Here are some comments I wrote for an introductory course on Chemical Equilibria (for Chem 162). I am giving it to you with the understanding that this is background information for you and may be of help here and there. If you had a course like this it might refresh old memories and clear away some of the cobwebs.

The Equilibrium and the Reaction Quotient
Consider a simple reaction: \( A \rightleftharpoons B \).
Equilibrium is the endpoint of all reactions. The reactions are still going on but the concentrations are balanced so that on net no species' concentration is changing. At equilibrium we find, for the simple reaction above, that: \( K = \frac{[B]}{[A]}_{eq} \). Therefore it is useful to ask at any point in time, are we at equilibrium? To answer this question we measure the quantity, \( Q \), which is called the reaction ratio, and defined to look just like \( K \) but not necessarily at equilibrium: \( Q = \frac{[B]}{[A]} \). Then when \( Q \), a time dependent, measured quantity, is the same as \( K \), we are at equilibrium, and otherwise we are not at equilibrium. Notice that the subscript 'eq' has been omitted from the definition of \( Q \), because \( Q \) can be measured at any time and with any set of concentrations consistent with the stoichiometric constraints.

We can also think of \( Q \) as a function of the extent of the reaction. \( X \) is a parameter, which controls the extent of the reaction. From stoichiometry:
\[
[A] = [A]_o - X \quad \text{and} \quad [B] = [B]_o + X.
\]
Therefore, from the initial conditions on the system we are now showing all possible combinations of \( A \) and \( B \) consistent with those initial conditions. Therefore we may write that \( Q \) is a function of \( X \):
\[
Q = Q(X) = \frac{[B]_o + X}{[A]_o - X}.
\]
Then, when \( Q = K \), we have equilibrium. Let's plot \( Q(X) \) as a function of \( X \). We know from the stoichiometry that \( X \) is constrained to be between: \( -[B]_o \leq X \leq [A]_o \). So if we plot \( Q(X) \) vs \( X \), we see that \( Q \) is very small at the minimum values of \( X \), because we have used up all the products (B) to make reactants (A), and then at large \( X \) we have used up all reactants to make products. No matter how complicated the reaction is, and we will get some complicated ones, this type of plot always occurs. It is best to plot \( Q \) on a log scale and then the dependence on \( X \) seems rather linear in the middle range of \( X \). In the plot here \( [A]_o = 3 \text{M} \), and \( [B]_o = 1 \text{M} \). Equilibrium can lie anywhere on this line, and occurs when \( Q \) takes on the numerical value given as \( K \). For illustration \( K = 1 \), the green icon (a square) shows where \( Q = K \).
The Equilibrium Constant

K is a constant, a number. It represents the ratio of reaction-product over reaction-reactants. The numerator contains the product of the concentrations of the reaction-products. The denominator contains the product of the concentrations of the reactants. K is always positive. K takes on a unique value for each chemical reaction. If K small (some sort of units are implied) then the reaction must have lots of reactants because the products are much less numerous than the reactants; the numerator is smaller than the denominator. Conversely, when K very large then the equilibrium lies heavily toward products being formed. Even when the system is far from equilibrium, K is the same, because it is a number, a constant.

Let’s now generalize the reaction to a more complicated one, but still a single overall reaction. Consider the reaction \[ aA + bB + \ldots \leftrightarrow \rightarrow k xX + yY + zZ \ldots \]. The gain and loss of A is still: \[ \frac{1}{a} \frac{\Delta [A]}{\Delta t} = -rate_f + rate_b \], and at equilibrium then \( rate_f = rate_b \). Assuming this reaction is the entire mechanism, you know how to write down the rates for the forward and reverse reactions: \[ k_f [A]^a [B]^b [C]^c \ldots = rate_f = rate_b = k_b [X]^x [Y]^y [Z]^z \ldots \] which leads to: \[ K = \frac{k_f}{k_b} \frac{[X]^x [Y]^y [Z]^z \ldots}{[A]^a [B]^b [C]^c \ldots} \] This expression is called the law of mass action, because it describes changes in the distribution of masses of material to come to balance or equilibrium. The reaction quotient, Q, has exactly the same dependence on concentrations except it is defined at any point along the kinetics pathway to equilibrium. The equilibrium constant can be expressed as the product of the reaction-products raised to their stoichiometric coefficients, divided by the products of the reaction-reactants. We can use our more general notation (using the signed stoichiometric coefficients) to summarize all of this:

Given a chemical reaction, the stoichiometric reaction is: \[ \sum_{i=1}^{N} c_i S_i = 0 \], then \[ K = \prod_{i=1}^{N} [S_i]^c \]

The coefficients, \( c_i \), in this case must have a sign; they are negative for reactants, and positive for products. Because of the sign on the coefficients, the products will be in the numerator and the reactants will be in the denominator. A picture of the equilibrium constant then is: \[ K = \frac{\prod_{\text{products}}^c}{\prod_{\text{reactants}}^c} \]. This might help you remember where the terms go, and show that large K means mostly products, and small K (<<1) means mostly reactants at equilibrium. When the reaction quotient (rhs of the above equilibrium equation) is not dimensionless, then the idea of size of K is difficult to quantify and is controlled by the nature of the expression. We will show this by examples soon.

Determining Chemical Equilibrium Constant

The way to determine the value of K is to measure the concentration of all substances in the definition of Q when at equilibrium, and Q=K. From the stoichiometric reaction you know
Consider a more visual way to imagine equilibrium and measuring the Equilibrium Constant, K. Let’s look inside a molecular reaction. We have a snapshot of the amounts of reactant and product. In this case the reaction is \( A_2 \leftrightarrow K \rightarrow 2A \) or \( N_2O_4 \leftrightarrow K \rightarrow 2NO_2 \), where A stands for the NO\(_2\) molecule. You can define a certain volume by a cubic box that is length \( L \) on a side (\( V = L^3 \)). Then count up the molecules of type A and type \( A_2 \) in the box and compute the concentration. You can then compute the molar concentrations of each of these and then compute the reaction quotient. We already know that water, and so NO\(_2\), will be much like spheres that are about 3 to 4 Å in diameter. So the dimer will be an ellipse that is about 3 by 6 Å. Around STP the distance between molecules is about 10 times the diameter, or about 30 Å. So let's pick a box with length \( L = 30 \) Å. Let's suggest that we find 3 A molecules and 3 \( A_2 \) molecules. What are the concentrations of the molecules? What is the pressure? What is Q?

\[
[\text{A}] = \frac{3 \text{ molecules}}{27 \cdot 10^3 \, \text{Å}^3} \cdot \left(10^8 \, \text{Å/cm} \right)^3 \cdot 10^3 \, \text{cc/liter} = \frac{10}{54.2} = 0.18 \, \text{M}
\]

An ideal gas at STP is about 45 mM. So the nitroxide gas we have is about 10 times more concentrated than typical air. For the example we are considering, \([A_2]=[A]=n/V\). The pressure is the sum of the two partial pressures (Dalton's Law),

\[
P = \frac{2n}{V} RT = 0.36 \cdot (0.082 \cdot 298) \, \text{Atm} = 8.8 \, \text{Atm}
\]

So what is Q? \( Q = \frac{[A]^2}{[A_2]} = 0.18 \). If the system is at equilibrium then \( K = 0.18 \, \text{M} \) also. This result gives an equilibrium constant very close to the actual one. Notice that in this case, unlike the A to B case, even though the reactants and products are in equimolar amounts, the equilibrium constant is not unity.

Now let's assume that the system is at equilibrium, but now imagine that one dimer falls apart, so that there are 5 A molecules and 2 \( A_2 \) molecules in this volume container. Now we are not at equilibrium. What is Q? \( Q = \frac{(\frac{5}{3})^2}{\frac{2}{3}} \cdot 0.18 = 12.2 \cdot 0.18 = 2.2 \). The change of the one dimer out of 3 to 2 monomers shifted Q by more than a factor of 10. The reaction quotient is much larger indicating that the system has moved to more products. It is now out of equilibrium because Q>K. Notice that the net number of moles increased in this process, so the pressure increased – only by a factor of \( 7/6 \) – (while out of equilibrium). As an exercise consider if the equilibrium moves the other way: Two of the three monomers join to form one dimer. Show that Q is reduced 12 fold, and Q<K, and the amount of reactants are in excess.

