

Lecture 21

It is possible to have forces between atoms or molecules that hold them together but are substantially weaker than covalent bonding forces. These forces, which are generally attractive at long to medium distances and are repulsive at short distances, are called **intermolecular forces**. The intermolecular forces that we will consider are between neutral molecules and not ions and are rather **weak in the gas phase**.

Both attractive forces and repulsive **forces depend strongly on the distance between two molecules**. The repulsive forces don't turn on, in fact, until the molecules are close enough to touch. The attractive forces, which have the effect of pulling the molecules closer together, have a strength proportional to $1/r^6$, where r is the separation between molecules. This means that as the molecules get farther and farther apart the forces rapidly become very, very weak. Thus in gases where there is typically a great deal of space between molecules, the forces are very weak and result only in very small attractions between atoms or molecules. However, in liquids and solids, the molecules are very close together, and the effect of these forces is much stronger.

There are three main types of forces that exist between uncharged species, dipole-dipole interactions, dipole-induced dipole interactions, and dispersion forces. There are also forces that involve ions, but we will treat those in later when we treat solutions.

The strongest forces between uncharged species are **dipole-dipole forces**. Remember that when I talk about a dipole moment, I am saying that there is an uneven distribution of electrons within a molecule, or in other words that the ends of a molecule will be slightly charged. Now imagine a liquid made up of polar molecules, i.e., molecules that have a dipole moment. Each will have a positive side and a negative side. By now we should all know that positives and negatives attract each other. **In a liquid, the molecules**

can move around fairly freely, so these dipoles can align so that the positive ends of molecules are pointing toward the negative ends of other molecules. The net result is an attraction that holds the liquid together. It is important to note that the molecules in a liquid are always moving, and that they have enough energy that often they can move away from this positive to negative arrangement. Nonetheless, at any given time, a liquid composed of polar molecules will have most of its molecules arranged in such a way that attraction can occur. An example of dipole-dipole interactions is the attraction between SO_2 molecules. The O atoms are more electronegative than the S, so the S will be slightly positive and both O atoms slightly negative. Since SO_2 is bent the whole molecule has a dipole moment as well. The dipole-dipole interaction is the attraction between the positive S and a negative O on different molecules.

A special case of a dipole-dipole interaction occurs when the polar bond is composed of a hydrogen atom bonded to a small electronegative atom like fluorine, oxygen or chlorine, as is the case with hydrochloric acid, hydrofluoric acid or water. For these special cases the dipole-dipole interactions are called **hydrogen bonds**. In all of these molecules the hydrogen will have a small positive charge, while the other atom will have a small negative charge. Therefore dipole-dipole interactions will occur between the negative and positive ends. Hydrogen bonds are special cases of dipole-dipole interactions for two reasons. First, the small size of the hydrogen atom means that the molecules can get closer together which makes the interaction stronger. This means that hydrogen bonds will be stronger than other dipole-dipole interactions. Second, because the H atoms are small and because of the close approach between the molecules involved in a hydrogen bond, actual orbital overlap occurs, and a weak bond, with bond order substantially less

than one, forms. This is in contrast to all other intermolecular forces between neutral molecules for which the dominant interactions are electrostatic.

An example of a hydrogen bond would be between molecules in pure ethanol, commonly known as grain alcohol. Its formula is $\text{CH}_3\text{CH}_2\text{OH}$. The oxygen is slightly negative and the hydrogen is slightly positive, so the O on one molecule will be attracted to the OH hydrogen on another molecule. It is important to realize that the other H's on the ethanol will not form hydrogen bonds. The reason is that the bonds between the carbons and hydrogens on ethanol are much less polar than those between the oxygen and the hydrogen, since the electronegativity of H is 2.1 and C is 2.5, while that of O is 3.5. Thus the H in the OH bond is much more positively charged than the H in the CH bond.

The hydrogen bonds with molecules containing O-H or N-H bonds are particularly important, in part because of the prevalence of these types of bonds in biological systems. Hydrogen bonding is responsible for the shapes of the DNA in your chromosomes, and for the shapes of the active sites of the enzymes which catalyze the reactions which allow life to occur. Hydrogen bonding is also responsible for the high boiling point of water. Water, since it is composed of two OH bonds, has the capability of forming hydrogen bonds with both ends. Thus instead of just holding two molecules together, the hydrogen bonds in water can link a whole network of molecules.

