Lecture 33

At the beginning of the semester I stated that we can describe the realms of kinetics and thermodynamics by stating that thermodynamics tells us what can happen, while **kinetics** tells us how fast it can happen. For example, thermodynamics tells us that the reaction

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

has an equilibrium constant greater than 10^{37}, yet we can place a mixture of H_2 and Cl_2 in a darkened container for upwards of a hundred years without a noticeable reaction occurring. Does this mean that thermodynamics is wrong? Of course not! What it does point out is that while **thermodynamics tells us a great deal about chemical equilibria, it tells us nothing about how quickly equilibrium is attained**.

Perhaps this last phrase with its emphasis on the word equilibrium helps bring about another level of understanding of the different realms of thermodynamics and kinetics. **Thermodynamics is limited to systems in equilibrium, while kinetics can treat systems in disequilibrium**.

Kinetics has a wide array of applications. By studying the concentration dependence of reactions we can determine the optimum concentration conditions for running a reaction, the rate-determining step of the mechanism, and the mechanism of the reaction itself. The temperature dependence of reactions tells us the optimum temperature for running reactions, the energy of activation for the reaction and information about microscopic mechanisms.

Most of the efforts of modern chemical kinetics have been focused on elucidation of **microscopic mechanisms.** To help understand the distinction between microscopic and macroscopic mechanisms consider the reaction

$$H_2 + 2ICl \rightarrow I_2 + 2\,HCl$$

When we study the concentration dependence of the reaction rates we discover that it is consistent with the reaction being broken down into two steps, both of which involve reactions between no more than two molecules.

$$H_2 + ICl \rightarrow HI + HCl$$

$$HI + ICl \rightarrow I_2 + HCl$$

These reactions are called elementary reactions because they proceed as written in a single chemical step. **This breakdown of a complex reaction into a series of elementary reactions is what we mean when we talk about a macroscopic mechanism.** Macroscopic mechanisms of reactions are the types of mechanisms we'll be focusing on in Chem 309. When we discuss **microscopic mechanisms**, we're considering an **elementary reaction** like the first step

$$H_2 + ICl \rightarrow HI + HCl$$

and asking questions like

- How do transitional, vibrational, and rotational energies affect the efficiency of the reaction?
- How do the bond lengths change as the reaction proceeds?
- What, if any, are the intermediates and how stable are they?
- How do reaction geometries affect reaction rates?
- How does energy flow between the various degrees of freedom of the molecule?

In other words, a microscopic mechanism is a detailed description of all of the processes that can affect an elementary reaction, and of the processes that occur during an elementary reaction.

On to **classical kinetics**. We begin with a quick review of elementary concepts. The first of these concepts is **reaction stoichiometry**. If we have a general reaction,

$$aA + bB + \ldots \rightarrow \ldots + yY + zZ$$

the lower case letters represent the stoichiometric coefficients. The stoichiometric coefficient for the i^th species is ν_i, where ν_i is greater than zero for products, and ν_i is less than zero for reactants. These ν_i are the same ν_i we used in studying the thermodynamics of chemical reactions.

It is important to note that **these stoichiometric coefficients are for the overall reaction, and may not be valid for the entire course of the reaction.** The reason is that an equation representing the overall reaction ignores any intermediates that may form in the course of the reaction. If these build up in appreciable amounts there will be times when the balance of reactants and products does not follow the overall stoichiometry. Such a reaction has **time dependent stoichiometry**. An example of this is the thermal decomposition of acetone, which has the stoichiometry

$$2CH_3COCH_3 \rightarrow 2CH_4 + C_2H_4 + 2CO$$

The overall **reaction mechanism** includes the steps

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4$$

and

$$2CH_2CO \rightarrow C_2H_4 + CO$$

In the course of the reaction significant amounts of ketene, CH_2CO, can build up. The presence of the ketene will clearly affect the stoichiometry at early and intermediate times in the reaction, since the presence of significant amounts of ketene means that less ethylene and carbon monoxide have formed.