**Pressure and Concentration Equilibrium Constants**

The equilibrium constant, and the reaction quotient, are both written and defined in terms of concentration. Moreover, the concentration must be molar (moles/liter). With this understanding, the Equilibrium constant is said, by some, to have no units. But it is often useful to keep track of the units to make sure you have not made a mistake. You do not have
to report your units as long as you are following the Molar convention. But how do you know others are following it, if they are not reporting their units? They put a c subscript by the K, called \(K_c\), to indicate that all substances are concentration and in molar. There are other examples of such double-speak. The use of radians is the same way. You cannot take the log or the sin of a number with units. So we claim we can evaluate log(\(K_c\)) because \(K_c\) has no units. Similarly we can evaluate the sin(\(x\)) when \(x\) has the units of radians, and not degrees. There is another convention, which is the convenient for reactions in the gas phase. If all substances in the equilibrium expression are in the gas phase, then it is convenient to express the equilibrium in terms of the partial pressures of each of the gaseous substances. Moreover the understood units are Atmospheres. With this understanding we denote the K with a subscripted p, called \(K_p\). Using the ideal gas relation we can relate the \(K_p\) to \(K_c\). For each substance, the ideal gas equation is \(P_i = [S_i]RT\). Because \(P\) is in Atmospheres and \([S]\) is in molar, \(R\) must be 0.082 liter-atm/mol-K. From this it follows that

\[
K_p = K_c \left(\frac{RT}{\sum_i c_i}\right)^\Delta n,
\]

where \(\Delta n = \sum_i c_i\). You can prove this from the definitions \(K_p = \prod_i P_i^{c_i}\).

The book does an excellent job describing the relation of \(K_p\) to \(K_c\).

Quantitatively Determining Chemical Equilibrium

Chemical Equilibria are just a matter of finding where along a reaction you are. The place you start is with an initial set of concentrations, called \(\{[S_i]_0\}\), the set of species in the stoichiometric reaction, written very generally, is:

\[
\sum_{i=1}^{N} c_i S_i = 0.
\]

In a stoichiometric equation, the concentration of each species, beginning with \(\{[S_i]_0\}\), is kept track of by a single variable, the extent of the reaction, \(X\):

\[
[S_i] = [S_i]_0 + c_i X.
\]

Again, the \(c_i\) are signed, and negative for reactants, so that as a reaction proceeds (to the right) the concentration of reactants drops and that of products increases. The concentration of each species is linearly related to \(X\). Because each and every species is now uniquely determined by \(X\), we can write the reaction quotient as a function of \(X\): \(Q(X) = \prod_{i=1}^{N} [S_i]^{c_i} = \prod_{i=1}^{N} [S_i(X)]^{c_i}\).

Therefore the reaction quotient is a function of \(X\). From the figure on page 3, you can see that \(Q(X)\) is in fact a simple function of \(X\), the log of which is almost linearly dependent on \(X\) over the middle of the graph. When we are at equilibrium then \(Q(X)\) is equal to a number, \(K\). Thus we have a single equation and a single unknown, \(X\), which we can solve for (eventually). Once \(X\) is known, then the stoichiometric equations give the concentrations of each and every species.

The Law of Mass Action

From the stoichiometric expression for the chemical reaction

\[
0 \rightleftharpoons \sum_{i=1}^{N} c_i S_i
\]

We can write the equation for chemical equilibrium (for \(X\)) in a very general form:
Notice that, in each term on the right for \( Q(X) \), the \( c_i \) (the signed coefficient) appears twice: it is the coefficient in front of the \( X \) and it is the power to which the concentration is raised. \( Q(X) \) is a function of the single variable \( X \). So it is straightforward to compute \( Q(X) \). However, if we set \( Q(X)=K \) and consider this an equation for \( X \), then we ask how to solve for \( X \). This equation, unfortunately is, in general, a nasty equation, as it is a polynomial in \( X \) of order either the sum of the product coefficients or the reactant coefficients, whichever is larger. So it can be a pretty nasty expression, and it has as many roots as the order; only one of which makes physical sense. Moreover, there is no known method to solve this expression above third order. But if you are that far into it, there are computer-based methods to find the answer. The best way to find the answer is by trial and error anyway. The physical constraints on \( X \) are quite good to limit the search. \( X \) cannot be so large that any reactant can become negative, nor so small (or negative) that any product can become negative. So given those constraints you have a bound or range in which to work. \( X \) must be real, but it need not be positive. Because \( Q(X) \) is a simple function of \( X \), if you guess a value of \( X \) and compute \( Q(X) \) and it is larger than \( K \), then you know to reduce \( X \) to a lower value. If you compute \( Q(X) \) for a different value and find it is lower than \( K \) then you have an upper and lower bound to \( X \) and can proceed to narrow down the range. This really does not take too long and for a higher order-polynomial problem it is the only way to go.