The second type of attractive force is called a **dipole-induced dipole force**. This type of force is weaker than the dipole-dipole force. This type of force is the strongest force between a polar molecule and a non-polar molecule. An example of such a pair would be HCl, a polar molecule, and ethane, C_2H_6 , a nonpolar molecule. This type of force comes about because electrons in an atom or molecule are constantly moving. If we put a

positive charged particle next to a non-polar molecule, it will attract the electrons in the non-polar molecule, so that they spend more of their time on the side of the molecule nearest the charged particle. This means that when a non-polar molecule sits next to a charged particle, its electron distribution will become uneven. In other words, because it is sitting next to a charged particle, a dipole moment will be created. We call such a created dipole an **induced dipole**. Notice that if we put a positive charge next to the non-polar molecule, it makes the side next to it more negative, and since opposites attract, the two molecules will be attracted to each other.

Not all non-polar molecules will form the same size induced dipole moment when faced with a charged particle. This is because atoms have different tendencies to bind valence electrons to themselves. For example, the fluorine atoms in F_2 hold their valence electrons more tightly than the iodine atoms in I_2 . Thus when we put a charged molecule next to I_2 its electrons will be able to move to the charged side more easily than the electrons in F_2 , and the induced dipole moment will be larger in I_2 than in F_2 . The tendency for the electrons in a molecule to move in response to an external charge is called the **polarizability** of the molecule. Thus since the electrons in I_2 can move more easily than the electrons in F_2 we say that I_2 is more polarizable than F_2 . In general polarizability follows the same periodic trends as the size of atoms. The polarizability increases as you go down a group and decreases as you go across a period. [Do a couple of examples from the periodic table.]

Now remember that a polar molecule, i.e., a molecule with a dipole moment, effectively has charged ends. This means that if we put a molecule with a dipole moment next to a non-polar molecule, it will induce a dipole moment in the non-polar molecule and

they will attract. Induced dipole moments are always weaker than normal dipole moments, so dipole-induced dipole interactions are always smaller than dipole-dipole interactions.

The third type of intermolecular attractive forces, which are known variously as London forces, van der Waals forces, or dispersion forces, are due to the interaction between **two induced dipoles**. Generally these are the forces which are responsible for the condensation of **non-polar molecules**. These forces, while new to some of you, are well known in the entertainment industry, to the point where the Clash even made a whole double album about these attractive forces, called "London Calling".

As was the case for the dipole-induced dipole interactions, London forces arise from the mobility of electrons in molecules. Even though on average, a non-polar molecule has a uniform distribution of electrons, the distribution is not uniform at all times. Sometimes, just for a fleeting moment, there will be more electrons on one side of the molecule than on the other side, so for this short time the molecule will have a dipole moment. If the molecule is sitting next to another molecule, because electrons can move really fast, the electrons in the second molecule will respond to the dipole in the first molecule, and will have more of its electrons on the side pointing to the positive side of the first molecule. Since this results in a positive side facing a negative side, attraction results. Since the dipole moments are around for a very short time, London forces can be very small.

However, **the strength of London forces depends on two factors, the size of a molecule and the polarizability of its atoms**. If an atom is more polarizable, it will have stronger London forces, because its electrons will be able to respond more quickly to any dipole moment they are exposed to. Thus iodine, which is non-polar but highly polarizable,

is a solid at room temperature because of strong London forces, while Cl_2 , which is substantially less polarizable, is a gas.

The reason that the size of a molecule affects the strength of London forces, is that **if the molecule is large enough, these short-lived dipole moments can be formed simultaneously on several places on a given molecule.** Thus for a pair of long molecules you can have London forces holding the molecules together in four or five places. This obviously would result in stronger attraction than a single interaction. As an example, hexadecane, $\text{C}_{16}\text{H}_{34}$, which is a medium sized molecule made only of carbon and hydrogen, is a liquid at room temperature, while propane, C_3H_8 , which is made of the same elements but is much smaller, is a gas. This is because the London forces between two propane molecules will be much weaker than those between two hexadecane molecules.

It is important to realize that a pair of non-polar molecules will exhibit only London forces. In contrast a non-polar and a polar molecule that interact will show both London forces and dipole-induced-dipole forces. Finally, two polar molecules will feel all three types of forces, dipole-dipole, dipole-induced dipole and London forces. Let's compare some pairs of molecules and see which will have the stronger intermolecular forces. [(SO_2 , CH_3OH), (CH_3OH , CH_4), (CH_4 , C_4H_{10}), (H_2 , O_2)]

As I said at the beginning of the lecture, these intermolecular forces are the forces that are responsible for matter existing in different phases, gases, liquids and solids. These forces are all distance dependent to a greater or lesser extent, and, with the exception of forces between charged species, are quite weak in the gas phase. However, liquids and solids are much denser than gases, with their molecules and atoms much closer together, and therefore these forces are much stronger for liquids and solids.