In contrast the reaction

$$H_2 + Br_2 \rightarrow 2HBr,$$

while having a very complex mechanism, results in little or no buildup of reactive intermediates so that the stoichiometry of the overall reaction is the reaction stoichiometry at all times. This type of stoichiometry is called **time independent stoichiometry**.

Suppose we have a reaction with time independent stoichiometry

$$2A + 3B \rightarrow Y + 2Z$$

and at time t, the amounts of our reactants are given by n_A, n_B, n_Y and n_Z, while initially at time 0, the amounts are n_{A0}, n_{B0}, n_{Y0}, and n_{Z0}. We can relate the changes in the amounts of these various reactants and products by

$$\frac{n_A - n_{A0}}{-2} = \frac{n_B - n_{B0}}{-3} = \frac{n_Y - n_{Y0}}{1} = \frac{n_Z - n_{Z0}}{2}$$

In general **the change in amount of the i^{th} substance in the reaction mixture is given by**

$$n_i - n_{i0} = \nu_i \zeta$$

where ζ is our extent of reaction from chemical thermodynamics. Note again that the extent of reaction is a positive number when our reaction proceeds from reactants to products, and is the same for all species in the reaction.

We are interested, of course, in **rates of reactions**, so we need to quickly define our terms. For our reaction

$$2A + 3B \rightarrow Y + 2Z,$$

the rate of consumption of A will be referred to as v_A. **If we assume that the volume of the solution is constant, the rate of consumption for a reactant is defined as the negative of the change in concentration of A per unit time,**

$$\mathbf{v_A} = \frac{-d[A]}{dt},$$

while for products, we speak of the rate of formation, given by

$$\mathbf{v_Y} = \frac{d[Y]}{dt}.$$

Note that if we plot [A] vs t, in general the slope changes with time so that the rate of change of concentration at time t_1 is not equal to the rate of change of concentration at some other time t_2. If we take the slope of the change of concentration with time at t = 0, we call the rate the **initial rate of consumption** for reactants, or the **initial rate of formation** for products.

The rates of change of the various species in the system are related by their stoichiometric coefficients by

$$v_A = 2/3 v_B = -2v_Y = -v_Z.$$

Clearly it is confusing to have a different rate describing the kinetics of each of the species in the reaction mixture. We can avoid this by defining **the rate of reaction as**

$$\mathbf{v} \equiv \frac{d}{dt}\left(\frac{\zeta}{V}\right).$$

With the simplifying assumption that the volume remains constant during the reaction this becomes

$$\mathbf{v} = \frac{1}{\nu_i}\frac{dc_i}{dt}$$

where c_i is the concentration of the i^{th} species in units of moles per liter. In the event that the volume also changes we find that the rate of reaction has two terms and for some substance B is given by

$$v = \frac{1}{\nu_B}\frac{d[B]}{dt} + \frac{[B]}{\nu_B V}\frac{dV}{dt}.$$

The first term is the derivative of extent of reaction normalized to unit volume, while the second term corrects for the effect of the change of volume on the concentration when the reaction composition changes.

The equation is derived as follows. We begin with our equation for rate of reaction for some substance B,

$$v = \frac{1}{\nu_B V}\frac{dn_B}{dt}.$$

At any given concentration we can write $n_B = [B]V$. Differentiating this for the case where both [B] and V can change yields

$$dn_B = [B]dV + Vd[B].$$

Inserting this into our first equation yields

$$v = \frac{1}{\nu_B}\frac{d[B]}{dt} + \frac{[B]}{\nu_B V}\frac{dV}{dt}.$$

It is usually not necessary to consider the terms for change of volume for reactions in solution, where volume changes are usually negligible. However for gas phase reactions at constant pressure, where volume changes can be substantial, the more complicated treatment can be necessary.

