We now turn to a topic of central importance in chemistry, chemical equilibrium. Chemical equilibrium is a well understood phenomenon of great power. It totally pervades chemistry. In our course, we will look only at what the concept can tell us about the relative yields of various reactions, but it also underlies most statistical theories of chemical reactions, gases, liquids and solids. It affects both our understanding of matter in bulk and the behavior of individual molecules.

We have mentioned equilibrium before, first when we discussed vapor pressure, and then when we discussed the related phenomenon of boiling point elevation. In both cases, the equilibrium, an unchanging vapor pressure, was the result of two opposing phenomena, evaporation and condensation, occurring at the same rate. Because our equilibrium didn't result from the two processes stopping, but rather from their occurring at the same rate, we called our equilibria by the special name of dynamic equilibria.

Like the phenomenon of vapor pressure, chemical reactions can come to equilibrium. Like the phenomenon of vapor pressure, these equilibria are dynamic. What are the opposing processes that lead to a dynamic chemical equilibrium? To see the answer to this question, consider the following reaction. When H₂(g) and I₂(g) are combined they form HI according to the reaction

\[ \text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g). \]

It just so happens that when any amount of HI is present, the opposite reaction,

\[ 2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g), \]
also occurs. The two reactions don't always occur at the same rate, but when they do there is no longer any change in the concentrations of the reactants or the products, and an equilibrium is established. It is a dynamic equilibrium, because it results from two opposing processes occurring at the same rate. We call the concentrations of our reactants and products when the system reaches equilibrium the equilibrium composition of our system. The concept of chemical equilibrium is important because all chemical reactions, left to themselves, will eventually reach equilibrium.

How do we know that these equilibria are dynamic? One piece of evidence is that the same equilibrium is achieved whether we begin with reactants or products. For example, in the example I've just given, if we begin with one mole of H₂ and one mole of I₂, when equilibrium is reached at 425°C, we will have 0.212 moles of H₂, 0.212 moles of I₂, and 1.58 moles of HI. However, if we start with two moles of HI under the same conditions, we will still end up with the same amount of each of our products and reactants. This is proof that both forward and backward reactions occur. It is a reasonable inference that both reactions occur simultaneously when at equilibrium. However, the dynamic nature of the equilibrium can be proved elegantly through the use of radioactive isotopes.

Remember that the composition of a reaction mixture at equilibrium is called the equilibrium composition. One equilibrium composition of our HI mixture is 0.212 moles of H₂, 0.212 moles of I₂, and 1.58 moles of HI. We make a new mixture with this equilibrium composition, except that in the 1.58 moles of HI, all the iodine is the radioactive isotope ¹³¹I. Since the reaction mixture has the equilibrium composition, there will be no overall change in
the amounts of HI, H₂ and I₂. However, the ¹²⁷I in the I₂ is gradually replaced by a mixture of ¹²⁷I and ¹³¹I, while the same mixing of stable and radioactive isotopes occurs in the HI. This demonstrates clearly that the equilibrium is dynamic, since the only way that the mixing can occur is if the forward and reverse reactions are both occurring.

It is useful to have a **quantitative** way to talk about the **balance between reactants and products that is present at equilibrium**. This is so because it is useful to compare the extent to which a reaction favors products or reactants, but also because such a quantitative tool would allow us to calculate the composition that a reacting mixture would have at equilibrium. In the case of vapor pressure, we only had to tabulate one number to quantify our equilibrium, but in chemical reactions we generally have the concentrations of several species to keep track of. Furthermore, because the equilibrium is a complex balance between the concentrations of several species, there is generally a large number of reaction mixtures which can satisfy the conditions for equilibrium. Fortunately, there is a number called the **equilibrium constant**, K, which **tells us the relationship between the concentrations of our reactants and products at equilibrium**.

We calculate K using the **equilibrium constant expression**. The equilibrium constant expression is a ratio. For a reaction of ideal gases, the numerator of the quotient is a function of the equilibrium partial pressures of the products, and the denominator of the quotient depends on the equilibrium partial pressures of the reactants. For a model reaction aA + bB ⇌ cC + dD, the **equilibrium constant expression** has the exact form $K_p = \frac{P_{C}^{c} P_{D}^{d}}{P_{A}^{a} P_{B}^{b}}$, where the subscript shows that the reaction quotient is calculated from partial pressures. Note that what we are doing is to
take the product of the partial pressures of the products raised to the power of their stoichiometric coefficients and divide by the product of the partial pressures of the reactants raised to the power of their stoichiometric coefficients. For example, for the reaction \( \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \),

\[
K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_2}p_{\text{I}_2}}.
\]

Since the stoichiometric coefficient for the HI is 2, its partial pressure is squared.

For the reaction \( \text{P}_4(\text{g}) + 6 \text{H}_2(\text{g}) \rightleftharpoons 4 \text{PH}_3(\text{g}) \), what would the equilibrium constant expression be?