Lecture 22

Now we turn to the study of **chemical kinetics**. Kinetics is **the study of the speed with which reactions occur under various conditions**. Why do we study kinetics? We all have an idea that **different reactions take different amounts of time**. When you're in lab and you add NaCl to AgNO₃ a precipitate forms instantaneously. On the other hand, if you combine H₂ gas and Cl₂ gas in a dark bulb, it can take over 100 years for the reaction to finish.

Kinetics also studies the processes that affect the speed of a reaction. For example, consider the reaction between H₂ and O₂. Without help this reaction is extremely slow. A mixture of H₂ and O₂ can sit around forever. Add a spark and boom, water forms instantly. Understanding what makes a given reaction go quickly or slowly is a practical goal of chemical kinetics.

There's another reason for the study of chemical kinetics than this practical one. One of the major goals of chemistry is to understand **how chemical reactions occur**. Along with quantum mechanics, chemical kinetics is one of the keys to this goal. By studying the factors that control the speed of chemical reactions, we can figure out the individual processes that occur in the course of the reaction. Some of these factors can be studied quite simply, and later in the semester you will do a kinetics lab. However, some of the processes that are important in controlling chemical reactions occur very quickly, on the timescale of 10⁻¹⁴ seconds, and substantial ingenuity has gone into studying these processes directly. Such experiments often involve sophisticated (and expensive) lasers and other complex technology. This aspect of kinetics, called chemical dynamics, is one of the most active areas in modern chemical research.

What controls the speed of a reaction? One factor is the **identity of reactants and products**. If one of the reactants is particularly stable, then the speed of the reaction is likely to be slow. If on the other hand a substance is intrinsically unstable, then it will react quickly. A second factor is the **concentrations of reactants and products**. This should make qualitative sense. In order for two compounds to react, they have to meet. If the concentration of the reactants is higher, then they will be closer together, and it won't take as long for them to come together and react. A third factor is **temperature**. The reason that it's bad for you to have a fever is that the elevated temperature increases the speed with which the reactions that allow you to live occur. A fourth factor is the presence of compounds which are neither products nor reactants called **catalysts**. Catalysts are widely used commercially to increase the speed of chemical reactions. We will expand on each of these in the next three lectures.

Kinetics is the study of the **rates of chemical reactions**. The word **rate** implies that **something changes with time**. For example, you hear a lot about the rate of inflation. The rate of inflation is the change of cost with time, i.e.,

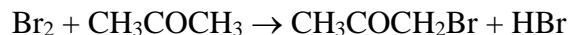
$$\textit{inflation rate} = \frac{\Delta \textit{cost}}{\Delta \textit{time}}$$

where the Greek letter Δ means "change in". When we talk about rates in chemistry, we are interested in how fast a reactant is consumed or a product is formed. In chemistry, the rate we are interested in is the **change in concentration of a reactant or product that occurs in a given time**,

$$\textit{reaction rate} = \frac{\Delta \textit{concentration}}{\Delta \textit{time}},$$

where time is usually measured in seconds. We will abbreviate concentration by using square brackets. For example, the concentration of Br₂ will be abbreviated [Br₂].

Let's **practice calculating a reaction rate** by considering a specific case, the bromination of acetone, in which bromine is reacted with acetone to form bromoacetone and hydrogen bromide. The overall reaction is



When we apply the idea of reaction rates to chemical reactions, we typically measure either rates of formation or rates of consumption. The rate of formation is defined as

$$\text{rate of formation} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$

Suppose in our bromination reaction, 0.047 moles/L of bromoacetone are formed in 300 s.

What is the rate of formation? According to our definition, this rate will be 0.047 moles/L/300s = 1.57 x 10⁻⁴ mol/L*s. IF 0.047 MOLES/L OF BROMOACETONE ARE FORMED,

HOW MANY MOLES/L OF HBR ARE FORMED? WHAT IS THE RATE OF FORMATION OF HBR?

Notice that because the stoichiometry is 1:1 the rates of formation are the same. IF 0.047

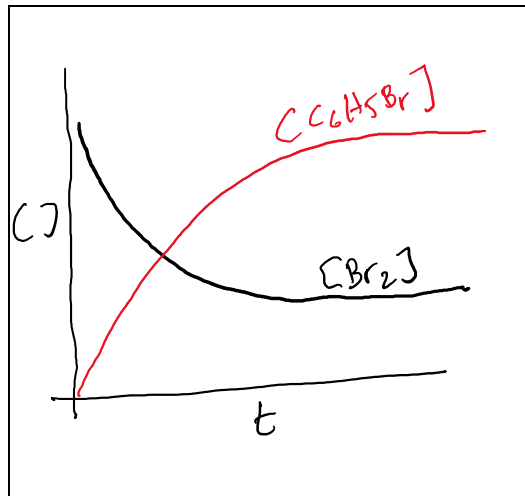
MOLES OF BROMOACETONE ARE FORMED, WHAT IS THE CHANGE IN CONCENTRATION OF THE

BROMINE? WHAT IS THE RATE AT WHICH THE BROMINE IS CONSUMED? Notice that **for a**

reactant, change in concentration is negative. For this reason the rate for

consumption of a reactant is given by $\text{rate of consumption} = -\frac{\Delta \text{concentration}}{\Delta \text{time}}$.