All of you should be familiar with rate equations from general chemistry. I'd like to review them quickly. In general, rate equations are equations that relate the rate of a chemical reaction to the concentrations of the species present in the reaction mixture, i.e.

$$\mathrm{v} = f([A],[B],[C]...)\ .$$

Note that this equation can be something very complicated such as

$$v = \frac{k_1[A]^{3/2}[C]}{k_2[A]+k_{-1}[B]}$$

or something as simple as

$$v = k_1[A]$$

In these example equations, the substances A, B, C etc, can be reactants, products, intermediates or catalysts.

For some reactions, the rate of reaction can be expressed by a particularly simple equation of the form

$$\mathrm{v} = \mathrm{k}[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}\ldots$$

where the concentrations of reactants and catalysts can be included in the equation and where k, α, and β are independent of the concentration and of time. It is important to emphasize that this simpler rate equation is not going to work for all reactions. It is also important to recognize that these rate equations are strictly empirical.

The rate of consumption of a given species will be represented by the equation

$$\mathrm{v}_\mathrm{A} = \mathrm{k}_\mathrm{A}[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}$$

where α and β are the same exponents as for the overall reaction, and k_A is related to k by

$$\mathrm{k}_\mathrm{A} = \mathrm{k}|\nu_\mathrm{A}|$$

So for our reaction

$$2A + 3B \rightarrow Y + 2Z,$$

$$k = k_A/2 = k_B/3.$$

The exponent α is called the **order of the reaction with respect to A**. Similarly the exponent β will be called the order of the reaction with respect to B. **α and β are called partial orders**. The sum of the partial orders,

$$\alpha + \beta + ... = n,$$

is called the **order of the reaction**. Once again I wish to emphasize that **α and β are empirical quantities**. They are not necessarily integral, not necessarily positive, and not necessarily related to the reaction stoichiometry.

The simplest case of a rate law is when the rate is linear with the concentration of a single reactant, i.e.

$$v = k[A].$$

This is called a **first order reaction**. If the rate depends on the square of the concentration of a single reactant, or the product of two reactant concentrations, i.e.,

$$v = k[A]^2$$

or

$$v = k[A][B],$$

the reaction is said to be **second order**. The constant k, once again is called the rate constant.

The rate constant depends on the temperature and the chemical identity of the reactants. Its dimensions depend on the order of the reaction. For example, for any reaction we have

$$v = \frac{1}{\nu_i V}\frac{dn_i}{dt}$$

which has units of moles L^{-1} s^{-1}. So for a first order reaction, since $v = k[A]$, and concentration has units of moles L^{-1}, the units of k must be s^{-1}. However, for a second order reaction with rate law $v = k[A]^2$, k must have units of $l\ mol^{-1}\ s^{-1}$.

It is important to note that **not all reactions have well defined orders**. The famous Michaelis-Menten Law of enzyme kinetics has the form

$$v = \frac{V[A]}{k_m + [A]},$$

which does not have a well-defined order.

At this point it is useful to distinguish between elementary and composite, or complex, reactions. An elementary reaction is one that occurs in a single chemical step, with no experimentally detectable reaction intermediates. If no such intermediates can be detected or need to be postulated to interpret the behavior of the system, a reaction is assumed tentatively to be elementary. However, it must be borne in mind that further experimental work may reveal that a reaction originally believed to be elementary in reality occurs in more than one step. For example, the reaction

$$H_2 + I_2 \rightarrow 2HI$$

was long believed to be elementary. However the reaction now is known to occur in part by a mechanism involving the following elementary steps:

$$I_2 \leftrightarrow 2I$$

$$I + H_2 \rightarrow HI + H$$

$$H + I_2 \rightarrow HI + I$$

The **molecularity of an elementary reaction** is the number of reactant particles (atoms, molecules, free radicals or ions) that are involved. If one reactant particle is involved then the reaction is said to be unimolecular. If two are involved the reaction is bimolecular, three trimolecular, etc. Note that in general, the molecularity is distinct from the order. In general, the molecularity tells us mechanistic details of a reaction, while the order simply tells us the dependence of the reaction rate on the concentration of a reactant.

