Lecture 25

I've said a couple of times in the past two lectures that **the rate constant k for a reaction depends on the temperature**. In fact, experiments over the years have shown that **the rate of the vast majority of chemical reactions will increase as the temperature increases**.

To understand why the rate depends on temperature we have to turn to a subject called **transition state theory**. According to transition state theory, **the rate of any elementary reaction depends on the frequency with which the reacting molecules collide, and the efficiency of the collisions, i.e. the fraction of the collisions that actually lead to a reaction**.

Let's consider these one at a time. Collisions that lead to reaction are more likely when a smaller number of molecules are involved in the reaction. This should make sense. Suppose I have a reaction involving two molecules. So I'm a molecule, and I'm waiting around for someone to react with me. Finally someone comes around and I react. O.K., fine. But suppose now I have to wait for two people to come around before I can react. It's got to take longer doesn't it? Thus the smaller the number of molecules which have to collide in order for a reaction to occur, the faster the reaction will be.

For a given number of molecules that have to collide, the reaction goes faster when the concentration is higher. Again, I’m waiting for someone to react with me. I’m more likely to collide with someone in the middle of New York City than I am in the middle of the Mojave Desert. Thus our rate should depend on the concentration of each of the species that collide in the reaction.

However, **for a given reaction, the frequency of these collisions also depends on the temperature**. This is because the average velocity of a molecule depends on the temperature, with the average velocity given by the equation

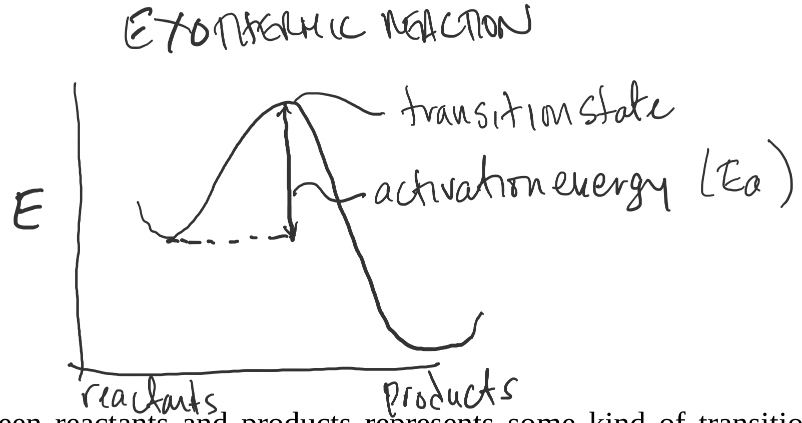
$$\langle v \rangle = \sqrt{\frac{3RT}{M}},$$

where the bracketed v stands for average velocity in meters second, R is the gas constant, 8.314 J K^{-1} mol^{-1}, T is the temperature in K, and M is the molar mass in kg/mol. The higher the temperature, the faster the molecule is moving. If the molecules are moving faster, the collisions have to be more frequent. So one effect of raising the temperature is to increase the number of collisions between molecules.

Now we need to talk about **the factors that make a collision effective or ineffective**. The most important of these are energy effects. Suppose that we have an endothermic reaction. IS THE ENERGY OF THE PRODUCTS HIGHER OR LOWER THAN THE REACTANTS? Let's make a graph that has reactants at one end and products at the other, and has energy on the y-axis. We can see from this that it takes energy to go from reactants to products. WHAT HAPPENS TO THE AVERAGE ENERGY OF A MOLECULE AS THE TEMPERATURE INCREASES? WHAT SHOULD HAPPEN TO THE RATE OF THIS REACTION AS THE TEMPERATURE INCREASES?

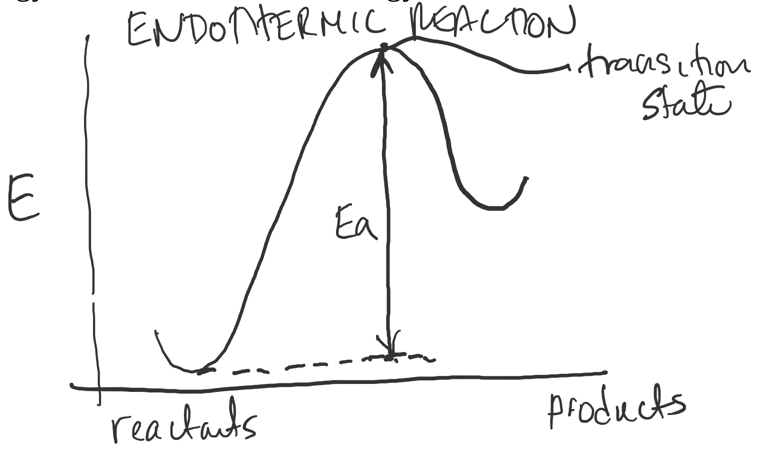
Now let's consider an exothermic reaction. WHICH HAS HIGHER ENERGY, THE REACTANTS OR THE PRODUCTS? Let's make the same kind of graph, with reactants at one end of the x axis, products at the other end and energy on the y axis. ACCORDING TO THIS GRAPH, SHOULD EXOTHERMIC REACTIONS DEPEND ON TEMPERATURE? However, experiments show that almost all exothermic reactions have rates which increase with increasing temperature.