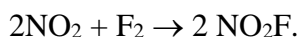
We can see the relative changes of product and reactant concentrations if we draw a graph that shows both the concentration of the bromine as a function of time, and the concentration of the bromoacetone as a function of time. We see that the concentration of our reactant decreases steadily over time. Because the stoichiometric ratio of the



product to the reactant is one to one, the curve of the growth of the bromoacetone is a flipped over version of the loss of the bromine, and the product grows steadily over time.

Note that there are two different ways we can calculate the rate of reaction from the data in this graph. One is the average rate of reaction. This is the change in concentration of one of our species over a finite period of time, and is defined as above. If the speed at which concentration changes varies over time, the average rate of reaction will depend on the length of time over which the average is taken. We can also calculate an instantaneous rate of reaction, the rate of change at any one instant of time. This rate is simply the slope of a concentration vs time curve at a given point. In general, average reaction rates are easier to determine, but whenever we can calculate them, instantaneous reaction rates are more useful.

The rates of change of product and reactant concentrations are not always so simply related. Consider the reaction



$\Delta[\text{F}_2] = -0.54 \text{ mol/L}$, $\Delta t = 130 \text{ s}$. In this case, the rates of consumption and reaction are related by the stoichiometric coefficients of the species. NO_2 will be consumed twice as

fast as F_2 , and NO_2F is formed twice as fast as F_2 is consumed. WHAT IS THE RATE OF CONSUMPTION OF F_2 ? [$4.15 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$] IF 0.54 MOL/L OF F_2 ARE CONSUMED, WHAT IS THE CHANGE IN CONCENTRATION OF NO_2 ? [$\Delta[NO_2] = -1.08 \text{ mol/L}$] WHAT IS THE RATE OF CONSUMPTION OF NO_2 ? [$9.30 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$] We can use similar reasoning to show that the rate of formation of NO_2F in this reaction is $9.30 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. It's confusing to have the reaction characterized by three different rates, one each for the NO_2 , F_2 and NO_2F . After all, sometimes all we want to know is the answer to the question, "How fast is this reaction?", which is ambiguous if the reaction is characterized by three different rates. To solve this problem, we define the **rate of reaction**. To calculate the rate of reaction, we divide the rate of formation or consumption by the stoichiometric coefficient. For this reaction the rate of reaction can be written three different ways,

$$rate = -\frac{1}{2} \frac{\Delta NO_2}{\Delta t} = -\frac{\Delta F_2}{\Delta t} = \frac{1}{2} \frac{\Delta NO_2F}{\Delta t}$$

Notice that all three give the same value, $4.15 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$, for each of the species in the reaction.

For a general reaction of the form $aA + bB \rightarrow cC + dD$, the rate of reaction is

$$rate = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Now I'll let you try a couple. [Rate of reaction and relative rate of formation/consumption for each component] $N_2O_5 \rightarrow 2 NO_2 + 1/2 O_2$. $\Delta[NO_2] = 2.4 \text{ M}$, $\Delta t = 75 \text{ s}$. $3ClO^- \rightarrow 2Cl^- + ClO_3$. $\Delta[ClO^-] = -0.87 \text{ M}$. $\Delta t = 3500 \text{ s}$.

Lecture 23

It is important to realize that **reaction rates generally change over the course of a reaction**. There are a couple of reasons for this. First, remember that we said that the **rate of reaction depends on the concentrations of the reactants, and these will decrease as the reaction proceeds**, so we would naturally expect the reaction rate to decrease. The other reason is that **sometimes the products** that form as a reaction proceeds **will have an effect on the rate of the reaction**. If the presence of a product speeds up the reaction, the reaction is said to be **self-catalyzing**. If the presence of a product slows down a reaction, the product is called an **inhibitor** and the reaction is referred to as **self-inhibiting**. Because the reaction rates change as the reaction proceeds, we will focus on the **initial reaction rates**, that is, the reaction rates that are observed immediately after the reactants are mixed.

The way that the rate of the reaction depends on the concentrations is usually expressed mathematically in the form of a **rate law**. **The rate law expresses the rate of a reaction as a function of concentrations raised to some powers**. Rate laws can be simple, as in the case of the reaction $3\text{ClO}^- \rightarrow 2\text{Cl}^- + \text{ClO}_3^-$ which follows the law

$$\text{rate} = k [\text{ClO}^-]^2,$$

or very complex as in the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ which follows the law

$$\text{rate} = \frac{k_1[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k_2 \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

Note that simple or complex, all rate laws are functions of concentrations raised to some power, which can be an integer or a real number, and constants.