Let’s see how we go about calculating \( K_p \) for a specific example, the gas phase reaction, \( \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \). As we said earlier, the equilibrium expression for this reaction is

\[
K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_2}p_{\text{I}_2}},
\]

so we need to find the equilibrium partial pressures of the reactants and products. If we start with only \( \text{H}_2 \) and \( \text{I}_2 \), as the reaction occurs the pressures of hydrogen and iodine decrease from their initial values, and the pressure of HI increases. As the reaction proceeds, the pressures of the reactants and products stop changing. The system has reached equilibrium and from then on the composition of the reaction mixture stays constant. The same thing would have happened if we started with HI. The HI pressure would decrease, and the \( \text{H}_2 \) and \( \text{I}_2 \) pressures would increase, but after a time, the pressures would
stop changing, and the system would achieve equilibrium. By measuring the equilibrium pressures of each product and reactant we can calculate the equilibrium constant using our equilibrium expression. For example, suppose we begin with a mixture at 699K in which \( p_{H_2} = 0.640 \text{ atm} \), \( p_{I_2} = 0.571 \text{ atm} \), and \( p_{HI} = 0 \). When the reaction reaches equilibrium, the pressures are \( p_{H_2} = 0.167 \text{ atm} \), \( p_{I_2} = 0.0980 \text{ atm} \) and \( p_{HI} = 0.946 \text{ atm} \). Then \( K_p = \frac{0.946^2}{(0.167 \times 0.0980)} = 54.7 \).

What's so special about the equilibrium constant? One thing that makes it important is that all chemical reactions, if left long enough, will come to equilibrium. So the equilibrium constant is a quantity which will be relevant to all chemical reactions. What is particularly important is that if we know the composition of our starting mixture, the equilibrium constant allows us to figure out the composition when our reaction reaches equilibrium. This is because no matter what mixture we start out with, our reaction always reaches a composition whose equilibrium expression equals the equilibrium constant.

To see this lets look at our synthesis of HI again, and consider several different starting mixtures. We've already done one example, but let's look at a few more,

<table>
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<tr>
<th>( p_0(H_2) ) (atm)</th>
<th>( p_0(I_2) ) (atm)</th>
<th>( p_0(HI) ) (atm)</th>
<th>( p(H_2),eq ) (atm)</th>
<th>( p(I_2),eq ) (atm)</th>
<th>( p(HI),eq ) (atm)</th>
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</tr>
</tbody>
</table>
[Have class calculate $K_p$ for each one.] Note that no matter what our starting concentrations, we get almost exactly the same value for our equilibrium constant. **It doesn't even matter if we start out with all products, all reactants or a mixture, our equilibrium constant will always come out the same.**

There are a couple of problems with our equilibrium expression as we've written it. The first problem is that **we don't always run reactions in the gas phase.** Often we run them in solution, and sometimes, we'll have mixtures of solids, solutions and gases. Obviously for solutions and solids we'll have to come up with an equilibrium expression which doesn't require pressures. We could (and will) define separate equilibrium expressions for each of these cases, but it would be even more useful to have a **general equilibrium expression which fits all of these cases.** The second problem is that later when we return to thermodynamics, we will have a couple of important equations which involve the natural log of the equilibrium constant, $\ln K$. The natural log is a very important function in chemistry, and is a logarithm to base $e$. This function is on all your calculators, and is reviewed in the math appendix in Chang. The most important thing for you to know about the natural log is that it is the inverse of the exponential function, i.e., $\ln(e^x) = x$ and $e^{\ln(x)} = x$. Why does this mean we need a new expression for $K$?

Consider the reaction $\text{C}_2\text{H}_4(\text{g}) \rightleftharpoons \text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g})$. **What would the equilibrium constant expression as we've learned to write it be?** The units would be atm$^2$/atm or atm. The problem is that **you can't take a logarithm of a unit.** We state this formally by saying that the argument of a log function must be dimensionless.
We solve this problem by redefining our equilibrium constant expression using a new quantity called the **activity, \( a \).** The activity represents the ability of a substance to take part in a reaction. The activity of a substance depends on its phase. For an ideal gas the activity is defined as its partial pressure in atm, divided by 1 atm. In solution, the activity is the molarity of the substance, divided by 1 M. Finally for a pure substance, like a pure solid or a pure liquid, or for a solvent, the activity is simply 1. Note that for this purpose we define a solvent as a component of a mixture whose mole fraction is \( \sim 1 \), ie, \( X_{\text{solvent}} \sim 1 \).

For example, let’s say we have 0.25 atm of CO\(_2\). Its activity is \( 0.25 \text{ atm/1 atm} = 0.25 \). If we had a sample of C(gr), a pure substance, its activity is 1. Finally if we have a 0.78M solution of NaCl(aq) its activity is \( 0.78 \text{ M}/1 \text{ M} = 0.78 \). What if we had 24 torr of Ar? How would we find its activity? [\( \frac{24}{760} = 0.032 \)]. Let’s say we have a 0.5 molar solution of NaF in water. What is the activity of the NaF? [\( a_{\text{NaF}} = \frac{0.5 \text{ M}}{1 \text{ M}} = 0.5 \)] What is the activity of water? [water is solvent so 1.]. To see this remember \( X_{\text{H}_2\text{O}} \) has to be \( \sim 1 \) for the activity to be one. \( n_{\text{NaF}} = 0.5 \). 1L \( \text{H}_2\text{O} \) has \( n_{\text{H}_2\text{O}} \sim 55 \), so \( X_{\text{H}_2\text{O}} = 55/55.5 \sim 1 \).

