ/mol, a 3% error. K calculated from this erroneous ΔG_r^0 = 3.91 x 10^5, a 33% error. The error is amplified because of the exponential relationship between ΔG_r^0 and K. For this reason, equilibrium constants calculated from ΔG_r^0 should be taken with a grain of NaCl(s).

Example 2: For the reaction $H_2 + I_2 \rightarrow 2$ HI at 298 K, the pressures of HI and H_2 were measured as 0.50 atm and 2.0 atm respectively. Is the system in equilibrium? ΔG_f^0 (HI) = 1.7 kJ/mol. The reaction quotient for the mixture is given by

$$Q = \left(\frac{a_{HI}^2}{a_{H_2} a_{I_2}}\right)$$

The activity of a solid is usually 1. This makes sense, since the activity measures the effective concentration, and the solid is for all practical purposes a pure substance, which by definition has an activity of one. For the gases we are forced as usual to assume ideality, so

$$Q = \frac{P_{HI}^2}{P_{H_2}} = \frac{.25}{2} = .125$$

K = $\exp(-\Delta G_r^0/RT)$ = exp (-1700 J/mol)/(8.314)(298) = .254. Since Q = K at equilibrium, and Q≠

K, the system is not at equilibrium.

In practice it is common to find systems that are not in equilibrium. There are two reasons for this. One is simply that energy is continually being pumped into systems and disturbing them from equilibrium. For, example, every time a photosynthetic system absorbs light, the energy storage proteins are removed from equilibrium. The second is that some systems can take a substantial time to reach a thermodynamic equilibrium. A classic example is the reaction between H_2 and Cl_2 to form HCl. This reaction takes years to reach equilibrium in the absence of light.

These considerations demonstrate one of the limits of thermodynamics - thermodynamics can tell us what will happen, but it can't tell us if it will occur in a finite amount of time. The latter question is answered by chemical kinetics, which we will be considering at the end of the semester.

At this point we've shown how to calculate equilibrium constants from free energies. However, it is useful to know how these equilibria will change when the reaction conditions, particularly temperature and pressure, change. Knowing this can help us choose the optimum conditions for running a reaction. For example, raising the temperature at which a reaction is run may dramatically increase the reaction yield, but it can also dramatically decrease the reaction yield. Only one of these outcomes is desirable.

Let's examine the **Temperature Dependence of K**. If we begin with $\Delta G° = -RT \ln K$, this can be arranged to

$$\ln K = -\frac{\Delta G^0}{RT}$$

If we remember that $\Delta G° = \Delta H° - T\Delta S°$ this becomes

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

This equation is the integrated form of the Van't Hoff equation. It can be used to determine ΔH° and ΔS° by plotting ln K vs. 1/T. It assumes that ΔH is constant over the temperature range.

If we take the derivative of ln K with regard to T we get

$$\frac{d\ln k}{dT} = \frac{\Delta H^0}{RT^2}$$

the Van't Hoff equation.

This shows us that if ΔH° > 0, ln K increases when T increases. This should match our intuition that raising the temperature of an endothermic reaction helps drive it to completion. On the other hand, if ΔH° < 0, ln K decreases when T increases. So for an exothermic reaction raising the temperature drives the reaction back toward products.

This is an example of **Le Chatelier's Principle**, which states that a system at equilibrium when subjected to a disturbance minimizes the effect of the disturbance by moving to a new equilibrium. Let's look at an example of applying Le Chatelier's Principle by asking what happens when we heat a system. According to Le Chatelier's Principle the system will act to minimize the effect of heating. In other words, the system will act by moving to a new equilibrium that requires that heat is absorbed.

If we have an endothermic reaction, heat is absorbed in going from reactants to products, which pushes the equilibrium toward products, in accord with our quantitative result. If we have an exothermic reaction, heat is absorbed going from products to reactants, which pushes the equilibrium toward reactants, again in accord with our quantitative result.

Let's do one last derivation on the temperature dependence of equilibria and actually calculate a new K when we raise the temperature. We begin with the Van't Hoff Equation

$$\frac{d\ ln\ K}{dT} = \frac{\Delta H^0}{RT^2}$$

and then integrate to yield

$$\int_{\ln k_1}^{\ln k_2} d\ln K = \int_{T_1}^{T_2} \frac{\Delta H^0}{RT^2} dT$$

This is the most general form of the equation. In general, ΔH will depend on the temperature, and we have to explicitly consider the temperature dependence of ΔH° in evaluating the integral. However, if the temperature range is reasonably small, we can assume that ΔH° is constant and pull it out of the integral to give

$$\int_{\ln k_1}^{\ln k_2} d\ ln\ K = \frac{\Delta H^0}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

which yields

$$\ln K_2 - \ln K_2 = -\frac{\Delta H^0}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

or

$$K_2 = K_1 e^{-\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

This equation is useful but has the disadvantage that once ΔH° varies much from its value at the initial temperature, it can introduce gross inaccuracies in the value of K at the new temperature.

If we wish to calculate accurate values of K(T) the best procedure is to turn to an accurate table of ΔG°(T) and use interpolation to get ΔG° if your value of T falls between the listed values. For example, if we want to know ΔG°(296) and we know ΔG°(298) and ΔG°(295), then ΔG°(296) ≈ ΔG°(295) + 1/3(ΔG°(298)-ΔG°(295)). K(296) can then be calculated from ΔG°(296) with reasonable accuracy.

Having considered the effect on our equilibrium composition of a change in temperature, it seems only natural to ask **how pressure affects equilibrium compositions**. We can see quickly that at constant temperature the equilibrium constant is independent of pressure, i.e., $(\frac{\partial K}{\partial p})_T = 0$.

We begin with

$$K = e^{-\frac{\Delta_r G^0}{RT}}$$

Then

$$\frac{\partial}{\partial p}(K) = \frac{\partial}{\partial p}\left(e^{-\frac{\Delta_r G^0}{RT}} \right) = 0 \ ,$$

since, in the final derivative, all three terms, T, R and $\Delta_r G^0$ are constant, so $(\frac{\partial K}{\partial p})_T = 0$.

However, and this is really important, **even though K is independent of pressure, the equilibrium composition may not be.** For example, consider again our reaction $2NO_2 \rightarrow N_2O_4$. If we have at equilibrium P_{N2O4} = 0.75 atm and P_{NO2} = 0.5 atm, plugging into the equilibrium expression, $K = (p_{N2O4}/p°)/(p_{NO2}/p°)^2$ yields K = 3. Now let's raise the total pressure by a factor of 10 while keeping the mole fractions constant. We find that $Q = (p_{N2O4}/p°)/(p_{NO2}/p°)^2 = 7.5/5^2 =$ .3. Therefore Q ≠ K, and the system is not in equilibrium. Since Q is less than K at this higher pressure, the equilibrium composition shifts toward products, and since 2 mols of NO_2 are consumed for every mole of N_2O_4 produced, the pressure is reduced. This is in keeping with Le Chatelier's principle since the disturbance, the increase in pressure, is reduced by the change in the equilibrium composition.