Some, but not all, reactions have rate laws that are functions of reactant and catalyst concentrations alone and have a particularly simple form. If we write our reaction as $aA + bB = cC + dD$, then this simple form of the rate law is simply

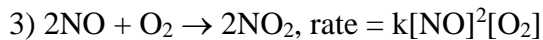
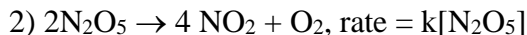
$$\text{rate} = k[A]^\alpha[B]^\beta\dots,$$

where α , and β can be any numbers, and k is a constant. The exponents α , and β are called **partial orders**. We say that α is the partial order of the reaction with respect to reactant A, β is the partial order of the reaction with respect to reactant B, and so on. It is important to realize that these partial orders are not necessarily related to the stoichiometric coefficient of a reaction. **The only way to determine these orders is experimentally.** The overall **order of the reaction is the sum of the partial orders**, i.e., the total order = $\alpha + \beta + \gamma + \dots$. When the overall order of a reaction is one, we say that the reaction is a **first order reaction**. When the overall order is two, the reaction is called a **second order reaction**, while if the order is three, the reaction is called **third order**.

Let's look at some examples. If we have a rate law

$$\text{rate} = k[A]^1[B]^2,$$

the partial order of A is 1, the partial order of B is 2 and the overall order is 3. Other possible examples of rate laws are $r = [A][B]^0$, which is first order with respect to A and has a total order of one, $r = [A]^0[B]$, which is first order with respect to B and has a total order of 1, and $r = [A][B]$, which is first order with respect to both A and B and has a total order of 2. WHAT DOES IT MEAN IF THE PARTIAL ORDER OF A REACTANT IS ZERO? Now some real examples. FOR THE FOLLOWING REACTIONS I'LL GIVE YOU THE RATE LAWS AND I'LL ASK YOU TO TELL ME THE PARTIAL ORDERS OF EACH OF THE REACTANTS, AND THE OVERALL ORDER OF THE REACTION.



What do these orders mean? **They tell us the way the rate changes when we change the concentration.** For example, in the $\text{H}_2 - \text{I}_2$ reaction if we double the hydrogen concentration, the reaction rate will double. IF WE TRIPLE THE IODINE CONCENTRATION WHAT WILL HAPPEN TO THE REACTION RATE? In contrast in the $\text{NO} + \text{O}_2$ reaction, if we double the concentration of nitric oxide, the rate will increase by a factor of four. WHAT WILL HAPPEN IF WE DOUBLE THE CONCENTRATION OF THE OXYGEN? IN THE ClO^- REACTION WITH THE RATE LAW RATE = $k[\text{ClO}^-]^2$, WHAT HAPPENS IF WE TRIPLE $[\text{ClO}^-]$?

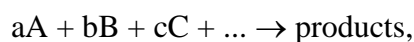
The only thing we have left to explain in our rate equation is the constant k . k is called the **rate constant**. It is simply a proportionality constant which relates the concentration terms in our equation to the actual rate. It **depends on the temperature** and like the order of the reaction, must be determined experimentally.

The units of rate constants depend on the order of the reaction. To see this, note that the units of rate are always M/s. A first order rate law has the form, rate = $k []$. If we look at the units of rate and concentration, we see that in order for both sides to have the same units, k must have units of 1/s. However now consider a second order reaction, which has a rate law, rate = $k []^2$. WHAT ARE THE UNITS FOR RATE? WHAT ARE THE UNITS FOR CONCENTRATION SQUARED? WHAT UNITS DOES k HAVE TO HAVE FOR THE UNITS TO BE THE SAME ON BOTH SIDES OF THE EQUATION? Let's look at a third order reaction as well. The rate law has a general form, rate = $k []^3$. WHAT ARE THE UNITS FOR RATE? WHAT ARE

THE UNITS FOR CONCENTRATION CUBED? WHAT UNITS DOES K HAVE TO HAVE FOR THE UNITS TO BE THE SAME ON BOTH SIDES OF THE EQUATION? So you see that **when we change the order of reaction we change the units of the rate constant** as well. We will study k more later.

We've just defined partial and total orders. Orders of reactions and partial orders are big pieces in the puzzle which allow us to figure out which sequence of steps occurs for a given reaction. Because of this we'll be spending some time learning **how to determine orders from experimental data**.