The reason that the rate increases with increasing temperature for the endothermic case is because **there is a barrier the molecules have to climb over in order for the reaction to occur**. The fact that exothermic reactions have rates which increase with temperature suggests that **even for exothermic reactions there is some energetic barrier that occurs between reactants and products.** This would make the reaction energy diagram look like this:



The highest energy between reactants and products represents some kind of transition between reactants and products. We could say, for example, that before we reach this high energy our molecules are still reactants, and that after we have passed it they are products. We call this transition region **the transition state of the reaction**. We call the energy barrier the **activation energy**. It is precisely the difference in energy between the reactant and the transition state.

If we were to look at the reverse of our reaction here we just have to reverse the curve. What kind of reaction is this, exothermic or endothermic? Notice that **the endothermic reaction also has an additional barrier between reactants and products**. Again, the activation energy is the difference in energy between the reactant and the transition state.



Again this tells us where the dependence of rate on temperature comes from. As temperature increases, the average energy of molecules increases, and more and more molecules have the energy necessary to climb over the activation barrier.

Why do reactions have these additional barriers to reaction? To see this lets consider the progress of an exothermic reaction, $F + CH_3I \rightarrow CH_3 + IF$. When the reaction starts we have a radical, F and a stable molecule CH_3I. As the fluorine atom approaches the iodine atom, two things happen. First, the C - I bond begins to break and second, the FI bond begins to form. What is happening is that essentially the F is tugging on the I and pulling it away from the CH_3. Since the bond is stable, it takes energy to begin to break it. As the reaction proceeds, the F continues to pull the I from the CH_3 until the C-I bond is half broken and the IF bond is half formed. At this point, the energy of the complex is pretty high, since we have these two half bonds which are pretty unstable. As the reaction proceeds from here, the IF bond gets stabler and stabler, and the energy goes to its final value. So you see, the activation energy comes from energy requiring processes like bond breaking that have to occur in order to get a reaction to work.

Therefore, rates increase with temperature for two reasons, because the collision rate increases with temperature, and because more molecules can cross the activation barrier as the temperature increases.

The temperature dependence of almost all reactions can be described well by a single equation, the **Arrhenius equation**. It is

$$k = Ae^{-\frac{E_a}{RT}},$$

where E_a is the activation energy in J/mol, R is the gas constant, 8.314 J mol^{-1} K^{-1}, and T is the temperature in Kelvin. This equation tells us that as T increases the rate increases, while if the activation energy increases the rate decreases.

The factor A is called the **preexponential factor**. It is a fairly complicated factor that includes the collision frequency and a factor called the **steric** factor, which recognizes that some collisions will always be ineffective no matter what the energy is. For example, in the reaction $K + CH_3I \rightarrow KI + CH_3$, the K can hit the CH_3I from the CH_3 end or the I end. If it hits on the I end reaction can occur if the energy is right. If it hits on the CH_3 end, you can't form KI no matter how hard you try.

Let's **practice using the Arrhenius equation** to determine the effect of changing temperatures on rate constants. The conversion of cyclopropane to propene, $(CH_2)_3 \rightarrow CH_3CH{=}CH_2$, has an activation energy of 272 kJ/mol and a preexponential factor of 1.5 x 10^{15} s^{-1}. What is the rate constant at 25°C? To answer this, we use the Arrhenius equation, and plug in our values for A, E_a and T. The only thing we need to watch out for is units. Our activation energy and gas constant must have the same energy units, either kJ or J, and our temperatures must be in K. Therefore our rate constant k is given by

$$k = Ae^{-\frac{E_a}{RT}} = 1.5x10^{15}s^{-1}e^{-\frac{272{,}000\,J/mol}{(8.314\,J/molK)(298K)}} = 3.14x10^{-32}s^{-1}$$

How do we find E_a from experiments? Let's go back to the Arrhenius equation,

$$k = Ae^{-\frac{E_a}{RT}}$$

If we take the log of both sides we get

$$\ln \mathrm{k} = \ln \mathrm{A} - \frac{E_a}{R} * \frac{1}{T} \ .$$

This has the same form as a straight line, where y = ln k, the intercept = ln A and the slope = $-E_a/R$. So one way to determine the activation energy is to measure rate constants at several different temperatures, and plot ln k vs 1/T. The slope of the plot will be $-E_a/R$. We can also figure out E_a using only two points, although this approach is less accurate. Suppose that we measure the rate constant at one temperature, T_1. We can write $\ln k_1 = \ln A - \frac{E_a}{R} * \frac{1}{T_1}$ At a second temperature, which we call T_2, we measure a new rate constant and the Arrhenius equation gives us $\ln k_2 = \ln A - \frac{E_a}{R} * \frac{1}{T_2}$ If we take the difference between these equations we get $\ln \frac{k_2}{k_1} = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. We can also use this to calculate the rate constant at one temperature if we have measured it at another temperature and know the E_a.