**Applying equilibria to a dimerization reaction**

This is one of my favorite reactions: The dissociation of a dimer molecule, \( A_2 \overset{K}{\rightarrow} 2A \) or, when viewed in the other direction, the dimerization of a molecule. In terms of the form where the coefficients can be negative numbers, the reaction may be written as: \( 0 \rightarrow 2A - A_2 \). The species \( A_2 \) is the dimer, or two \( A \) molecules bonded together.

The stoichiometric reaction expressions are:

\[
[4_2] = [A_2]_o - X \quad \text{and} \quad [A] = [A]_o + 2X
\]

The mass balance on entity \( A \) is: \( [A] + 2[A_2] = [A]_o + 2[A_2]_o \). This is found by adding up the reaction expressions so that the terms in \( X \) drop out. An example in the text is the formation of \( N_2O_4 \), which is \( (NO_2)_2 \), made from two \( NO_2 \) molecules combining by bonding through the nitrogens as \( O_2N-NO_2 \). ‘\( A \)’ is easier to write than \( NO_2 \), and hopefully easier to follow as well.

Now let’s show that we have a single equation and a single unknown. The reaction quotient is \( Q(X) = \frac{[A]^2}{[A_2]} = \frac{([A]_o + 2X)^2}{([A_2]_o - X)} \), based on the law of mass action. At equilibrium \( Q(X) = K \).
The equation for which we find $X$ is: 

$$K = \frac{[A]^2}{[A_2]_{eq}} = \frac{([A]_o + 2X)^2}{([A]_o - X)^2}.$$ 

Notice that the sign in front of the $X$ in the numerator term is positive and the sign in front of the $X$ in the denominator is negative. This is always the case, because the same coefficient that is used to make the power, or exponent, such as the 1 in the denominator (as a $-1$ in the numerator) or 2 (in numerator), is the same coefficient that multiplies the $X$. Compare this with the general form above.

Before we solve it, there are lots of things to notice about the expression. 1) The larger $X$ is, the larger the numerator is, but more to the point we can drive the denominator to zero, which makes $Q(X)$ infinite. 2) $X$ can't be larger than $[A_2]_o$, or we would be taking more reactant than we have. 3) And $X$ can't be any smaller than $[A_2]_o/2$, or we would be using up product we don't have. Usually one starts with no product in a reaction, so that $X$ must come out positive. 4) This range in $X$ covers the range of all possible positive numbers, which is where $K$ lies. 5) The general problem can be solved by resorting to the quadratic equation. You must multiply both sides by the denominator. Then you have a quadratic equation in $X$. You know how to solve that. So in principle, the most general conditions can be dealt with and solved. 6) The equilibrium position is controlled by $K$. 7) Once $X$ is obtained from this expression then the concentration of each of the species is found from the equation for that species, because $X$ is known.

Now let's solve this for the case where we initially have only reactant, so $[A]_o=0$. Then $X$ cannot be larger than $[A_2]_o$, no matter how large $K$ becomes, and $X$ cannot be negative no matter how small $K$ becomes. The rearranged expression becomes:

$$K \cdot ([A_2]_o - X) = (2X)^2.$$ 

This can be solved using the quadratic expression. [This is a skill you should practice many times on your own.] The answer is:

$$X = \frac{-K \pm \sqrt{K^2 + 4 \cdot ([A_2]_o - K)}}{2 \cdot (4)}.$$ 

Of the two solutions only the + term in front of the square-root is possible to keep $X$ positive, and so that $X$ goes to zero when $[A_2]_o$ goes to zero. If $K$ is small, \( i.e. \ K < [A_2]_o \), then \( X = \frac{\sqrt{([A_2]_o \cdot K)}}{2} \). As $K$ goes to infinity we know from the original form that $X= [A_2]_o$. However, this is very difficult to see from the above solution. One way to see this is to factor $K$ out of the numerator: \( X = K \left( \frac{\sqrt{1 + 16 \cdot [A_2]_o / K} - 1}{8} \right) \). This helps because we can use the approximation that \( \sqrt{1 + 2\varepsilon} \approx 1 + \varepsilon \), when $\varepsilon$ is small. Using this approximation, for $K$ larger than $[A_2]_o$, or small $\varepsilon = 8 \cdot [A_2]_o / K$, we find that $X$ goes to the correct limiting value. Now consider a different regime: When $1 = [A_2]_o / K$, then $X=0.4K=0.4[A_2]_o$. So the “middle region”, when there are approximately equal amounts of
products and reactants at equilibrium, occurs when the concentration is on the order of the equilibrium constant (both have the same units in this case).