Composite reactions are those that involve more than one elementary reaction. The term molecularity has no meaning for a composite reaction.

It is convenient to number the reactions that make up a composite reaction in such a way that reverse reactions are identified easily. For this reason the reverse of reaction 1 is referred to as reaction -1, and the rates and rate constants are denoted by corresponding subscripts, for example v_1, v_{-1}, k_1 and k_{-1}.

A composite reaction mechanism sometimes includes a cycle of reactions such that certain reaction intermediates consumed in one step are generated in another. If such a cycle is repeated more than once, the reaction is known as a chain reaction.

For example, if hydrogen and bromine react in the gas phase and the product HBr is removed as fast as it is formed the reaction is believed to proceed by the following steps:

(1) $Br_2 \xrightarrow{k_1} 2Br$ Initiation

(2) $Br + H_2 \xrightarrow{k_2} HBr + H$ Chain Propagation

(3) $H + Br_2 \xrightarrow{k_3} HBr + Br$ Ditto

(-1) $Br + Br \xrightarrow{k_{-1}} Br_2$ Termination

Reactions (2) and (3) constitute a cycle and are known as chain-propagating steps; in reaction (2) a bromine atom is produced which is consumed in reaction (3) while in reaction (3) a hydrogen atom is produced which is consumed in reaction (2). Under normal conditions this cycle occurs a number of times, and the reaction is therefore a chain reaction. Reaction (1), which produces active intermediates, is known as an initiation reaction, and its reverse, reaction (-1) is called a termination step or chain ending step. Chain reactions always involve initiation and termination steps and two or more chain-propagating steps.

Lecture 34

Last time we noted that one of the goals of chemical kinetics is to determine the way in which reaction rates depend on concentration. There are **two primary methods of analyzing concentration data** to determine its effect on reaction rates, the differential method and the integral method. In both methods the basic data are concentration vs. time curves.

In the **differential method**, the **slope of the concentration versus time curve** is analyzed. To see how this is done, remember that if a reactant has order n with respect to a given reactant, then the rate can be written as

$$\mathrm{v} = \frac{1}{\nu_i}\frac{dc}{dt} = kc^n$$

If we take the log of both sides we get

$$\log \mathrm{v} = \log kc^n = n \log c + \log k.$$

Thus **a plot of log v vs log c will have a slope equal to the order**.

Empirically there are two ways to get the concentration data. In both methods, it is critical to remember that a rate is determined from the slope of a concentration vs time curve. The first method is to change the initial concentrations, determine the initial slope, and plot the log of the initial rate vs the log of the initial concentration. The order is then the slope of the log-log plot. The order determined by this method is labeled n_c, to indicate that the initial concentrations were changed.

The alternative method is to follow the concentration of one sample over time, and to determine the rate at various points in the course of the reaction. Plots of log v vs log [ ] then yield the order. Orders determined this way are labeled n_t. It is important to note that **n_t is not necessarily equal to n_c**. The reason is that **when the reaction is followed over time, intermediates may build up which change the rate of reaction, and therefore the apparent order of the reaction**. We see from this that n_c and n_t each provide useful information that the other does not. n_c shows the concentration dependence under initial conditions. n_t shows us the order based on conditions averaged over the whole course of the reaction. In addition, comparison of the two shows whether additional species need to be considered in the rate law. Once n_c or n_t is determined for one of the reactants, the procedure is repeated for each reactant, catalyst and product to determine the overall rate law.

The alternative method for determining the order of reaction for each substance is called the **method of integration.** Basically this method is to **guess an order for the reaction, see what the concentration dependence should be and compare the prediction with the experimental results**. We will solve the concentration equation for four cases - first order, second order in one substance, second order overall with two reactants having partial orders of one, and then finally the general case of nth order in one substance.