Examples. For $2N_2O_5 \rightarrow 2N_2O_4 + O_2(g)$, k = 7.87×10^{-7} s^{-1} at 0°C and 4.98×10^{-4} s^{-1} at 45°C. What is E_a? [104 kJ/mol]

For 2 NOCl(g) → 2 NO(g) + $Cl_2(g)$, E_a = 100 kJ/mol and k = 6.0×10^{-4} M^{-1} s^{-1} at 500K. What is k at 1000K? [2.7×10^{-1}]

$2N_2O \rightarrow 2\ N_2 + O_2$ has k = .86 $M^{-1}s^{-1}$ at 1030K and 3.69 M^{-1} s^{-1} at 1085 K. What is E_a? [272 kJ/mol]

By now we've discussed most of the factors which affect the rate of a chemical reaction. At this point I'd like to turn to the topic of **reaction mechanisms**. A reaction mechanism is a sequence of **elementary reactions** that occurs during the conversion of reactants to products. Most reactions don't occur in a single step as written, but involve a sequence of steps. For example, consider the reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$. Suppose that the reaction occurs in one step as written. In order for the reaction to occur all four of the reactant molecules must simultaneously collide. If we think about it, we'll realize that at any given concentration, it is more likely to have two molecules collide than three, and more likely for three to collide than four. In fact, the fewer molecules we have involved in the collision, the more likely the collision is.

Reactions in which four molecules simultaneously collide are extremely rare. Yet the reaction we've written actually occurs, and occurs pretty quickly. How can this be? The answer is that **if the reaction we write down involves four or more reactant molecules, it almost certainly occurs as a sequence of reactions that involve collisions of two or three molecules or even reactions of a single molecule.**

Such a sequence of simpler reactions is called a **mechanism**. The one, two and three reactant reactions that make up the mechanism are called **elementary reactions**. We define an elementary reaction as any reaction that occurs in a single step as written, rather than being composed of a sequence of simpler reactions. We call the number of reactant molecules in an elementary reaction the **molecularity** of the reaction. If an elementary reaction involves only one reactant molecule it has a molecularity of one and is called a **unimolecular reaction**. If it involves two reactant molecules it has a molecularity of two and is called a **bimolecular reaction**. If it involves three reactant molecules it has a molecularity of three and is called a **trimolecular reaction**. A reaction that is made up of a sequence of elementary reactions is called a **complex or composite reaction**.

One difference between elementary and composite reactions is that **we can write down the rate law of an *elementary* reaction just by looking at the chemical equation**. Suppose we have the elementary reaction $NOCl + Cl \rightarrow NO + Cl_2$. This is a bimolecular reaction, and its rate law is given by rate = k[NOCl][Cl]. Notice that **for an elementary reaction, the partial orders are equal to the stoichiometric coefficients**. Let's look at a couple more examples. The reaction $2\ NO_2 \rightarrow NO_3 + NO$ is also an elementary reaction. Since two molecules collide in the reaction, its molecularity is two and it's a bimolecular reaction. Its rate law is rate = $k[NO_2]^2$. Notice again that the exponent in the rate law is the same as the stoichiometric coefficient in the balanced reaction. This is an immediate observable difference between elementary and complex reactions. Let's do an example together. Consider the elementary reaction $O_3 \rightarrow O_2 + O$. WHAT IS THE MOLECULARITY OF THE REACTION? WHAT IS THE RATE LAW FOR THIS REACTION?

We can obtain information about whether a given reaction is elementary or complex by comparing its rate law with the rate law we would expect if it were elementary. Consider the reaction

$$2NO_2\ (g) + F_2(g) \rightarrow 2\ NO_2F\ (g).$$

WHAT WOULD ITS RATE LAW BE IF IT WERE AN ELEMENTARY REACTION? We do an experiment to determine the rate law and find out that it is actually rate = $k[NO_2][F_2]$. WHAT DO WE CONCLUDE? Now I have to warn you that even though we can decide conclusively that a reaction is not elementary, it is substantially more difficult to prove that a reaction *is* elementary.

Once we decide that a reaction is complex, the next goal is to determine what the steps in the mechanism are. This can be very difficult. A classic example is the decomposition of N_2O_5 by heat. When heated, N_2O_5 decomposes according to the reaction

$$2N_2O_5 \rightarrow N_2O_4 + O_2.$$

This is a first order reaction, with rate law rate = k $[N_2O_5]$. IS THIS AN ELEMENTARY REACTION? I won't show you how the mechanism was determined, because that could be the subject of a lecture in itself. The mechanism consists of six elementary reactions and is

$$N_2O_5 \rightleftharpoons NO_2 + NO_3$$

$$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$$

$$NO + N_2O_5 \rightarrow 3NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4.$$

I said that there were six elementary reactions yet I've written only four equations. WHERE ARE THE SIX REACTIONS? Notice that each of the six elementary reactions involves the collision of only one or two molecules.

How does a complex reaction like this lead to such a simple rate law? The answer is that **in many cases the overall rate of a composite reaction is equal to the rate of the slowest step**. For this reason, the slowest step in a composite reaction is called the **rate determining step**. A good analogy would be if you were driving down a four lane highway in heavy traffic, and suddenly three lanes were closed for construction. All of a sudden there's this huge traffic jam because even though you can get to the single lane quickly, and you can get away quickly, you still have to wait in line to get through. It turns out that in this reaction the rate determining step is the very first reaction, $N_2O_5 \rightarrow NO_2 + NO_3$. WHAT IS THE RATE LAW FOR THIS ELEMENTARY REACTION? So you see, the rate law for the rate determining step matches the rate law for the overall reaction.

Figuring out the mechanism of a reaction is very hard work, and sometimes requires the development of new experimental technology. It took from 1921 to 1950, 29 years, to figure out the mechanism for this reaction.