If we have a general reaction, \( aA + bB \rightleftharpoons cC + dD \), the equilibrium constant expression is given by \( K_{\text{act}} = \frac{a_c^c \cdot a_d^d}{a_a^a \cdot a_b^b} \), where for example \( a_A \) indicates the activity of substance A, and \( a_B \) indicates the activity of substance B, etc. Let’s look at a couple of quick examples. For the reaction we just mentioned the partial pressure of ethylene is 0.25 atm, the partial pressure of acetylene is 0.3 atm, and the partial pressure of H\(_2\) is 0.8 atm. The activity of each of these gases is just \( p/1 \text{ atm} \). Therefore the equilibrium constant expression is
\[ K_{ac} = \frac{a_{c,H_2}a_{H_2}}{a_{c,H_2}} = \frac{0.3 \times 0.8}{0.25} = 0.96 \]

Notice that the equilibrium constant expression is now dimensionless so we can take the natural log with no problem.

We've already discussed two types of equilibrium constants, \( K_p \) and the more general, \( K_{act} \). Another type of equilibrium constant you will often see is \( K_c \), which is based on concentrations of reactants and products. Having defined \( K_p \) and \( K_{act} \), the definition of \( K_c \) is simple. For a model reaction \( aA + bB \rightleftharpoons cC + dD \),

\[ K_c = \frac{[C][D]^c}{[A]^a[B]^b} \]

For example if we were to measure the amount of products and reactants in our \( HI \) reaction in concentration units, then given the reaction \( H_2 + I_2 \rightleftharpoons 2HI \),

\[ K_c = \frac{[HI]^2}{[H_2][I_2]} \]

An important thing to realize is that most of the time for a given reaction, \( K_p \) and \( K_c \) will have different values. Consider the reaction \( N_2 + 3H_2 \rightleftharpoons 2 NH_3 \). At equilibrium at a temperature of 500°C, \( p_{H_2} = 6.15 \text{ atm} \), \( p_{N_2} = 30.8 \text{ atm} \), and \( p_{NH_3} = 0.505 \text{ atm} \). What is the form of \( K_p \)? Calculate \( K_p \) \((3.56 \times 10^{-5} \text{ ATM}^{-2})\) If we use concentrations instead the values are \([H_2] = 0.150 \text{ M}, [N_2] = 0.750 \text{ M}, [NH_3] = 1.23 \times 10^{-2} \text{ M} \). What is the form of \( K_c \)? Calculate \( K_c \) \((5.97 \times 10^{-2} \text{ M}^{-2})\) Are the two equilibrium constants the same? Since the two equilibrium constants are different, it would be useful to know how to convert between them.

Only gas phase reactions can have both \( K_p \) and \( K_c \) as equilibrium constants. Why? [\( p \) is partial pressure of reactant, for most liquid solutions reactant won't have a partial pressure., i.e. what is the partial pressure of 1M NaCl(aq)] Notice that \( K_c \) uses \( M \), moles/liter in its equilibrium constant expression, while \( K_p \) uses \( p \). Since we are working with gases we'll turn to the ideal gas
law to link the two quantities. Let’s illustrate this by converting from $K_c$ to $K_p$ first. We do this by noting that moles/liter is moles per unit volume, ie, $n/V$. According to the ideal gas law, $n/V = p/RT$. So to convert from $K_c$ to $K_p$, our first step is to take our expression for $K_c$ and replace $[\cdot]$ by $p/RT$. For example, for the reaction $2A(g) \rightarrow 2B(g) + C(g)$, $K_c = \frac{[B]^2[C]}{[A]^2}$. If we substitute $p/RT$ for each of our concentrations, we get $K_p = \frac{p_B^2p_C}{p_A^2}. \frac{1}{RT} = \frac{K_p}{RT}$.

Note that this result is only for this reaction. To relate $K_c$ and $K_p$ for other reactions, we simply replace the concentration with $p/RT$, just as we did here. What if we have $K_p$ and want to find $K_c$? In this case the ideal gas law tells us that $p = RT(n/V) = RTM$. For this case we would just replace the pressures with $RT[\cdot]$, and proceed as before.