The simplest example of a **first order reaction** would be an elementary reaction of the form

$$A \rightarrow Z,$$

but more complex reactions like

$$2A \rightarrow Z$$

or

$$A + B \rightarrow Z$$

could be first order reactions as well. Remember, there is not necessarily any relationship between the stoichiometry of a reaction and its order.

For the first of these reactions, at t = 0, we have [A] = a_0, and at some time t later we have [A] = a_0 – x, where x is the amount of A consumed at time t. Therefore the rate of consumption of A is given by

$$v_A = -\frac{d(a_0 - x)}{dt} = \frac{dx}{dt}.$$

Since the reaction is first order we can write

$$\frac{dx}{dt} = k_A(a_0 - x)$$

Separation of variables and integration yields

$$-\ln(a_0 - x) = k_A t + c$$

Finally evaluation of the constant of integration yields our integrated rate equation

$$\ln\left(\frac{a_0}{a_0 - x}\right) = k_A t$$

Therefore if our reaction is first order, a plot of $\ln\left(\frac{a_0}{a_0 - x}\right)$ vs t will be linear with a slope of k_A.

Note that this result is exactly equivalent to

$$\ln\left(\frac{[A_0]}{[A]}\right) = k_A t\ .$$

There are two possibilities for **second order reactions**. The first is that the reaction is second order in a single reactant, i.e.,

$$v_A = k_A(a_0 - x)^2,$$

where a_0 - x is the concentration of A at time t. Once again note that this rate law could arise from the same range of reactions as our first order reaction, including

$$A \rightarrow Z$$

$$2A \rightarrow Z$$

and

$$A + B \rightarrow Z.$$

The differential rate law for a reaction which is second order in one reactant is

$$\frac{dx}{dt} = k_A(a_0 - x)^2$$

When we collect variables, integrate and evaluate the constant of integration, we find that our integrated rate law is

$$\frac{x}{a_0(a_0 - x)} = k_A t$$

Therefore a plot of $\frac{x}{a_0(a_0 - x)}$ vs t will yield a straight line with slope k_A when the reaction is second order in one reactant. Note that this result is equivalent to

$$\frac{1}{[A]} - \frac{1}{[A_0]} = k_A t\ .$$

Interestingly, if we have a reaction which has an overall order of two, but which has partial orders of 1, i.e., for reactants A and B,

$$v = k\,[A][B],$$

the result is completely different. If we let $[A] = a_0 - x$ and $[B] = b_0 - x$, then our differential equation is

$$\frac{dx}{dt} = k_A(a_0 - x)(b_0 - x)$$

This is a fairly difficult integral to solve, but can be solved in one of three ways. The oldest and least recommended is to use the method of partial integration. It works fine but it's just too much work. The second is to look it up in a table of integrals. Third, you could use a symbolic manipulation program like Mathematica or Maples to do the integration. No matter what method you use, when you carry out the integral and evaluate the constants of integration, the rate law is

$$\frac{1}{a_0 - b_0}\ln\left[\frac{b_0(a_0 - x)}{a_0(b_0 - x)}\right] = kt$$

There are tables available where you can find the integrated rate laws for a wide variety of reaction orders and a wide variety of initial conditions. **In each case you determine the order of your reaction by plotting your data according to the appropriate integrated rate equation and testing for linearity.**

A reaction of general order n in one reactant, where n is greater than one, would have the rate expression

$$v = -\frac{d[A]}{dt} = k[A]^n .$$

A simple integration of this expression yields the result

$$\frac{1}{(n-1)}\left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) = kt ,$$

where [A] is the concentration of A at time t, and $[A]_0$ is the initial concentration of A.