Most mechanisms start with one set of reactants which leads directly to one set of products, i.e., in our N_2O_5 decomposition,

$$N_2O_5 \rightleftharpoons NO_2 + NO_3$$

$$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$$

$$NO + N_2O_5 \rightarrow 3NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4.$$

Each time you want to start the reaction you need to break up another N_2O_5. However, there is a special class of complex reactions called **chain reactions**. Their characteristic is that they contain steps in their mechanism that are self-perpetuating, so that one initial step can yield many molecules of products. Chain reactions are important commercially - most polymers are made through chain reactions; nuclear fission reactors work through nuclear chain reactions, and most explosive materials have chain reactions as their explosive reactions.

Example: $CH_3CHO \rightarrow CH_4 + CO$

Mechanism: $CH_3CHO \rightarrow CH_3 + CHO$

$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$

$CH_3CO \rightarrow CH_3 + CO$

$2\ CH_3 \rightarrow C_2H_6$

Note that the two intermediate steps are self-perpetuating. In other words, the products of the second step include CH_3CO, a crucial reactant for the third step, while the products of the third step include CH_3, a crucial reactant for the second step. These steps are called **chain propagating steps.** The first step is called the initiation step. The final step is called the termination step, because it removes chain molecules without producing any. The number of times the propagating step repeats is called the chain **length**. It is not unheard of to have chain lengths which are greater than 100. This means that each acetaldehyde which breaks up yields 100 molecules of each product.

I'd like to briefly mention one final topic of chemical kinetics, catalysis. A **catalyst** is substance which is neither produced nor consumed in a reaction and which increases the rate of reaction. Let's figure out how catalysis works. WHAT ARE THE FACTORS THAT AFFECT RATE OF REACTION? [collision rate, temperature, activation energy] LET'S ELIMINATE THESE ONE BY ONE. **Catalysts must affect activation energy**. They do this by providing an alternate mechanism in which activation energies are lower.[Illustrate]

There are two main types of catalysts - **homogeneous and heterogeneous**. A catalyst is homogeneous if it is in the same type of state as the reactants and products. I.e., if a reaction occurs in aqueous solution, then a homogeneous catalyst will be aqueous as well. As an example, for the decomposition of ozone, $O_3(g) + O \rightarrow 2O_2(g)$, an effective catalyst is gas phase Cl atoms. Since the catalyst is gas phase and the reactants are gas phase as well, the catalysis is homogeneous. Note that the mechanism is different than the direct mechanism. Instead of the direct attack of the oxygen atom on the ozone that we see in the absence of the catalyst, the following two reactions occur,

$$Cl + O_3 \rightarrow ClO + O_2$$

$$\underline{ClO + O \rightarrow Cl + O_2}$$

The net reaction is the sum of the two reactions, and is the same as our original reaction, but differs in that each step has a lower activation energy than the uncatalyzed reaction. Since the overall activation energy is lower the reaction will be faster in the presence of the catalyst. H^+, and OH^- are common homogeneous catalysts in organic chemistry.

Heterogeneous catalysis involves two different phases of matter. I.e., a solution may be flowed over a metal surface, or a metal powder may be stirred into a liquid reaction mixture. The study of the mechanisms of heterogeneous catalysis and the search for new catalysts is an intense area of research.

Enzymes are proteins that act as biological catalysts. They have the special property that each usually catalyzes only one reaction, i.e. the selectivity is high, and is unusually efficient. Intensive research is currently going on to understand how enzymes work, and therefore to gain the ability to make artificial enzymes.

Lecture 26

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.

Equilibrium is the name for the situation in which there are no observable changes in a system. There are two types of equilibria, static and dynamic equilibria. An example of a static equilibrium is a table sitting on the floor. There is no motion because the forces acting on the table are in balance. The fact that there is no motion tells us that the table and floor are in equilibrium and that the equilibrium is static. The other type of equilibrium is called a dynamic equilibrium. **In dynamic equilibrium there is no *net* change because two opposing processes are occurring at equal rates.** As a simple example, the undergraduate population at the University of Richmond is constant. However, it is not constant because the same students stay here forever, but because the opposing processes of graduation and matriculation occur at the same rate, i.e., the same number of students enter each year as graduate.

The reason that we are interested in this concept is that all **chemical reactions can come to equilibrium**. These **chemical 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 $H_2(g)$ and $I_2(g)$ are combined they form HI according to the reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g).$$

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

$$2HI(g) \rightarrow H_2(g) + I_2(g),$$

also occurs. The two reactions don't always occur at the same rate, but if we wait long enough they will. When they occur at the same rate 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 t**he 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 H_2 and one mole of I_2, when equilibrium is reached at 425°C, we will have 0.212 moles of H_2, 0.212 moles of I_2, 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 H_2, 0.212 moles of I_2, 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 ^{131}I. Since the reaction mixture has the equilibrium composition, there will be no overall change in the amounts of HI, H_2 and I_2. However, the ^{127}I in the I_2 is gradually replaced by a mixture of ^{127}I and ^{131}I, 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. Calculating such a composition in chemical reactions in which we generally have the concentrations of several species to keep track of would be difficult without the use of such constants. Furthermore, because the equilibrium is a complex balance between the concentrations of these species, there are 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. We can define equilibrium constants for any phase, gas, liquid or solid. We'll begin by defining the equilibrium constant expression for gases, but before we do we need to define some terms, and introduce a new law of chemistry.