A useful number is the sum of the signed coefficients: \[ \Delta n = \sum c_i \text{ summed over all species} \]

present. This quantity, \( \Delta n \), is the net change in the number of moles for the reaction (per mole of \( X \)). This sum tell you the units of \( K \) – Warning: see above on units – or the net order in the reaction. In this particular case, because the sum of the coefficients is not zero, but 1, then it is not whether \( K \) is large or small but whether \( K \) is larger than the concentration of reactant or smaller than the concentration of reactant that determines whether the reaction goes to product or stays reactant. I hope this helps clarify the comments in the text (Pg. 717).

In the simple \( A \rightleftharpoons k B \) reaction discussed at the beginning, \( \Delta n = 0 \). This implies that if the initial concentration of reactant is increased, then at equilibrium the ratio of \( [B]/[A]_{eq} \) will not change. However in the dimer reaction, \( A_2 \rightleftharpoons K 2A \), the ratio of products to reactants, \( [A]/[A_2]_{eq} \), does depend on the initial concentration of reactant. Work and compare each of these problems to see for yourself how this assertion is true.

**The dissociation of a heteromolecule.**

Above we considered the reaction \( A_2 \rightleftharpoons K 2A \). Now we compare and contrast this reaction with that of a molecule that consists of two distinct parts, (AB): \( AB \rightleftharpoons K A + B \).

The associated reaction quotient is: \( Q = \frac{[A][B]}{[AB]} \). When all species are at equilibrium, then \( Q = K \), the equilibrium constant. Let’s examine how the system reaches equilibrium for this dissociation and compare it to how the homodimer (\( A_2 \)) reaches equilibrium. This particular reaction is very important in the study of weak acids and bases, and (in a slightly modified form) the solubility of salts, which are the main applications of the chemical equilibrium principles that we will be developing. Therefore it is good to get a good grounding on this reaction now. Often there are techniques such as spectroscopy or ion selective electrodes that can monitor the concentration of just A or just B in the presence of other species, and so give a direct measurement on the equilibrium quotient and constant. We will work many examples soon. Let’s take the somewhat specific case where we know the total amount of AB one used at the start; \( [AB]_o \) is known, and there are no products initially. This is definitely the usual case. Then we can keep track of each species using the reaction advancement parameter, \( X: [AB] = [AB]_o - X \) and \( [A] = [B] = X \). From these expressions you can derive the mass balance relation \( [AB]_o = [AB] + [A] \). The reaction quotient is then a function of \( X: Q = Q(X) = \frac{X \cdot X}{[AB]_o - X} \). Equilibrium occurs when \( Q(X) = K \), the equilibrium constant.
How is the equilibrium any different from the case where $A_2$ dissociated? We can answer this by examining the two reaction quotients, both written in terms of $X$. Let’s assume that in both cases the concentration of the dimmers are the same and are the only species present at the start of the reaction. Let’s also assume that the equilibrium constants are the same for the two reactions. If you compare closely you realize that, in the case of $A_2$ dissociation, there is an extra 4 in the numerator. This comes about because the two products (2A) are indistinguishable when the homodimer dissociates whereas A and B are distinguishable products when AB dissociates. This leads to around a two fold increase in product at equilibrium for the AB dissociation. Let’s take a specific case, where we have around half dissociated when $K = [AB]_o = [A_2]_o$. At equilibrium the total concentration of $[A] + [B]$ when (AB) dissociates is $1.6\times[A]$ when $A_2$ dissociates. The heterodimer makes more product. Does this make any sense? We see the beginnings of a very general principle here. If we think of concentration effects as a crowding, we see that each species seems to ignore other species but they are crowded by their own kind. The crowding of the A type molecules in the homodimer case retards the generation of monomers. It is a great principle of chemistry that molecules will move away because they do not like to crowd together and will expand to fill all accessible space to avoid high concentrations. We will come back to this point when discussing entropy, as this is an entropy effect.