What do we do if we want to calculate an equilibrium constant for a reaction like

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq),$$

where the equilibrium involves both a solution and a solid. In this case

$$K_{act} = \frac{a_{\text{Ag}^+(aq)}a_{\text{Cl}^-(aq)}}{a_{\text{AgCl(s)}}}.$$

The activities of the $\text{Ag}^+$ and $\text{Cl}^-$ will just be $[\text{Ag}^+]/1M$, and $[\text{Cl}^-]/1M$. The $\text{AgCl}$, since it is a pure solid, has an activity of 1. Thus $K_{act} = \frac{[\text{Ag}^+] [\text{Cl}^-]}{1M \cdot 1M}$. Now this is really important. If we want to calculate $K_c$, even though we use the concentration for our two solutes, we still use the
activity for the solid in our equation, i.e., $K_c = [\text{Ag}^+] [\text{Cl}^-]$. Let's look at another example. For the reaction

$$\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq),$$

$[\text{H}_3\text{O}^+] = .1 \text{ M}$, $[\text{Cl}^-] = .1 \text{ M}$, and $[\text{HCl}] = .0001 \text{ M}$. What is the form of $K_{\text{ACT}}$? What is the activity of $\text{HCl}$, $\text{H}_3\text{O}^+$, $\text{Cl}^-$, $\text{H}_2\text{O}$? What will the form of $K_c$ be? So we find in general that the concentrations of pure solids, liquids or solvents don't appear in $K_c$ or $K_p$.

At this point we've learned the basics about defining equilibrium constants. We can use the rules that I've given to calculate, and calculate with, just about any equilibrium constant. However, there are a few situations that appear so frequently that solving equilibria for these problems will be easier if we learn just a few new rules. The first of these is when we have two consecutive reactions, both of which reach equilibrium. If we have two consecutive reactions, their equilibrium constant is given by the product of the two equilibrium constants. This fact will be important when we consider acidic equilibria. So for example, suppose we have two consecutive reactions,

$$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$$

$$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$$

If we add the two reactions to see what the overall reaction is, we get

$$\text{H}_3\text{PO}_4 + 2 \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + 2\text{H}_3\text{O}^+.$$ 

The equilibrium constants for the first and second reactions are

$$K_1 = \frac{a_{\text{H}_3\text{O}^+}a_{\text{H}_2\text{PO}_4^-}}{a_{\text{H}_3\text{PO}_4}a_{\text{H}_2\text{O}}},$$
The equilibrium constant for the overall reaction is

\[ K = \frac{a_{H_2O}^2 a_{H_3PO_4}^-}{a_{H_2O} a_{H_3PO_4}} \]

But this is just the same as the product between \( K_1 \) and \( K_2 \) [Demonstrate]. So our general rule is that if we have two successive reactions with equilibrium constants \( K_1 \) and \( K_2 \), then the overall equilibrium constant \( K = K_1 \times K_2 \).

Another case we need to consider is the case where we look up an equilibrium constant in a book, and the reaction for the equilibrium constant is written differently than we've written our reaction. Suppose you want to find out the equilibrium constant for the reaction

\[ H_2 + I_2 \rightleftharpoons 2HI \]

but while the book you use has the reaction, it is written as

\[ \frac{1}{2} H_2 + \frac{1}{2} I_2 \rightleftharpoons HI. \]

The equilibrium constant for the reaction as it is first written is

\[ K_1 = \frac{a_{HI}^2}{a_{H_2} a_{I_2}} , \]

while for the second case we have

\[ K_2 = \frac{a_{HI}}{a_{H_2} a_{I_2}^2} \].
We see that for this case, where our first reaction is just two times our second reaction, that the first equilibrium constant is the square of the second, i.e., $K_1 = K_2^2$. In general, if we can write one reaction as

$$\text{reaction 1} = aA + bB \rightarrow cC + dD$$

with equilibrium constant equal to $K_1$, and we can write the second reaction as a multiple of the first, i.e.,

$$\text{reaction 2} = n (aA + bB \rightarrow cC + dD)$$

then $K_2 = K_1^n$.

Another common situation is that we want the equilibrium constant of a given reaction, i.e.,

$$2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2,$$

but the equilibrium constant tabulated is for the opposite reaction. The rule for this is easy to see. **What is the equilibrium constant expression for the reaction as written? What is the equilibrium constant expression for the reverse reaction,**

$$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}?$$

Our general rule is that the rate constants of forward and reverse reactions are related by $K_r = 1/K_f$.

Now we have a number of rules for determining equilibrium constants. How do we use them? **First, the equilibrium constant can tell us qualitatively whether products or reactants are favored in a reaction.** This is clearest for the simple reaction $A \rightleftharpoons B$. The
equilibrium constant expression for this reaction is $K_c = \frac{[B]}{[A]}$. Suppose that the products are favored. This means that $[B]$ is larger than the $[A]$, and $K_c$ will be greater than 1. If reactants are favored, then $[A]$ is greater than $[B]$ and $K_c$ will be less than 1. Finally if the products and reactants are exactly balanced, then $K_c = 1$. Although the exact relations are more complicated for most other reactions the general conclusions are still valid. If $K > 1$ then products are favored at equilibrium. If $K < 1$ then reactants are favored at equilibrium. Finally if $K \approx 1$, then neither products nor reactants are particularly favored at equilibrium.

Another use of the equilibrium constant is that by comparing it with a new quantity called the reaction quotient, we can determine whether a reaction has reached its equilibrium composition or not. Furthermore, we can use this comparison to determine whether the mixture will react to produce more products or more reactants as it moves toward equilibrium.