Here's the basis for our method. As we said before, for many reactions of the form



we can write

$$\text{rate} = k[A]^\alpha[B]^\beta[C]^\gamma \dots$$

There are two ways to use this equation. In both cases we measure the **initial rates** (the rates at $t=0$) while changing the concentration of one of our reactants and holding all the others constant. Suppose that we do two experiments. In experiment one, the concentrations are A_1 , B_1 and C_1 and we measure rate r_1 . Now in the second, we keep the concentrations of B and C the same, and double the concentration of A. The concentrations for our second experiment are $2A_1$, B_1 and C_1 and we measure the rate r_2 for this second set of concentrations. Let's suppose that the rate increases by a factor of 4, i.e., $r_2 = 4r_1$. WHAT IS THE RATE EXPRESSION FOR THE FIRST EXPERIMENT ACCORDING TO OUR GENERAL FORMULA FOR A RATE LAW? WHAT IS THE RATE EXPRESSION FOR THE SECOND? To determine the partial order with respect to [A], let's take the ratio of the two rates. Notice that k , [B], and [C] cancel and we're left with $4 = (2)^\alpha$, and it's apparent that $\alpha = 2$ and the

partial order of the reaction with respect to A is 2. Does anyone know what to do if the value of the exponent isn't apparent from inspection? [Use log] Let's do an example together.

Suppose we have a reaction $A + 2B \rightarrow C + D$. When the reaction is run with the following concentrations of A and B in the first two columns, the rates in the third column are observed.

[A](M)	[B](M)	rate(M s ⁻¹)
2.0×10^{-3}	2.0×10^{-4}	1.5×10^{-6}
4.0×10^{-3}	2.0×10^{-4}	6.0×10^{-6}
4.0×10^{-3}	6.0×10^{-4}	1.8×10^{-5}

Find α , the partial order with respect to A, β , the partial order with respect to B, and k , the rate constant.

Here's a second way we can use initial concentrations to determine orders.

Let's take our rate equation,

$$r = k[A]^\alpha[B]^\beta[C]^\gamma..$$

and take the ln of both sides. Now this becomes

$$\ln r = \ln (k[A]^\alpha[B]^\beta[C]^\gamma).$$

There are two rules of logarithms that we can use to put this in a more useful form. The first is

$$\ln (a*b*c) = \ln a + \ln b + \ln c.$$

Using this gives us

$$\ln r = \ln k + \ln [A]^\alpha + \ln [B]^\beta + \ln [C]^\gamma.$$

The second rule of logarithms is $\ln x^a = a \ln x$. This makes our equation

$$\ln r = \ln k + \alpha \ln [A] + \beta \ln [B] + \gamma \ln [C].$$

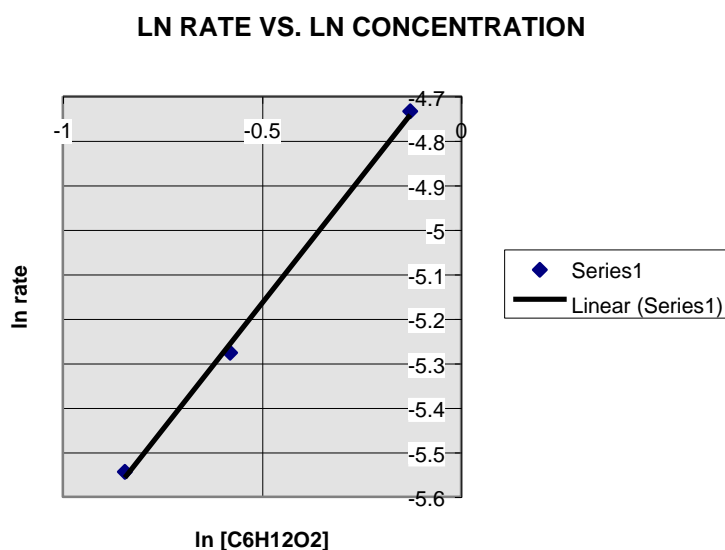
Now suppose that we follow the same experimental procedure we did for our first method and do a series of experiments where we hold the concentrations of B and C constant and vary only the concentration of A. Now the terms $\beta \ln B$, $\gamma \ln C$ and $\ln k$ are all constant so we can group them all together and write,

$$\ln r = \alpha \ln [A] + \text{constant}.$$

Notice that this equation has the same form as a straight line, $y = mx + b$, where α is the slope. If we take our data and plot $\ln r$ vs $\ln [A]$, the slope will be the partial order of [A]. If we now do a sequence of experiments with [A] and [C] constant and vary [B], plotting $\ln r$ vs. $\ln [B]$ yields a straight line with a slope of β . Repeating this for all reactants yields all of the partial orders and the overall order.

Example. For the reaction $\text{C}_6\text{H}_{12}\text{O}_2 \rightarrow 2 \text{C}_3\text{H}_6\text{O}$ we collect the following data.