The state of a pure gas can be defined by determining the value of four variables. These variables are the mole number, n; the temperature T; the volume, V; and the pressure, p. Mole number and volume are things that we've already covered in the earlier part of this class. The temperature, T, is a measure of the thermal energy of a system, i.e. the energy contained in the random motion of the atoms and molecules making up the system. It is expressed in units of either degrees celsius, °C, or Kelvin, K. The two are related by

$$K = {}^{\circ}C + 273.15$$

When we do calculations involving temperature (T) in equilibrium calculations or in thermodynamics (which we will continue soon!), we always have to express our temperatures in K. However, if a calculation requires the temperature change ($\Delta T \equiv T_f - T_i$), then we can use either K or °C.

Pressure is defined as force divided by area. There are several units commonly used to describe pressure. The oldest is the atmosphere, which is approximately the pressure exerted upon an object by the earth's atmosphere at room temperature, and which has the abbreviation atm. Another old unit is the Torr, which has the abbreviation torr, and is equal to the pressure exerted by a 1 mm column of mercury at a temperature of 298.15K. An atmosphere is exactly 760 torr. Neither atmosphere nor torr is an SI unit for pressure. The SI unit for pressure is the Pascal, abbreviated Pa. It is 1 N/m^2, and is a tiny unit of pressure. One atmosphere is actually 101,325 Pa. Because it is convenient to have an SI unit similar in value to the atmosphere, the Bar has been defined as 1 Bar = 10^5 Pa. Therefore 1 Atm = 1.01325 Bar.

It turns out that these four variables, p, V, n, and T, are not independent, but are related. The simplest of the equations that relates them is called the ideal gas law, and is

$$pV = nRT.$$

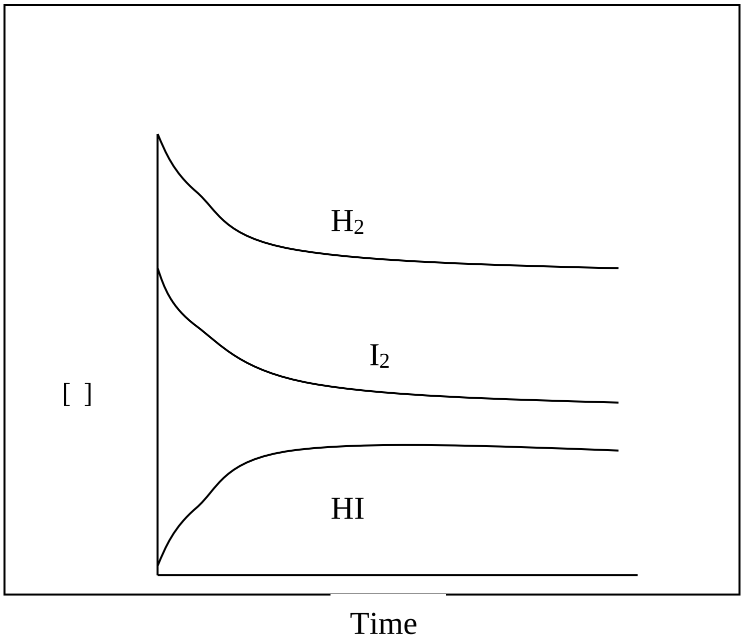
In this equation, R is a constant called the ideal gas constant. If p is expressed in atm, V in L, n in mol, and T in K, then R has the value $0.08206\frac{L\ atm}{mol\ K}$. If we use SI units instead, with V in m^3 and p in Pa, then it has the value 8.314 J mol^{-1} K^{-1}. (Note that $1Pa*1m^3 = 1\frac{kg\ m^2}{s^2} = 1J$) .

For a reaction of ideal gases, the equilibrium constant expression is a function of the equilibrium partial pressures of the products and reactants. The partial pressures are the pressures that each substance in a mixture of gases exerts. The partial pressure of substance A in a mixture will still be described by the ideal gas law: $p_A = \frac{n_A RT}{V}$, where n_A is the number of moles of A. The denominator of the quotient depends on the equilibrium partial pressures of the reactants, while the numerator of the quotient depends on the equilibrium partial pressures of the products. For a model reaction

$$\text{aA + bB} \rightleftharpoons \text{cC + dD},$$

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 then divide by the product of the partial pressures of the reactants raised to the power of their stoichiometric coefficients. For example, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_p = \frac{p_{HI}{}^2}{p_{H_2} p_{I_2}}$. Since the stoichiometric coefficient for the HI is 2, its partial pressure is squared. FOR THE REACTION P_4(G) + 6 H_2(G) $\rightleftharpoons$ 4 PH_3(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, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. As we said earlier, the equilibrium expression for this reaction is $K_p = \frac{p_{HI}{}^2}{p_{H_2} p_{I_2}}$, so we need to find the equilibrium partial pressures of the reactants and products. If we start with only H_2 and 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 H_2 and 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 $p_{H2} = 0.640$ atm, $p_{I2} = 0.571$ atm, and $P_{HI} = 0$. When the reaction reaches equilibrium, the pressures are $p_{H2} = 0.167$ atm, $p_{I2} = 0.0980$ atm and $p_{HI} = 0.946$ atm. Then $K_p = .946^2/(.167 * .0980) = 54.7$.