The reaction quotient is a ratio with a definition very similar to the equilibrium constant expression. In terms of activities, the reaction quotient $Q_a$ for the reaction

$$aA + bB \rightleftharpoons cC + dD$$

is given by the equation

$$Q_a = \frac{a^c a^d}{a^a a^b}$$

Similarly, we can define reaction quotients in terms of concentration and partial pressure, with

$$Q_p = \frac{p^c p^d}{p^a p^b}$$
and

\[ Q_e = \frac{[C][D]^d}{[A][B]^f}. \]

Notice that the form of the reaction quotient is identical to that of the equilibrium constant expression. The only difference between \( Q \) and \( K \) is that when calculating \( K \), the only activities or pressures or concentrations that can go into our ratio are the values at equilibrium. Once again, because this is important, the only pressures that can go into \( K_p \) are equilibrium pressures. The only concentrations that can go into \( K_c \) are equilibrium concentrations. The only activities that can go into \( K_{\text{act}} \) are what kind of activities? In contrast, we can plug the activity of any mixture into a reaction quotient.

The reaction quotient can take on a wide variety of values. For example, for the reaction \( \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI(}\text{g}) \), if we have a reaction mixture with very little HI and large amounts of H2 and I2, the quotient will be very small. If there's lots of HI and little H2 and I2, the quotient will be very large. As the reaction proceeds and the pressures of our reactants and products change, the value of our reaction quotient changes.

Now we have two ratios, \( Q_{\text{act}} \), the reaction quotient, and \( K_{\text{act}} \), the equilibrium constant, which is the reaction quotient at equilibrium. By comparing them we can tell if our system is at equilibrium. For example if \( Q = K \), then our system is in equilibrium. If \( Q \) is not equal to \( K \) then the system is not in equilibrium. This should make sense, since from our definitions, we can see that \( K \) is just the equilibrium value of the reaction quotient. We can also use the ratio of \( Q/K \) to determine whether the reaction mixture will proceed toward products or reactants. The
rule here is that if \( Q/K > 1 \), then we have more products than we should have at equilibrium, and the reaction mixture will produce more reactants. If \( Q/K < 1 \), then we have more reactants than we should have at equilibrium, and the reaction mixture will produce more products as it moves toward equilibrium.

One feature of this ratio is that since \( Q \) and \( K \) have the same form, any units they have will cancel out. For example, for the reaction \( C_2H_4 \rightleftharpoons C_2H_2 + H_2 \), \( Q_p = \frac{p_{C_2H_2}p_{H_2}}{p_{C_2H_4}} \), which will have units of \( \text{atm}^2/\text{atm} = \text{atm} \), and \( K(p) = \frac{(P_{C_2H_2}P_{H_2})_{eq}}{P_{C_2H_4}} \), and will also have units of \( \text{atm} \). Thus the ratio \( Q_p/K_p \) will be dimensionless, since the units cancel out. Since the units cancel out we can use the ratio \( Q_{act}/K_{act} \), or \( Q_p/K_p \) or \( Q_c/K_c \) to determine which way a reaction will go. We just choose whichever is easiest for a given situation.

**Example 1: Calculating Equilibrium Constants**

When a sample of \( \text{PCl}_5 \), initially with a pressure of 1.0 atm, is heated to 189°C, some of the \( \text{PCl}_5 \) decomposes according to the reaction

\[
\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)
\]

The equilibrium partial pressure of \( \text{Cl}_2 \) is 0.244 atm. What is \( K_{act} \)?

\[
K = \frac{a_{\text{Cl}_2}a_{\text{PCl}_3}}{a_{\text{PCl}_5}} = \frac{(P_{\text{Cl}_2} / 1\text{atm})(P_{\text{PCl}_3} / 1\text{atm})}{(P_{\text{PCl}_5} / 1\text{atm})}
\]

We need to find \( P_{\text{Cl}_2}, P_{\text{PCl}_3}, \) and \( P_{\text{PCl}_5} \). We use a pressure table to find the pressures.
Plugging the equilibrium pressures into our equilibrium expression yields

\[ K = \frac{(0.244)(0.244)}{0.756} = 0.787 \]

**Example 2: Calculating the Equilibrium Composition from K.**

For the reaction

\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}, \]

\( K_p = 2.7 \times 10^{-8} \) at 750°C. What is the equilibrium pressure of NO if the initial pressure of \( \text{N}_2 \) is 22.5 atm and the initial pressure of \( \text{O}_2 \) is 7.50 atm?

\[ K_p = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = 2.7 \times 10^{-8} \]

Once again we set up a pressure table.