$[\text{C}_6\text{H}_{12}\text{O}_2]$ (M)	Rate (M s^{-1})
0.43	3.91×10^{-3}
0.56	5.11×10^{-3}
0.88	8.79×10^{-3}



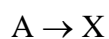
If we plot the natural log of the concentration vs. the natural log of the rate we get a slope = 1.14, and therefore the order of the reaction is 1.14 as well.

As we mentioned earlier, the way that order affects reactions is that it

determines the way that **the concentration of a species changes with time**. We are interested in this because it allows us to know before we run a reaction how long it will take for a reactant to be 90% consumed or half consumed. In order to do this, we are going to determine equations that relate the concentration of a reactant with time.

This involves the use of integral calculus. It gets very complicated very quickly, but is relatively simple for first order and some second order reactions. I don't expect you to know integral calculus yet, since almost all of you are either taking it now or have not taken it at all. I will use it to derive two equations, so that those of you who are interested can see how it is done, but I only expect you to learn the equations I obtain, not the derivation.

Let's begin with a **first order reaction**. Two examples of reactions which could be first order in A would be



and



with the rate equation rate of consumption = $k[A]$. WHAT IS EXPRESSION FOR THE RATE OF CONSUMPTION OF THIS REACTION? [$rate = -\frac{\Delta[A]}{\Delta t}$] Since these are both expressions for the

rate of consumption, they must be equal, so we can write

$$-\frac{\Delta[A]}{\Delta t} = k[A]$$

If we look at the change of concentration for an infinitesimally small time we can represent the change of concentration with time by a derivative, and our equation becomes

$$\frac{-d[A]}{dt} = k[A]$$

Collecting all terms with the concentration of A on one side gives us

$$\frac{d[A]}{[A]} = -kdt$$

Integrating this will give us our equation for concentration versus time, but first we need to decide what our limits of integration should be. What we'll do is say that we start at time 0 with some initial concentration $[A]_0$. After some time t , the new concentration is $[A]$. Thus we integrate concentration from $[A]_0$ to $[A]$ and time from 0 to t . Now our integral becomes

$$\int_{[A]_0}^A \frac{d[A]}{[A]} = \int_0^t -kdt,$$

which after integration yields the equation for concentration as a function of time for first order reactions.

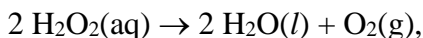
$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt.$$

This is often rewritten in the form

$$[A] = [A]_0 e^{-kt}$$

We can use this equation, which is called an **integrated rate equation**, to determine $[A]$, $[A]_0$, k or t , as long as the other three variables are known.

Let's do an example of using this equation. In dilute NaOH, the decomposition of hydrogen peroxide to water and oxygen,



is first order in H_2O_2 with a rate constant of 0.052 min^{-1} at a certain temperature. If the original concentration is 0.450 M , what is its concentration after 7.50 minutes? How long will it take for its concentration to decrease from 0.450 M to 0.225 M ? To answer the first question we note that for a first order reaction, $[A] = [A]_0 e^{-kt}$. Since we know the initial concentration, the rate constant and the elapsed time, we need only plug in to find the concentration of H_2O_2 after 7.50 min.

$$[\text{H}_2\text{O}_2] = 0.450 \text{ M} e^{-(0.052 \text{ min}^{-1})(7.50 \text{ min})} = 0.305 \text{ M}$$

For the second question, the more useful form of our equation is $\ln \frac{[A]}{[A]_0} = -kt$.

Since we want to find the time which elapses before the concentration drops from $.450 \text{ M}$

to $.225 \text{ M}$ we need only solve this equation for t , i.e., $t = -\ln \left(\frac{[A]}{[A]_0} \right) / k$. Thus

$$t = -\frac{\left(\ln \frac{0.225 \text{ M}}{0.450 \text{ M}} \right)}{.052 \text{ min}^{-1}} = 13.3 \text{ min}.$$

Lecture 24

We can also find the integrated rate equation for a second order reaction, for example the reaction $A \rightarrow C$, or $2A \rightarrow C$ or $A + B \rightarrow C$. IF THE REACTION IS 2ND ORDER IN A, WHAT IS THE RATE LAW? [rate = $k[A]^2$]. IF OUR REACTION IS $A \rightarrow C$, WHAT IS THE EXPRESSION FOR THE RATE OF CONSUMPTION IN TERMS OF THE CONCENTRATION OF A? AS before we equate these to get

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2$$

For an infinitesimal change this becomes

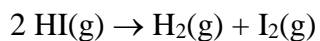
$$-\frac{d[A]}{dt} = k[A]^2$$

Collecting terms and integrating the concentration from $[A]_0$ to $[A]$ and the time from 0 to t , yields our equation for the change of concentration with time for second order reactions,

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt.$$

Once again, this equation can be used to solve for $[A]$, $[A]_0$, t or k , as long as the other three terms are known.