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. Furthermore, **at a given temperature, no matter what starting mixture we use, the equilibrium constant obtained once equilibrium is achieved will always be the same.** This means that if we know the composition of our starting mixture, the equilibrium constant allows us to figure out the new composition when our reaction reaches equilibrium.

To see this let's 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,

$p_0(H_2)$ (atm)	$p_0(I_2)$ (atm)	$p_0(HI)$ (atm)	$p(H_2)$,eq (atm)	$p(I_2)$,eq (atm)	p(HI),eq (atm)
0.64	0.571	0	0.167	0.098	0.946
0.6464	0.43	0	0.258	0.0423	0.776
0	0	0.259	0.027	0.0274	0.202
0	0	0.614	0.0655	0.0655	0.483

[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 is a problem with our equilibrium expression as we've written it. The 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**.

We solve this problem by redefining our equilibrium constant expression using a new quantity called the **activity, a.** The a**ctivity 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 ~ 1, ie, $X_{\text{solvent}} \sim 1$. The mole fraction is the ratio of the moles of a given substance in a mixture to the total number of moles in the mixture, i.e.,

$$X_A = \frac{n_A}{n_T},$$

where X_A is the mole fraction of substance A, n_A is the number of moles of substance A, and n_T is the total number of moles in the system. So for our current purposes, we're saying a solvent has an activity of one, when the solvent constitutes almost almost all the moles of the solution.

For example, let’s say we have 0.25 atm of CO_2. Its activity is 0.25 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 0.78M / 1M = 0.78. WHAT IF WE HAD 24 TORR OF AR? How would we find its activity? [24/760=.032]. Let’s say we have a 0.5 molar solution of NaF in water. WHAT IS THE ACTIVITY OF THE NAF? [a_{NaF} = 0.5M/1M = 0.5] WHAT IS THE ACTIVITY OF THE WATER IN THIS SOLUTION? [water is solvent so 1.] To see this remember X_{H2O} has to be ~1 for the activity to be one. n_{NaF} = .5. 1L H_2O has n_{H2O} ~ 55, so X_{H2O} = 55/55.5 ~ 1.

If we have a general reaction, aA + bB $\rightleftharpoons$ cC + dD, the equilibrium constant expression is given by $K_{act} = \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}$**,** 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

$$C_2H_4(g) \rightleftharpoons C_2H_2(g) + H_2(g)$$

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 atm. Therefore the equilibrium constant expression is $K_{act} = \frac{a_{C_2H_2} a_{H_2}}{a_{C_2H_4}} = \frac{0.3 * 0.8}{0.25} = 0.96$.

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,

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

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_{H2} = 6.15 atm, p_{N2} = 30.8 atm, and p_{NH3} = 0.505 atm. WHAT IS THE FORM OF K_P? CALCULATE K_P (3.56×10^{-5} ATM^{-2}) If we use concentrations instead the values are $[H_2]$ = 0.150M, $[N_2]$= 0.750M, $[NH_3] = 1.23 \times 10^{-2}$ M. WHAT IS THE FORM OF K_C? CALCULATE K_C (5.97×10^{-2} 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 [ ] by p/RT**. For example, for the reaction 2A(g) → 2B(g) + C(g), $K_c = \frac{[B]^2[C]}{[A]^2}$. If we substitute p/RT for each of our concentrations, we get $K_c = \dfrac{\left(\dfrac{p_B}{RT}\right)^2\left(\dfrac{p_C}{RT}\right)}{\left(\dfrac{p_A}{RT}\right)^2} = \dfrac{p_B^2 p_C}{p_A^2} * \dfrac{1}{RT} = \dfrac{K_p}{RT}$ 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 Kp and want to find Kc**? In this case the ideal gas law tells us that p = RT(n/V) = RT M. **For this case we would just replace the pressures with RT [], and proceed as before.**

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

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

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

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

The activities of the Ag^+ and Cl^- will just be $[Ag^+]$/1M, and $[Cl^-]$/1M. The AgCl, since it is a pure solid, has an activity of 1. Thus $K_{act} = \dfrac{[Ag^+]}{1M}\dfrac{[Cl^-]}{1M}$. 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., $K_c = [Ag^+][Cl^-]$. Let's look at another example. For the reaction

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq),$$

$[H_3O^+]$ = .1 M, $[Cl^-]$ = .1 M, and [HCl] = .0001 M. WHAT IS THE FORM OF K_{ACT}? WHAT IS THE ACTIVITY OF HCL, H_3O^+, CL^-, H_2O? 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.

Lecture 27

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, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the consecutive reactions. This fact will be important when we consider acidic equilibria. So for example, suppose we have two consecutive reactions,

$$H_3PO_4 + H_20 \rightleftharpoons H_2PO_4^- + H_30^+$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{-2} + H_30^+$$