<table>
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<tr>
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<th>Initial Pressure (atm)</th>
<th>Change (atm)</th>
<th>Final Pressure (atm)</th>
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<td>-x/2</td>
<td>22.5 - x/2</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>7.5</td>
<td>-x/2</td>
<td>7.5 - x/2</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Substituting into our equation for \( K_p \) gives
\[ K_p = \frac{x^2}{(22.5 - \frac{x}{2})(7.50 - \frac{x}{2})} = 2.7 \times 10^{-8} \]

If we multiply out all terms and collect them, this becomes

\[ x^2 + 4.05 \times 10^{-7} - 4.55 \times 10^{-6} = 0 \]

Using the quadratic formula to solve for \( x \) yields

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.05 \times 10^{-7} \pm \sqrt{(4.05 \times 10^{-7})^2 - 4(-4.5 \times 10^{-6})}}{2} \]

\[ = 2.13 \times 10^{-3} \text{ or } -2.13 \times 10^{-3} \text{ atm} \]

Since choosing the negative value for \( x \) would yield a negative final pressure for NO, our solution is \( x = 2.13 \times 10^{-3} \) atm, and our equilibrium pressures are 22.5 atm for \( \text{N}_2 \), 7.50 atm for \( \text{O}_2 \), and 2.13 \times 10^{-3} \text{ atm} \) for NO.

Since the pressures of our starting materials were essentially unchanged by the reaction, we could have used a short cut in solving this problem. We will be able to use this short cut, or approximation, whenever \( K \) is small. Let's set up our table again.

<table>
<thead>
<tr>
<th></th>
<th>Initial Pressure (atm)</th>
<th>Change (atm)</th>
<th>Final Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>22.5</td>
<td>-x/2</td>
<td>22.5 - x/2 = 22.5</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>7.50</td>
<td>-x/2</td>
<td>7.50 - x/2 = 7.50</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
This time we make that approximation that since $K$ is small, that $x/2$ will be insignificantly small compared to 22.5 atm or 7.50 atm. Thus the final pressures for N\textsubscript{2} and O\textsubscript{2} which we put into our equilibrium expression will be 22.5 and 7.50 atm respectively.

\[ K = \frac{P_{N_2}^2}{P_{N_2}P_{O_2}} = 2.7 \times 10^{-8} \]

\[ 2.7 \times 10^{-8} = \frac{x^2}{(22.5)(7.5)} \]

\[ x = 2.13 \times 10^{-3} \text{.} \]

Notice that for this set of conditions, $x$ is the same as when we solve the equation exactly.

Whenever we use this approximation we have to check to see whether it is reasonable. We will say that our assumption is valid if the initial pressure or concentration is changed by less than 5\%. Let’s check our approximation.

\[ P_{N_2} = 22.5 \text{atm} - \frac{2.13 \times 10^{-3} \text{atm}}{2} = 22.5 \text{atm} \]

\[ P_{O_2} = 7.5 \text{atm} - \frac{2.13 \times 10^{-3} \text{atm}}{2} = 7.5 \text{atm} \]

Since the initial pressures are unchanged, our assumption is valid.

**Example 3. Using Q and K to Determine Whether a System is in Equilibrium**

For the reaction

\[ \text{CO (g) + 2H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH (g)}, \]

$K_p = 36$ atm\(^{-2}\) at 700 K. What net reaction, if any, will occur in a system containing 15 atm CO, 30 atm H\textsubscript{2}, and 50 atm CH\textsubscript{3}OH at 700 K?
A net reaction will occur only if the system is not at equilibrium, i.e., if $Q \neq K$. If $Q = K$, the system is in equilibrium. If $Q/K > 1$, then the reverse reaction will be spontaneous and the observed net reaction will be

$$\text{CH}_3\text{OH} (g) \rightarrow 2\text{H}_2(g) + \text{CO}(g)$$

If $Q/K < 1$, the forward reaction will be spontaneous, and the observed net reaction will be

$$\text{CO} (g) + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH} (g).$$

Let’s evaluate $Q_p$ and take its ratio with $K_p$

$$Q_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}}p_{\text{H}_2}} = \frac{50\text{atm}}{(15\text{atm})(30\text{atm})^2} = 3.70\times10^{-3}$$

$$Q / K = \frac{3.70\times10^{-3} \text{ atm}^{-2}}{36 \text{ atm}^{-2}} = 1.0\times10^{-4} < 1$$

Since $Q/K < 1$, the net reaction will be the forward reaction,

$$\text{CO(g) + 2H}_2(g) \rightarrow \text{CH}_3\text{OH}(g).$$

**Example 4: Calculating Equilibrium Constants**

Ethylene, $\text{C}_2\text{H}_4$, and water react under appropriate conditions to give ethanol. The reaction is

$$\text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(g).$$

The equilibrium mixture at a certain temperature had the following concentrations, $[\text{C}_2\text{H}_4] = 0.0148 \text{ M}$, $[\text{H}_2\text{O}] = 0.0336 \text{ M}$ and $[\text{C}_2\text{H}_5\text{OH}] = 0.180 \text{ M}$. What is $K_c$?

$$K_c = \frac{[\text{C}_2\text{H}_5\text{OH}]}{[\text{C}_2\text{H}_4][\text{H}_2\text{O}]} = \frac{0.180 \text{ M}}{(0.0148 \text{ M})(0.0336 \text{ M})} = 362 \text{ M}^{-1}$$

**Example 5: Calculating Equilibrium Compositions**
At 25°C, $K_c = 0.145$ for the following reaction in CCl₄:

$$2\text{BrCl} \rightleftharpoons \text{Br}_2 + \text{Cl}_2.$$  

A solution was prepared with the following initial concentrations: $[\text{BrCl}] = 0.0400$ M, $[\text{Br}_2] = 0.0300$ M, $[\text{Cl}_2] = 0.0200$ M. What will the equilibrium concentrations be?

$$K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]} = 0.145$$

Once again we set up an equilibrium table, this time using concentrations.