When the reaction rate depends on the concentration of only one reactant, it is relatively easy to determine the rate law. It is more work for a reaction in which the rate depends on several species, whether they are reactants, products, or catalysts. If the rate of consumption is relatively slow, then we can simply use the method of initial rates, varying the initial concentration of each species in turn. However, this method presupposes that the concentrations of the species which we are not varying are either constant or are changing slowly enough that their changes do not affect the apparent order of the reaction. As an example, consider the bromination of acetone. The reaction here is

$$CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr.$$

The rate of reaction is a function of the concentrations of bromine, acetone, and a catalyst, H^+, so our rate equation is

$$v = k\,[H^+]^\alpha[CH_3COCH_3]^\beta[Br_2]^\gamma,$$

where α, β and γ are the orders we wish to determine. Now suppose that while we are examining the effect of changing the bromine concentration on the reaction rate, the acetone concentration is also changing rapidly. This would distort the results of the bromine study.

One solution to this is the **method of isolation** in which all of the species in the reaction except one are present in large excess. In effect what this does is to keep the concentrations of all species but one approximately constant. This means that the observed order of the reaction will be the partial order of the species under consideration. Thus if our rate law is

$$v = k\,[A]^\alpha[B]^\beta[C]^\gamma,$$

and we isolate A, the order of the reaction will be α. If we now repeat the experiment isolating B and C in turn, we can determine the overall rate law for the reaction.

The fact that we can isolate a single component, and therefore simplify the rate law means that the method of integration can still be used for relatively complex systems, since the integrated rate laws involving only a single substance are all simple.

Another measure of reaction rates that can also be used to distinguish between reaction orders is the **half-life**. The **half-life is the time necessary for the concentration of a substance**

to be reduced to half its initial value. The half-life of a substance is determined by the integrated rate law of the reaction. For a first order reaction the rate law is

$$\ln\left(\frac{a_0}{a_0 - x}\right) = k_A t$$

If we substitute $t = t_{1/2}$ and $x = a_0/2$, we find that **for a first order reaction**

$$t_{1/2} = \frac{.693}{k}$$

We will find in general that the half-life is inversely proportional to the rate constant.

For a reaction that is **second order in one reactant**, the rate law is

$$\frac{x}{a_0(a_0 - x)} = k_A t$$

Substituting $t = t_{1/2}$ and $x = a_0/2$ yields

$$t_{1/2} = \frac{1}{a_0 k_A}$$

Note that **for this case, the half-life depends on the initial concentration**. In fact we find that **for all reactions with orders other than one that the half-life depends on the initial concentration**. Note that once again we are talking of the half-life of the reactant, and not the reaction. Consider the reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{Z},$$

where $a_0 \neq b_0$. Since the initial amounts of the substances are not equal, the half-lives cannot be equal. Clearly in this case it is not meaningful to speak of reaction half-lives. In general, **it is meaningful to speak of reaction half-lives only when the reactants are present in their stoichiometric ratios**. For example, in the case we just discussed, if $a_0 = b_0$, then we can talk about reaction half-lives. Similarly for a reaction with stoichiometry

$$A + 3B \rightarrow Z,$$

we can only talk about reaction half lives if $b_0 = 3a_0$. Otherwise it is only meaningful to speak of reactant half-lives.

We can write an equation for the half life of a general reaction of order n>1 for a single reactant, based on our integrated equation for a reaction with order n. It is

$$t_{1/2} = \frac{\left(2^{n-1} - 1\right)}{k\left(n-1\right)\left[A\right]_0^{n-1}}.$$

We can see from this equation that a plot of the log of $t_{1/2}$ vs the log of $[A]_0$ can be used to determine the reaction order. To see this we take the log of the equation above to get

$$\log t_{1/2} = \log \frac{\left(2^{n-1} - 1\right)}{k\left(n-1\right)} - \left(n-1\right)\log\left[A\right]_0.$$

Thus a plot of log $t_{1/2}$ vs log $[A]_0$ will have a slope of n-1, where n is the order.

Half-lives have the useful property that they can be used to compare how fast two reactions with different orders will proceed. This is one case where the half life is more transparent than the rate constant, since the rate constants for reactions with different orders will have different units and will be difficult to compare. We can also use half-lives for a relatively quick determination of whether a reaction is first order. If the reaction is first order we can measure the half-life for two or more different initial concentrations, and it will not change, while for higher order reactions the half life will be dependent on the initial concentration.

