

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  $\Delta G$  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  $\Delta G$  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  $\Delta G_{\text{sys}}$  decreases for processes in which  $\Delta S_{\text{tot}}$  increases, it is logical that a graph of  $G_{\text{sys}}$  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**. Suppose we have our generic chemical reaction,

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

where  $S_i$  is the  $i$ th substance, and  $\nu_i$  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,  $\Delta n_i$ , is proportional to its stoichiometric factor  $\nu_i$ . The proportionality constant is called the extent of

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

For example in the reaction  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$ , suppose that 20 mol of  $\text{N}_2$  reacts. Then 60 mol of  $\text{H}_2$  will have reacted and 40 mol of  $\text{NH}_3$  will have formed. We have  $\Delta n(\text{N}_2) = -20 \text{ mol} = -1 (20 \text{ mol})$ ,  $\Delta n(\text{H}_2) = -60 \text{ mol} = -3 (20 \text{ mol})$  and  $\Delta n(\text{NH}_3) = 40 \text{ mol} = 2 (20 \text{ mol})$ , where the numbers -1, -3, and 2 are the stoichiometric coefficients. The extent of reaction here is 20 mol.

$\zeta$  is a measure of how far the reaction has progressed. Since  $\nu_i$  is dimensionless, and  $\Delta n_i$  has units of moles,  $\zeta$  has units of moles as well.  $\zeta$  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  $\text{O}_2$  reacts according to  $3\text{O}_2 \rightarrow 2 \text{O}_3$ . Find  $\zeta$ .

The change in number of moles of species  $i$  during a reaction is proportional to its stoichiometric coefficient  $\nu_i$ , where the proportionality constant is the extent of reaction,  $\zeta$ ;  $\Delta n_i = \nu_i \zeta$ . Since  $\nu_{\text{O}_2} = -3$  and  $\Delta n_{\text{O}_2} = -0.6 \text{ mol}$ , we have  $-0.6 \text{ mol} = -3\zeta$  and  $\zeta = 0.2 \text{ mol}$ .

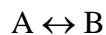
For our generalized reaction,

$$0 = \sum_j \nu_j S_j$$

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

$$dn_j = \nu_j d\zeta$$

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



We already know that at constant temperature and pressure,

$$\begin{aligned}
 dG_{T,p} &= \mu_A dn_A + \mu_B dn_B \\
 &= -\mu_A d\zeta + \mu_B d\zeta
 \end{aligned}$$

If we divide both sides by  $d\zeta$  we get

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

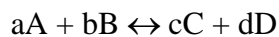
We can see the significance of this expression if we use this to calculate  $dG$ , the change in the Gibbs free energy for the reaction. The equation is

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

Let's see if we can interpret this equation. Remember that as the reaction proceeds from reactants to products,  $d\zeta > 0$ . This means that if  $\mu_A > \mu_B$ , then  $dG_{T,p} < 0$  and the reaction  $A \rightarrow B$  will be spontaneous. If  $\mu_A < \mu_B$ , then  $dG_{T,p} > 0$  and it will be the reverse reaction,  $B \rightarrow A$ , 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  $\mu$  not  $\mu^\circ$  to determine the  $dG$ . Since  $\mu$  changes as the composition of a system changes, this means that as the reaction proceeds the value of  $\mu$  changes, and therefore the value of  $dG$  changes. Remember the difference.  $\mu^\circ$  is a constant for any substance at a given  $T$ .  $\mu$  depends on composition and pressure.

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



$$\Delta G_r = c\mu_C + d\mu_D - a\mu_A - b\mu_B.$$

Finally for our most general form of a chemical reaction,

$$0 = \sum v_j S_j$$

We have

$$\Delta G_r = \sum_j v_j \mu_j$$

If we compare this with our result for the two component case we just studied, we see that the **condition for equilibrium** is  $\Delta G_r = 0$ . If  $\Delta G_r < 0$  the reaction has a tendency to proceed from reactants to products, and is called **exergonic**. If  $\Delta G_r > 0$  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,  $\Delta G_r = \sum_{j=1}^n v_j \Delta G_f(S_j)$ . In addition, if we define **standard Gibbs free energies of formation**, we can use these to calculate standard Gibbs reaction functions.  $\Delta G_f^0$  is the standard Gibbs free energy change for the formation of a compound from its elements in their reference states. Q: WHAT WOULD  $\Delta G_f^0$  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

$$\Delta G_r^0 = \sum_j v_j \Delta G_f^0(j)$$

Note that  $\Delta G^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0$  and is also given by  $\Delta G^0 = c\Delta G_f^0(C) + d\Delta G_f^0(D) - a\Delta G_f^0(A) - b\Delta G_f^0(B)$ . 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  $\Delta G_r$  and  $\Delta G_r^0$ .

$$\Delta G_r \neq \Delta G_r^0.$$

$$\Delta G_r = \mu_B - \mu_A. \quad \Delta G_r^0 = \mu_B^\circ - \mu_A^\circ$$

$\Delta G_r$  changes as the reaction proceeds.  $\Delta G_r^0$  is a constant.