Let's look at an example of using this equation. The decomposition of hydrogen iodide to hydrogen and iodine,



is a second order reaction with a rate constant of 0.11 L/mol s at 650 K. How long does it take for the HI concentration to decrease from 0.120 M to 0.030 M? If the initial concentration of HI is 0.120 M, what will be its concentration after 2.00 minutes? For this first problem we just take our second order integrated rate equation and solve for t ,

$$\left(\frac{1}{[A]} - \frac{1}{[A]_0} \right) / k = t. \quad \text{Thus in this case } t = \left(\frac{1}{0.030 \text{ M}} - \frac{1}{0.120 \text{ M}} \right) / 0.11 \text{ M}^{-1}\text{s}^{-1} = 227 \text{ s}.$$

For the second problem we manipulate the equation so that we are solving for [A]. [Do it.]

Now we plug in our values for [A]₀, k and t, and determine that [A] = 0.046 M. Notice that we have to be careful to have the same time units in our rate constant and time, or our time units will not cancel and we will get the wrong answer.

Let's consider one more case, a zero order reaction. A zero order reaction is one in which the rate of the reaction is independent of the concentrations of the reactants. let's say our reaction is the simple reaction:



In this case our rate of reaction is

$$\text{rate} = -\frac{\Delta[A]}{\Delta t},$$

which for an infinitesimal change in t becomes

$$\text{rate} = -\frac{d[A]}{dt}$$

Our rate law for the zero order reaction is

$$\text{rate} = k[A]^0 = k.$$

Now we set the two equations for the rate equal and get our differential rate law,

$$-\frac{d[A]}{dt} = k$$

To solve for the integrated equation, we collect terms and then integrate:

$$\int_{[A]_0}^{[A]_t} d[A] = \int_0^t -k dt$$

Yielding

$$[A]_t - [A]_0 = -kt \quad \text{or} \quad [A]_t = [A]_0 - kt .$$

What this tells us is that after we start with a given concentration of our reactant, that it decreases with a constant rate, with a slope of $-k$.

A consequence of these integrated rate equations is the concept of **half-lives**. In short, the half-life is the time it takes for a **reactant** to reach 1/2 of its initial concentration. We find the half-life for a reactant by using our integrated rate equations, inserting $[A]_0/2$ as the final concentration, and solving for t . Let's do this first for a first order reaction. FOR A FIRST ORDER REACTION WHAT IS OUR INTEGRATED RATE EQUATION? We take this equation and substitute $[A]_0/2$ as the final concentration, and $t_{1/2}$ as the time at which we reach this concentration. Solving for $t_{1/2}$ yields $t_{1/2} = \frac{0.693}{k}$. Notice that **for a first order reaction, the time it takes for the concentration of a reactant to go down to half of its initial value depends only on the rate constant and not on the concentration of the substance.**

Now let's figure out the equation for the **half-life of a second order reaction**. The integrated rate equation is $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$. Inserting $[A]_0/2$ as our final concentration and $t_{1/2}$ as our time and solving for the half-life, yields the equation

$$t_{1/2} = \frac{1}{[A]_0 k}$$

Therefore, for a second order reaction, the half-life, $t_{1/2}$, depends on the initial concentration.

Let's practice. WHAT IS THE HALF-LIFE OF A FIRST ORDER REACTION WHOSE RATE CONSTANT IS $5.78 \times 10^{-5} \text{ s}^{-1}$? WHAT IS THE RATE CONSTANT FOR A FIRST ORDER REACTION WHOSE HALF-LIFE IS 480 s?

We can also **use integrated rate equations to graphically determine the order of a reaction**. To see this let's begin with our integrated rate law for a **first order reaction**. By taking the natural log of both sides we get

$$\ln[A] = \ln [A]_0 - kt.$$

Note that this equation has the exact form of a straight line, $y = mx + b$, with $\ln[A] = y$, $t = x$, and the rate constant k the slope. Thus **if a reaction is first order, a plot of $\ln [A]$ vs t should yield a straight line**. If such a plot does not yield a straight line, then the reaction is not first order. If it does yield a straight line, then we have an extremely reliable way to determine the rate constant k .

Similarly, note that we can express our integrated rate equation for the second order reaction as $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$. Once again, if we graph $\frac{1}{[A]}$ vs kt this has the same form as a straight line, $y = mx + b$, except this time $y = 1/[A]$. Thus for this case, **if we have a second order reaction, a graph of $1/[A]$ vs t will give us a straight line** with a slope of k . So you see that we can use graphical methods to determine the order of a reaction and the rate constant.