Effects of Temperature and Pressure on Equilibrium (The Principle of LeChatelier)

There are 3 ways to change the system that we will consider. The first is to change the amount of one species of the material in a reaction. This type of change and system response is often grouped with the Principle of LeChatelier, but that is a bit of a misnomer. We will explain why later. The other two ways to change the balance of a system is to change the pressure (at constant temperature), and the third is to change the temperature (at constant pressure). These two ways illustrate the principle of LeChatelier.

**Adding more of one substance**

The question is, what does the system do in response to an increase in one species. The way to solve this is to know the initial concentration of each species and to solve for equilibrium, then you will find out how all the species changed, and what the equilibrium concentrations are. We can get some qualitative sense of what goes on. Lets assume that the system is at equilibrium, and some amount of each species is present. Now add a little of one of the species. So the concentration of that species goes from $[S_i]_{eq}$ to $[S_i]_{eq} + \Delta S$. Now the system will respond and come back to a new equilibrium. You will find that the new $[S_i]_{eq}$ is between $[S_i]_{eq}$ and $[S_i]_{eq} + \Delta S$. The system responds to absorb the effect, but not all of it. If $S$ is a reactant and you increase the amount then all other reactant concentrations must drop some and all product concentrations will rise some. How else can the system distribute the new amount of material around? Now consider a simple example of how a system responds to a change in concentration. We go back to the A to B example: $A \xrightleftharpoons[K]{\text{K}} B$, and imagine that we are at equilibrium:

$$K = \frac{[B]}{[A]_{eq}}.$$  

Now we increase the concentration of $A$ to what we call a starting amount.

$$[A]_o = [A]_{eq} + \Delta A$$  by adding a small additional amount of A, $\Delta A$. The initial concentration
of B is: \[ [B]_0 = [B]_{eq} = K[A]_{eq}. \]

From these initial conditions A will decrease by X and B will increase by X. The reaction ratio, or mass action expression is:

\[ K = \frac{Q(X)}{\left(\frac{K[A]_{eq} + X}{[A]_{eq} + \Delta A - X}\right)} \]

From this we can solve for X, and find that

\[ X = \left(\frac{K}{1 + K}\right) \cdot \Delta A \]

This shows that X is bounded \(0 \leq X \leq \Delta A\) in such a way that the equilibrium amount of A is greater than the old equilibrium amount but less than that suggested by the addition of \(\Delta A\). This demonstrates the general claim that the system responds to reduce the effect of the change.

A second example is the reaction: \(PCl_3 + Cl_2 \xrightleftharpoons{K} PCl_5\) or \(0 \xleftarrow{K} PCl_3 - Cl_2 + PCl_5\). The system is at equilibrium with the three species having concentrations of 0.2, 0.125 and 0.6 M respectively. Because the system is at equilibrium, K=Q, and

\[ K = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.6}{0.2 \times 0.125} = 24 \]

The Cl_2 species is increased from 0.125 to 0.2M. This disturbs the equilibrium, and the system must readjust. The degree of advancement is used to compute the new levels of each of the species. [Practice writing out each of these expressions for yourself.] The system will move according to

\[ K = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.6 + X}{(0.2 - X) \times (0.2 - X)} = 24 \]

[Practice solving for X using the quadratic formula.] X=.037M, which is less than the .075M increase the Cl_2 experienced at the initial imbalance. The point here is that the system responded to the increase in Cl_2 by removing some (about ½) of the increase. In so doing all other reactants were decreased, the PCl_3 was reduced by the same amount, and the products increased, from 0.6 to 0.637M.

**The Effect of Pressure Change on Equilibria**

The text does an excellent job explaining the effects of pressure on chemical equilibria. Therefore, I will only summarize the salient features here. The equilibrium constants (both Kp and Kc) are rigorously independent of pressure. We now consider the effects of changing pressure at constant temperature. When changing the pressure, but keeping the temperature fixed, the value of the constants does not change. What changes is the volume of the container. The change in volume changes the concentrations (or partial pressures) of the individual gasses. The system will respond, according to LeChatelier, by moving the chemical equilibria so that the total number of moles of gas is reduced. The quickest way to determine, in which direction the reaction will move, is to compute \(\Delta n\). If it is positive that means more moles of gas are produced as the reaction moves to the right. If the pressure is increased then the system will move back to reactants. In heterogeneous reactions, where solids sublime to give a gas, you only want the stoichiometric terms of the gasses, i.e. you want to calculate \(\Delta n_{gas} = \sum c^gas_i\), so be sure to note which species are solids and liquids and do not count them in the sum. Moreover, the sum contains the signed coefficients, so a minus sign goes with the reactants.
You can convince yourself of the correctness of this statement by comparing Q with K. Begin with the system in equilibrium at volume, V₀. Q = K. Now change the pressure so that you have new volume V. Now how does Q compare to K? Each new concentration for each species is: 

\[ [S_i] = \frac{n_i}{V} = \frac{n}{V} \cdot \frac{V_o}{V} = \left[ S_i \right]_{eq} \cdot \frac{V_o}{V}. \]