$\Delta G_r$  predicts spontaneity..... $\Delta G_r^0$  predicts equilibrium composition

Now lets 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

$$\Delta G_r = \mu_B - \mu_A.$$

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

$$\Delta G_r = \mu_B^\circ + RT \ln \frac{P_B}{P^\circ} - \mu_A^\circ - RT \ln \frac{P_A}{P^\circ}.$$

Since  $\Delta G_r^0 = \mu_B^\circ - \mu_A^\circ$ , and since  $\ln a - \ln b = \ln a/b$ , we can rewrite this as

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{P_B}{P_A}.$$

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:

$$\Delta G_r = \Delta G_r^0 + RT \ln Q_p$$

At equilibrium  $\Delta G_r = 0$  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

$$\Delta G_r^0 = -RT \ln K_p.$$

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

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

$$\begin{aligned} \Delta G_r &= \mu_B - \mu_A = \mu_B^0 - \mu_A^0 + RT \ln f_B/p^\circ - RT \ln f_A/p^\circ \\ &= \Delta G_r^0 + RT \ln f_B/f_A \end{aligned}$$

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

$$\mu_i = \mu_i^\circ + RT \ln a_i.$$

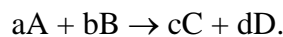
For a real gas the activity  $a_i = f_i/p^\circ$ . In general, the chemical potential of any substance in its reference state is  $\mu_i^\circ$ . This means that the activity of any substance or mixture in its reference state is 1.

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

$$\begin{aligned}\Delta G_r &= \mu_B - \mu_A = \mu_B^\circ - \mu_A^\circ + RT \ln a_B - RT \ln a_A \\ &= \Delta G_r^0 - RT \ln a_B/a_A.\end{aligned}$$

This leads to new 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



For this reaction

$$\begin{aligned}\Delta G_r &= c\mu_C + d\mu_D - a\mu_A - b\mu_B \\ &= c(\mu_C^\circ + RT \ln a_C) + d(\mu_D^\circ + RT \ln a_D) - a(\mu_A^\circ + RT \ln a_A) - b(\mu_B^\circ + RT \ln a_B) \\ &= \Delta G_r^0 + RT(c \ln a_C + d \ln a_D - a \ln a_A - b \ln a_B)\end{aligned}$$

Which yields

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

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

$$\begin{aligned} \Delta G_r &= \sum_j \nu_j \mu_j \\ &= \sum_j \nu_j (\mu_j^0 + RT \ln a_j) \\ &= \Delta G_r^0 + RT \left( \sum_j \nu_j \ln a_j \right) \\ &= \Delta G_r^0 + RT \ln \left( \prod_j a_j^{\nu_j} \right) \end{aligned}$$

where

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

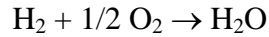
and therefore

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

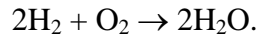
Since at equilibrium,  $\Delta G_r = 0$ , we have for any reaction  $\Delta G_r^0 = -RT \ln K$ .

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



will be different than the equilibrium constant for the reaction



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,  $a_j = f_j/p^\circ$ . So

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

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 will depend only on the temperature of the system.

For ideal gases, the form of the equilibrium constant is

$$K = \left( \prod_j \left( \frac{p_j}{p^\circ} \right)^{v_j} \right)_{eq}$$

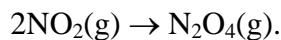
If we use this equation to calculate the equilibrium constant for real gases, it will depend on both temperature and pressure, since in general the ideal gas pressure will not equal the fugacity. To

see this note that we can rewrite the equilibrium constant based on fugacities as

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

Since  $\gamma$  depends on pressure and temperature, the apparent equilibrium constant calculated using pressures will change with pressure.