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

$$H_3PO_4 + 2\ H_2O \rightleftharpoons HPO_4^{--} + 2H_3O^+.$$

The equilibrium constants for the first and second reactions are

$$K_1 = \frac{a_{H_3O^+}a_{H_2PO_4^-}}{a_{H_2O}a_{H_3PO_4}}$$

and

$$K_2 = \frac{a_{H_3O^+}a_{H_2PO_4^=}}{a_{H_2O}\ a_{H_2PO_4^-}}$$

The equilibrium constant for the overall reaction is

$$K = \frac{a_{H_3O^+}^2 a_{H_2PO_4^=}}{a_{H_2O}^2 a_{H_3PO_4}}$$

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 $K = K_1 * K_2$.**

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

$$1/2\ H_2 + 1/2\ I_2 \rightleftharpoons HI.$$

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

$$K_2 = \frac{a_{HI}}{a_{H_2}^{1/2} a_{I_2}^{1/2}}.$$

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.,

$$2HI \rightleftharpoons H_2 + I_2,$$

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,

$$H_2 + I_2 \rightleftharpoons 2HI?$$

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 ≈ 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

$$\text{aA} + \text{bB} \rightleftharpoons \text{cC} + \text{dD}$$

is given by the equation

$$Q_a = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

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

$$Q_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

and

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}.$$

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_{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 $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$, if we have a reaction mixture with very little HI and large amounts of H_2 and I_2, the quotient will be very small. If there's lots of HI and little H_2 and I_2, 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_{act}, the reaction quotient, and K_{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 atm^2/atm = atm, and $K_p = (\frac{p_{C_2H_2} p_{H_2}}{p_{C_2H_4}})_{eq}$, and will also have units of 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.

Let's practice by doing several of the types of equilibrium calculations we'll need to master.

Example 1: Calculating Equilibrium Constants

When a sample of PCl_5, initially with a pressure of 1.0 atm, is heated to 189°C, some of the PCl_5 decomposes according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The equilibrium partial pressure of Cl_2 is 0.244 atm. What is K_{act}?

$$K = \frac{a_{Cl_2} a_{PCl_3}}{a_{PCl_5}} = \frac{(P_{Cl_2} / 1atm)(P_{PCl_3} / 1atm)}{(P_{PCl_5} / 1atm)}$$

We need to find p_{Cl_2}, p_{PCl_3}, and p_{PCl_5}. We use a pressure table to find the pressures.

	Initial Pressure (atm)	Change (atm)	Final Pressure (atm)
Cl_2	0	+.244	.244
PCl_3	0	+.244	.244

PCl_5	1.00	-.244	.756

Plugging the equilibrium pressures into our equilibrium expression yields

$$K = \frac{(.244)(.244)}{.756} = .787$$

Example 2: Calculating the Equilibrium Composition from K.

For the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\ NO,$$

$K_p = 2.7 \times 10^{-8}$ at 750°C. What is the equilibrium pressure of NO if the initial pressure of N_2 is 22.5 atm and the initial pressure of O_2 is 7.50 atm?

$$K_p = \frac{P^2_{NO_2}}{P_{N_2} P_{O_2}} = 2.7x10^{-8}$$

Once again we set up a pressure table.

	Initial Pressure (atm)	Change (atm)	Final Pressure (atm)
N_2	22.5	-x/2	22.5 - x/2
O_2	7.5	-x/2	7.5 - x/2
NO	0	x	x

Substituting into our equation for K_p gives

$$K_p = \frac{x^2}{(22.5 - \frac{x}{2})(7.50 - \frac{x}{2})} = 2.7x10^{-8}$$

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

$$x^2 + 4.05 \text{ x } 10^{-7} - 4.55 \text{ x } 10^{-6} = 0$$

Using the quadratic formula to solve for x yields

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.05x10^{-7} \pm \sqrt{(4.05x10^{-7})^2 - 4(-4.5x10^{-6})}}{2}$$

$$= 2.13 \text{ x } 10^{-3} \text{ or } -2.13 \text{ x } 10^{-3} \text{ atm}$$

Since choosing the negative value for x would yield a negative final pressure for NO, our solution is x = $2.13 \text{ x } 10^{-3}$ atm, and our equilibrium pressures are 22.5 atm for N_2, 7.50 atm for O_2, and $2.13 \text{ x } 10^{-3}$ 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.

	Initial Pressure (atm)	Change (atm)	Final Pressure (atm)
N_2	22.5	-x/2	22.5 - x/2 ≈ 22.5
O_2	7.50	-x/2	7.50 - x/2 ≈ 7.50
NO	0	x	x

This time we make the approximation that since K is small, x/2 will be insignificantly small compared to 22.5 atm or 7.50 atm. Thus the final pressures for N_2 and O_2 which we put into our equilibrium expression will be 22.5 and 7.50 atm respectively.

$$K = \frac{P^2_{NO_2}}{P_{N_2} P_{O_2}} = 2.7x10^{-8}$$

$$2.7x10^{-8} = \frac{x^2}{(22.5)(7.5)}$$

$$x = 2.13 \text{ x } 10^{-3}.$$

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.

$$P_{N_2} = 22.5atm - \frac{2.13x10^{-3}atm}{2} = 22.5atm$$

$$P_{O_2} = 7.5atm - \frac{2.13x10^{-3}atm}{2} = 7.5atm$$

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

$$CO\ (g) + 2H_2(g) \rightleftharpoons CH_3OH\ (g),$$

$K_p = 36 \text{ atm}^{-2}$ at 700 K. What net reaction, if any, will occur in a system containing 15 atm CO, 30 atm H_2, and 50 atm CH_3OH 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

$$CH_3OH\ (g) \rightarrow 2H_2(g) + CO(g)$$

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

$$CO\ (g) + 2H_2(g) \rightarrow CH_3OH\ (g).$$

Let's evaluate Q_p and take its ratio with K_p

$$Q_p = \frac{p_{CH_3OH}}{p_{CO}\, p_{H_2}^2} = \frac{50atm}{(15atm)(30atm)^2} = 3.70x10^{-3}$$

$$Q / K = \frac{3.70x10^{-3}\, atm^{-2}}{36atm^{-2}} = 1.0x10^{-4} < 1$$

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

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g).$$

Lecture 28

Example 4: Calculating Equilibrium Constants

Ethylene, C_2H_4, and water react under appropriate conditions to give ethanol. The reaction is