The new reaction quotient is 

\[ Q = \prod_i [S_i]^{c_i} = \prod_i \left[ S_i \right]_{eq}^{c_i} \left( \frac{V_o}{V} \right)^{c_i} = K \prod_i \left( \frac{V_o}{V} \right)^{c_i} = K \left( \frac{V_o}{V} \right)^{\Delta n}. \]

From this form: If the pressure is increased, then V₀/V > 1, and if \( \Delta n > 0 \), then Q > K. When Q is greater than K you need to make more reactants and reduce the concentration of the products.

An interesting consequence is that the volume will not be what you would have guessed initially given the pressure change. Consider an increase in pressure at constant temperature. The volume is reduced (according to the I.G. law). So you would think you could compute the new volume. However, the system is dynamic and will respond by shifting the equilibrium so that there are fewer moles of gas present. Well, this will cause the new volume to be even smaller than you would have expected had it not been a system in equilibrium, capable of changing the number of moles.

One way to visualize the effect of increasing (or decreasing) the volume, is to think about molecules combining to make fewer, but bigger molecules. If the volume decreases then the pressure is on (so to speak) to push the molecules together to make bigger (and fewer) molecules. But if you give large molecules a lot more room (by increasing the volume) then you would expect that they would fall apart more and so make more (and smaller) molecules if given a chance. And that, in fact, is how molecular reactions behave.

A final word of caution on a comment in the text. The text suggests that one may add an inert gas at constant volume to increase the total pressure on the gas. When done at constant volume, an increase in pressure will not affect the equilibrium. However, if the inert gas is added at constant pressure, then the volume does change, and this moves the system equilibrium to produce more total moles of material. So the addition of an inert gas does not always have no effect. How it is added must be examined carefully.

**The Effect of Temperature Change on Equilibria**

The major effect of changing the temperature, at constant pressure, is to actually change the value of the equilibrium constant. This seems inconsistent with the above discussion. Changing pressure at constant temperature changed the volume, and that caused the shift in equilibrium. Now changing the temperature, at constant pressure, will also change the volume. This is true but not the major factor (usually). The equilibrium constant (Kp or Kc) is independent of pressure but it strongly depends on temperature.

The relation is: 

\[ K = A \exp \left\{ -\frac{\Delta H^{\circ}}{RT} \right\}, \]

and it is independent of the mechanism. If we take the natural log of both sides we find 

\[ \ln(K) = \left( -\frac{\Delta H}{R} \right) \cdot \frac{1}{T} + \ln(A). \]

A plot of \( \ln(K) \) vs 1/T would
give a straight line. This is called a van’t Hoff plot. The slope of the plot is $\frac{-\Delta H}{R}$, and the intercept of this plot corresponds to $T \rightarrow \infty$. Because the slope is the rise over run, or just the ratio of two points on the ordinate (or y axis values), $K_1$ and $K_2$, over the two points on the abscissa (the x axis), $T_1$ and $T_2$:

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

We can use this expression to determine how the increase in temperature will move the system. If the reaction is endothermic, $\Delta H = \Delta H^o dX > 0$, and the system absorbs heat as the reaction proceeds to products. Now, if $T_2 > T_1$ then $K_2 > K_1$. So an increase in temperature makes the equilibrium constant larger, which means that the equilibrium shifts to more products. The upshot then is that the increase in $T$ means that heat goes into the system, and the system responds by moving in the direction that will absorb the heat.

A way to visualize the result is to think of heat as a part of the stoichiometric reaction. For the case of endothermic reactions heat is put in (like a reactant). Then a rise in temperature, like an increase in reactants, will drive the system in the direction of making more products.