<table>
<thead>
<tr>
<th>Initial [ ] (M)</th>
<th>Change (M)</th>
<th>Equilibrium [ ] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrCl</td>
<td>0.04</td>
<td>-2x</td>
</tr>
<tr>
<td>Br₂</td>
<td>0.03</td>
<td>x</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.02</td>
<td>x</td>
</tr>
</tbody>
</table>

Plugging the equilibrium concentrations into our equilibrium constant expression gives us

$$K_c = 0.145 = \frac{(0.0200 + x)(0.0300 + x)}{(0.0400 - 2x)^2}$$

When we multiply out all terms this becomes

$$0.420 x^2 + 0.0732 x + 3.68 \times 10^{-4} = 0$$

Applying the quadratic formula gives

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0732 \pm \sqrt{0.0732^2 - (4)(0.420)(3.68 \times 10^{-4})}}{0.840}$$
x = -0.169, -0.00523

Only one of these values makes physical sense, since if x = -0.169 the final concentration of Br₂, which we said equaled 0.0300 + x would have to equal 0.0300 - 0.169 M = -0.139 M. Since we obviously can't have negative concentrations, -0.00523 is our correct value for x. This gives us final values of [BrCl] = 0.0400 - 2x = 0.0400 - (2)(-0.00523) = 0.0504 M, [Br₂] = 0.0300 + x = 0.0300 - 0.0053 = 0.0248 M, and [Cl₂] = 0.0200 - 0.00523 = 0.0148 M.

Example 6: Calculating Equilibrium Compositions From K

The reaction

\[ 2\text{HCl}(g) \rightleftharpoons \text{H}_2(g) + \text{Cl}_2(g) \]

has \( K_c = 3.2 \times 10^{-34} \) at 25°C. If a reaction vessel initially contains 0.0500 M of HCl and then reacts to reach equilibrium, what will be the equilibrium concentrations of HCl, H₂ and Cl₂?

\[
K_c = \frac{[H_2][Cl_2]}{[HCl]^2}
\]

Since K is small, we use our approximation for the concentration of HCl in this calculation.

<table>
<thead>
<tr>
<th>Initial [ ] M</th>
<th>Change</th>
<th>Final [ ] M</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.0500</td>
<td>-2x</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>x</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0</td>
<td>x</td>
</tr>
</tbody>
</table>

Substituting into the formula for \( K_c \) yields
and therefore $x = 4.0 \times 10^{-18}$ M. Whenever we use this approximation, as in this case where we assume that $.0500 - 2x = .0500$, we need to check at the end to make sure that it was a reasonable assumption. In this case $.0500 - (2)(4.0 \times 10^{-18}) = .0500$, since the number we subtract does not affect any of our significant figures. Therefore our equilibrium concentrations are $[\text{HCl}] = .0500$ M, and $[\text{H}_2] = [\text{Cl}_2] = 4.0 \times 10^{-18}$ M.

**Example 7: Using Q and K to Determine Whether a System is in Equilibrium**

At 460°C, the reaction

$$\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \text{SO}_3(g)$$

has $K_c = 85.0$. A reaction flask at 460°C contains gases at the following concentrations. $[\text{SO}_2] = .00200$ M, $[\text{NO}_2] = .00350$ M, $[\text{NO}] = .0250$ M and $[\text{SO}_3] = .0400$ M. What, if any, net reaction will occur?

As before, we need to calculate our reaction quotient and compare it to $K$. If $Q = K$, then our system is at equilibrium. If $Q/K > 1$ then the reaction will proceed toward reactants, while if $Q/K < 1$, then the reaction will proceed toward products. For this reaction,

$$Q_c = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(.0400)(.0250)}{(.00200)(.00350)} = 114$$

Since $Q_c/K_c = 1.34$, the reaction will go toward reactants, and the observed net reaction will be

$$\text{SO}_3(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{SO}_2(g).$$

**Example 8: Manipulation of Equilibrium Constants.**

a) For the reaction
\[ \frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}), \]

\[ K_p = 7.75 \times 10^2 \text{ at } 25^\circ \text{C}. \] What is \( K_p \) for the reaction

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})? \]

Since reaction 2 is 2 x reaction 1, \( K_2 = K_1^2 \), and \( K_2 = (7.75 \times 10^2)^2 = 6.0 \times 10^5 \).

b) The equilibrium constant, \( K_p \), for the reaction

\[ \text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \]

is 11.5 atm at 300\(^\circ\)C. What is the equilibrium constant for the reverse reaction

\[ \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})? \]

Since the second reaction is the reverse of the first, the equilibrium constant for the second is the inverse of the first, \( K_2 = K_1^{-1} = 1/11.5 \text{ atm} = .0870 \text{ atm}^{-1} \).

c) Carbonic acid has two acidic protons, which are released in the following two reactions:

\[ \text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \quad K_1 = 4.2 \times 10^{-7} \]

\[ \text{HCO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \quad K_2 = 4.8 \times 10^{-11} \]

What is the equilibrium constant for the reaction

\[ \text{H}_2\text{CO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + 2\text{H}_3\text{O}^+(\text{aq})? \]

The reaction in question can be written as the sum of the two reactions for which we know the equilibrium constants, i.e., reaction 3 = reaction 1 + reaction 2. Therefore, the equilibrium constant \( K_3 = K_1 \times K_2 = (4.2 \times 10^{-7})(4.8 \times 10^{-11}) = 2.02 \times 10^{-17} \).