The  $p^\circ$  in this equation has important ramifications. Remember that  $\Delta G_r^0 = -RT \ln K$ . 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



For this reaction  $K$  is given by

$$K = \left( \frac{p_{\text{N}_2\text{O}_4}}{p^\circ} \right) / \left( \frac{p_{\text{NO}_2}}{p^\circ} \right)^2$$

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

For example, if at equilibrium,  $p_{\text{eq}}(\text{N}_2\text{O}_4) = 0.75 \text{ atm}$  and  $p_{\text{eq}}(\text{NO}_2) = 0.5 \text{ atm}$  then if we don't divide by  $p^\circ$ ,  $K = .75/.5^2 = 3 \text{ atm}^{-1}$ . However, if we measure  $p$  in torr, then  $K = 570 \text{ torr}/(380 \text{ torr})^2 = 3.95 \times 10^{-3} \text{ torr}^{-1}$ . This is all resolved if we divide by  $p^\circ$ . In the first case  $K$  remains the same:

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

For the calculation in torr,

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

Let's look at a couple of examples.

Example 1: What is K for the reaction  $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$  at 298K? To answer this we first need to calculate  $\Delta G_r^0$ .  $\Delta G_f^0(\text{H}_2) = \Delta G_f^0(\text{N}_2) = 0$ .  $\Delta G_f^0(\text{NH}_3) = -16.45 \text{ kJ/mol}$ . Therefore  $\Delta G_r^0 = -32.9 \text{ kJ/mol}$ .  $\Delta G_r^0 = -RT \ln K$  and therefore

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

So this reaction is highly favored.

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

Example 2: For the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$  at 298 K, the pressures of HI and  $\text{H}_2$  were measured as 0.50 atm and 2.0 atm respectively. Is the system in equilibrium?  $\Delta G_f^0(\text{HI}) = 1.7 \text{ kJ/mol}$ .

The reaction quotient for the mixture is given by

$$Q = \left( \frac{a_{\text{HI}}^2}{a_{\text{H}_2} a_{\text{I}_2}} \right)$$

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

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

$K = \exp(-\Delta G_r^0/RT) = \exp(-1700 \text{ J/mol})/(8.314)(298) = .254$ . Since  $Q = K$  at equilibrium, and  $Q \neq K$ , 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. 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  $\Delta G^\circ = -RT \ln K$ , this can be arranged to

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

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

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

This equation is the integrated form of the Van't Hoff equation. It can be used to determine  $\Delta H^\circ$  and  $\Delta S^\circ$  by plotting  $\ln K$  vs.  $1/T$ .

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

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

the Van't Hoff equation.

This shows us that if  $\Delta H^\circ > 0$ ,  $\ln K$  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  $\Delta H^\circ < 0$ ,  $\ln K$  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 responds in a way that tends to minimize the effect of the disturbance. 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 so 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,  $\Delta H$  will depend on the temperature, and we have to explicitly consider the temperature dependence of  $\Delta H^\circ$  in evaluating the integral.

However, if the temperature range is reasonably small, we can assume that  $\Delta H^\circ$  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

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

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  $\Delta H^\circ$  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  $\Delta G^\circ(T)$  and use interpolation to get  $\Delta G^\circ$  if your value of  $T$  falls between the listed values. For example, if we want to know  $\Delta G^\circ(296)$  and we know  $\Delta G^\circ(298)$  and  $\Delta G^\circ(295)$ , then  $\Delta G^\circ(296) \approx \Delta G^\circ(295) + 1/3(\Delta G^\circ(298) - \Delta G^\circ(295))$ .  $K(296)$  can then be calculated from  $\Delta G^\circ(296)$  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

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

Then

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

In the final derivative, all three terms,  $T$ ,  $R$  and  $\Delta_r G^\circ$  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  $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ .

If we have at equilibrium  $P_{\text{N}_2\text{O}_4} = 0.75$  atm and  $P_{\text{NO}_2} = 0.5$  atm, plugging into the equilibrium expression,  $K = (P_{\text{N}_2\text{O}_4}/P^\circ)/(P_{\text{NO}_2}/P^\circ)^2$  yields  $K = 3$ . Now lets raise the total pressure by a factor of 10 while keeping the mole fractions constant. We find that  $Q = (P_{\text{N}_2\text{O}_4}/P^\circ)/(P_{\text{NO}_2}/P^\circ)^2 = 7.5/5^2 = .3$ . Therefore  $Q \neq K$ , 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  $\text{NO}_2$  are consumed for every mole of  $\text{N}_2\text{O}_4$  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.