**Equilibrium**

So far we have talked about a chemical reaction as a single equilibrium reaction. When working problems in this chapter and in future ones be sure that there really is only one reaction. When we have two reactions, sometimes one will not be stated. So be sure you know the rules of the problem before you try to solve it. The first thing to do on equilibrium problems is get the stoichiometric reaction. Make sure it is balanced; be clear on which species are reactants. Decide in advance if you want to treat the reactants as having negative or positive coefficients. Now, just set up the mass balance expressions. These are the stoichiometric constraints that you know from previous courses. Now you add to your constraints the reaction quotient expression for $Q$, which you can express in terms of the degree of advancement. At equilibrium $Q=K$. When we have multiple reactions with common species, the degree of advancement does not always work, and must be used carefully. For a single reaction the degree of advancement, $X$, is a convenient way to express what is unknown. Before you try to solve the problem be sure you have as many equations as you have unknowns.

Let's try an example that will set the stage for the next chapter. Suppose you throw into water a weak acid that dissociates somewhat. $HA \rightleftharpoons K H^+ + A^-$. Now, you don’t know how much you added, but you know $K$ and you measured the $[H^+]$. {For now we will ignore the fact that water dissociates. We really have a single reaction going on. Next chapter we will have to think about the effects of water auto-ionizing or dissociating.} So the unknown is $C_a=|HA|_0$. The reaction quotient $Q=K$ now at equilibrium. This gives us the reaction quotient, which we can write out in terms of $X$. $[HA] = [HA]_o - X$ and $[A^-] = X$. If we use the reaction quotient at this point we find:

$$\frac{[A^-]}{[HA]} = \frac{K}{[H^+]}$$

where the quantity on the r.h.s. is known. So substituting in for the initial amount and $X$, unfortunately gives us an equation for $X$ which is in terms of $C_a$, which is also unknown, so we made no progress in trying to solve
the problem this way. The secret is in writing out all of the mass balance expressions before continuing, as they will provide the clue for solving this puzzle. One more mass balance comes from \([H^+] = X\), assuming no \(H^+\) ions present before acid dissociation, as was stated in the problem (but not obviously). It may have seemed odd writing out \([H^+]\) in terms of \(X\), when \([H^+]\) was known, but the utility is not to solve for \([H^+]\), but to solve for \(X\). From this we get the mass balance \([H^+] = X = [A^-]\). This is also the charge balance expression, in this particular case. Because \([H^+]\) is known, now we know \([A^-]\). Now we can use the mass action rule to find \([HA]\)

\[
[HA] = \frac{[A^-][H^+]}{K} = \frac{[H^+]^2}{K}.
\]

From this now we can get the total amount or the initial amount of acid: \([HA]_o = [H^+] \left(1 + \frac{[H^+]}{K}\right)\). Hopefully, this demonstrates that we all run into unexpected outcomes as we solve problems. But if we write down all that we know, sometimes it helps.

**Chemists use these ideas**

These ideas are of tremendous practical importance to working chemists. We all think that to make a reaction go faster we heat it up. The Arrhenius form of the rate constants reinforces that this idea is true. However, we may not really accomplish much. One might say “I only got 30% yield on my product and I heated it and waited all day but didn’t get any more.” You can say to that person: well you probably reached equilibrium (although you should check that more thoroughly) and if the reaction is exothermic you were reducing the yield by heating it, not increasing it. But if you cool the reaction you might make more product but the tradeoff is it will take longer. So one thing one can do is to begin a reaction warm to get the kinetic advantage, and then slowly cool to move the system when it is near equilibrium to get the thermodynamic advantage. There are tradeoffs to this strategy, and reading about how ammonia is made, in the text, will illuminate these tradeoffs by example. And there are other things one can do. From the principle of mass action we know that adding more reactants produces more products. You can use this in a clever way: If you have two reactants, one of which is expensive and the other cheap, you can drive the reaction by adding more of the cheap reactant. This will help you consume and use up the expensive reactant (making it the limiting reagent). This way you get your money’s worth from the reaction. Even though you can’t beat the equilibrium constant you can stack the deck in your favor.

**Charge Balance  An additional stoichiometric constraint**

From the rules of stoichiometry you know the mass balance expression for each of the atoms in the expression. Because the system is electrically neutral (no net charge in the container) but some of the individual species may be charged, we also have the charge balance

\[
\sum_{i=1}^{N} q_i [S_i] = 0,
\]

where the \(q_i\) are the charges on each of the species, which could also be written as \(\left[S_i\right] = \left[S_i^{q_i}\right]\). We have not encountered many charged species yet, but that will
soon change. We did notice in the acid dissociation that we obtained an expression similar to the charge balance. This is just a little note to let you know what is coming.