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g).$$

The equilibrium mixture at a certain temperature had the following concentrations, $[C_2H_4] = 0.0148$ M, $[H_2O] = 0.0336$ M and $[C_2H_5OH] = 0.180$ M. What is K_c?

$$K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]} = \frac{.180M}{(.0148M)(.0336M)} = 362M^{-1}$$

Example 5: Calculating Equilibrium Compositions

At 25°C, $K_c = .145$ for the following reaction in CCl_4:

$$2BrCl \rightleftharpoons Br_2 + Cl_2.$$

A solution was prepared with the following initial concentrations: $[BrCl] = 0.0400$ M, $[Br_2] = 0.0300$ M. $[Cl_2] = 0.0200$ M. What will the equilibrium concentrations be?

$$K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2} = .145$$

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

	Initial [ ] (M)	Change (M)	Equilibrium [ ] (M)
BrCl	0.04	-2x	.0400 - 2x
Br_2	0.03	x	.0300 + x

Cl_2	0.02	x	.0200 + x

Plugging the equilibrium concentrations into our equilibrium constant expression gives us

$$K_c = .145 = \frac{(.0200 + x)(.0300 + x)}{(.0400 - 2x)^2}$$

When we multiply out all terms this becomes

$$.420\ x^2 + .0732\ x + 3.68 \times 10^{-4} = 0$$

Applying the quadratic formula gives

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-.0732 \pm (.0732^2 - (4)(.420)(3.68x10^{-4}))^{1/2}}{.840}$$

$$x = -.169,\ -.00523$$

Only one of these values makes physical sense, since if x = -.169 the final concentration of Br_2, which we said equaled .0300 + x would have to equal .0300 - .169 M = -.139 M. Since we obviously can't have negative concentrations, -.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, [Br_2] = 0.0300 + x = 0.0300 -0.0053 = 0.0248 M, and [Cl_2] = 0.0200 - 0.00523 = 0.0148 M.

Example 6: Calculating Equilibrium Compositions From K

The reaction

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

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, H_2 and Cl_2?

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

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

	Initial [ ] M	Change	Final [ ] M
HCl	0.0500	-2x	0.0500-2x ≈ 0.0500
H_2	0	x	x
Cl_2	0	x	x

Substituting into the formula for K_c yields

$$3.2x10^{-34} = \frac{x^2}{0.0500}$$

and therefore x = 4.0 x 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 x 10^{-18}) = .0500, since the number we subtract does not affect any of our significant figures. Therefore our equilibrium concentrations are [HCl] = .0500 M, and [H_2] = [Cl_2] = 4.0 x 10^{-18} M.

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

At 460°C, the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

has K_c = 85.0. A reaction flask at 460°C contains gases at the following concentrations. [SO_2] = .00200 M, [NO_2] = .00350 M, [NO] = .0250 M and [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,

$$Q_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(.0400)(.0250)}{(.00250)(.00350)} = 114$$

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

$$SO_3(g) + NO(g) \rightarrow NO_2(g) + SO_2(g).$$

Example 8: Manipulation of Equilibrium Constants.

a) For the reaction

$$1/2\ N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g),$$

$K_p = 7.75 \times 10^2$ at 25°C. What is K_p for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)?$$

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

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

is 11.5 atm at 300°C. What is the equilibrium constant for the reverse reaction

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)?$$

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

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \qquad K_1 = 4.2 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{-2}(aq) + H_3O^+(aq) \qquad K_2 = 4.8 \text{ x } 10^{-11}$$

What is the equilibrium constant for the reaction

$$H_2CO_3(aq) + 2H_2O(l) \rightleftharpoons CO_3^{-2}(aq) + 2H_3O^+(aq)?$$

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 $K_3 = K_1 \text{ x } K_2 = (4.2 \text{ x } 10^{-7})\ (4.8 \text{ x } 10^{-11}) = 2.02 \text{ x } 10^{-17}$.

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 complete our treatment of thermodynamics later. However, there is 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**. **LeChatelier's principle says that if a system is in equilibrium, and if we do something to disturb that equilibrium, the system will move toward a new equilibrium 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

$$C_2H_4 \rightleftharpoons C_2H_2 + H_2.$$

After the reaction reaches equilibrium, we increase the pressure of our C_2H_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? Therefore, in this case, 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 C_2H_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 $C_2H_4 \rightleftharpoons C_2H_2 + H_2$. 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

$3H_2 + N_2 \rightleftharpoons 2\ NH_3$ 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 $H_2 + CO_2 \rightleftharpoons H_2O + CO$? 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,

$$3H_2 + N_2 \rightleftharpoons 2\ NH_3 \qquad\qquad \Delta H^\circ_f = -46.19\ \text{kJ/mol.}$$

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

$$3H_2 + N_2 \rightleftharpoons 2\ NH_3 + 46.19\ \text{kJ.}$$

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 that there is none. **Catalysts will affect the rate at which a system will approach equilibrium, but will not affect the equilibrium constant or the equilibrium composition itself.**