It is useful to ask what the effect of changing temperature, and other parameters of our system, such as pressure, volume, and amounts of reactants and products, will be on the equilibrium constant. In order to predict these things quantitatively, we need to know more about
thermodynamics, and we will indeed address these questions when we return to thermodynamics in Chapter 19. However, we already have a tool that will allow us to figure out what the qualitative effect of changing these parameters will be. This tool is **LeChatelier's principle**, which we introduced when we were discussing solubilities at the beginning of the semester.

Once again, **LeChatelier's principle says that if a system is in equilibrium, and if we do something to disturb that equilibrium, the system will react in a way that reduces the disturbance.** In order to determine the effect of a change on the equilibrium, we just have to decide what the disturbance is, and how the system has to react to reduce the disturbance.

Let's start with the **effect of increasing the pressure**. Consider the reaction

\[
\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2.
\]

After the reaction reaches equilibrium, we increase the pressure of our \( \text{C}_2\text{H}_4 \). LeChatelier's principle says that if we disturb a system in equilibrium, the system will react to reduce the disturbance. **In this case what is the disturbance? What do we have to do to reduce the disturbance?** So increasing the pressure of a reactant pushes the reaction toward products.

**What if we had increased the pressure of the acetylene? What is the disturbance now? What do we have to do to reduce the disturbance?** So increasing the pressure of a product pushes the reaction toward reactants. Suppose instead we reduced the pressure of the \( \text{C}_2\text{H}_2 \). This is the same as saying that we are removing some of our product. **What would happen to the reaction then?** Here is a practical consequence of LeChatelier's principle. If we can design a synthesis so that we are either continually adding one of the reactants, or
removing one of the products, we can keep the reaction going until one of the reactants is completely consumed, i.e., we can make a reaction go to completion.

We will see an identical effect for solution phase reactions. If we increase the concentration of reactants, it pushes the equilibrium toward products. If we increase the concentration of products, it pushes the equilibrium toward reactants.

What happens if we decrease the volume? Suppose we have a gas phase reaction like \( \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2 \). We decrease the volume. All of our pressures increase, because of the ideal gas law. What is our disturbance? LeChatelier's principle says the system must respond to reduce the disturbance. Therefore, the reaction will go in the direction that reduces the total pressure. If we go from reactants to products we create two product molecules for every reactant we consume. What will this do to the pressure? If we go from products to reactants, we produce one molecule for every two we consume. What does this do to the pressure? So for this example, decreasing the volume favors the side of the reaction with the least molecules. We will find this in general - decreasing the volume favors the side of the reaction that has the fewest molecules. For the reaction \( 3\text{H}_2 + \text{N}_2 \rightleftharpoons 2 \text{NH}_3 \) what will happen if we decrease the volume? Which side has the most molecules? In this case since the product side has the fewest molecules, the product will be favored if the volume is decreased. What about \( \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \)? Since neither side has more molecules, the equilibrium will stay the same when the volume is decreased.

Finally, what is the effect of changing the temperature on equilibrium? Let’s consider the case of an exothermic reaction,
\[ 3H_2 + N_2 \rightleftharpoons 2 \text{NH}_3 \quad \Delta H^\circ = -46.19 \text{ kJ/mol}. \]

What happens to the reaction when we raise the temperature? In answering this question, it helps to include the heat as a reactant or product. **Is the heat a reactant or product for this reaction?** So we can write the reaction as

\[ 3H_2 + N_2 \rightleftharpoons 2 \text{NH}_3 + 46.19 \text{ kJ}. \]

**If we raise the temperature what is the disturbance? Which way does the reaction have to go to reduce the disturbance?** So in short, **if we have an exothermic reaction**, increasing the temperature moves the equilibrium toward reactants, while lowering the temperature moves the equilibrium toward products. In contrast, **if we have an endothermic reaction**, increasing the temperature moves the equilibrium toward products, while lowering the temperature moves the equilibrium toward reactants.

Now I want to point out an important distinction. Changing the pressure, volume, temperature, and amounts of reagents will all change the equilibrium composition. However, the only one of these that affects the equilibrium constant is changing the temperature. To repeat, changing the temperature changes both the equilibrium constant and the equilibrium composition, while changing initial composition, pressure or volume changes only the equilibrium composition.

Our final topic is the effect of catalysts on equilibria. The answer, in short, is there is none. **Catalysts will affect the rate at which a system will approach equilibrium, but will not affect the equilibrium constant itself.**