How do these methods for determining rate laws compare? **If you know very little about the reaction the differential method is best** for the following reasons. First, if the log-log plot is linear, then the reaction has an order. Second, by distinguishing between n_t and n_c it helps us detect the presence of intermediates in the reaction. Third, it allows us to find non-integral orders if they are present. **The main advantage of the integral method is that it may provide more accurate rate constants than the differential method**. A disadvantage is that a reaction may have a non-integral order, yet fit one of our integrated rate laws fairly well. This means that it is not too hard to get at least slightly incorrect orders from the integral method. A second disadvantage is that the integral method gives us only n_t, since n is obtained by following the concentration over time.

Lecture 34

At this point we've covered rate laws for first and second order reactions that go only toward products, i.e.,

$$A \rightarrow Z$$

or

$$A + B \rightarrow Z.$$

However, **many reactions proceed in both directions** under normal reaction conditions, i.e.,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z$$

where k_1 is the rate constant for the forward reaction and k_{-1} is the rate constant for the reverse reaction. Suppose that both the forward and the reverse reactions are first order, the initial concentration of A is a_0 and the initial concentration of Z is 0. After a time t has elapsed, the concentration of A is $a_0 - x$, and the concentration of Z is x. Therefore at time t, the rates for the two reactions are

$$v_1 = k_1 (a_0 - x),$$

where v_1 is the rate of production of Z, while for the reverse reaction

$$v_{-1} = k_{-1} x$$

where v_{-1} is the rate of consumption of Z. Thus the overall rate of the reaction should be given by the difference between the rates of the forward and reverse reactions,

$$v = \frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x .$$

If the two reactions proceed until equilibrium is achieved, then there is no longer a net production or consumption of Z, so the overall rate becomes 0 and we can write

$$0 = k_1 (a_0 - x_e) - k_{-1} x_e$$

where x_e is the equilibrium concentration of Z. If we use this to eliminate k_{-1} from our rate equation, our differential equation becomes

$$\frac{dx}{dt} = \frac{k_1 a_0}{x_e}(x_e - x)$$

If we integrate this equation and apply the boundary condition that x = 0 at t = 0, we get

$$\frac{x_e}{a_0}\ln\left(\frac{x_e}{x_e - x}\right) = k_1 t$$

Note the similarity of this equation to the integrated rate law for a first order reaction, which we derived earlier.

The first conclusion we draw from this is that **if both opposing reactions are first order, equilibrium is approached exponentially**. It is also apparent that we can determine k_1 by plotting $\frac{x_e}{a_0}\ln\left(\frac{x_e}{x_e - x}\right)$ vs t. **How could we determine x_e?** [By measuring x(t). x_e will be the asymptotic value.] Note that **the biggest difference between a simple first order reaction and opposing first order reactions is that the simple first order reaction approaches a concentration of reactants of 0 exponentially, while the opposing first order reactions approach equilibrium exponentially**.

Once we have determined k_1 we can also determine k_{-1} because the equilibrium constant is given by

$$K_{eq} = \frac{k_1}{k_{-1}}$$

To see this remember that at equilibrium the change in concentration of Z = 0, so the reaction rate is zero. This means that we can write

$$0 = k_1 (a_0 - x_e) - k_{-1} x_e.$$

This can be rewritten as

$$\frac{k_1}{k_{-1}} = \frac{x_e}{a_0 - x_e}$$

But $x_e = [Z]_{eq}$, and $a_0 - x_e = [A]_{eq}$. Making this substitution yields

$$\frac{k_1}{k_{-1}} = \frac{[Z]_{eq}}{[A]_{eq}} = K_{eq}$$

We've noted already that for opposing first order reactions the equilibrium is approached exponentially, but what will be the rate constant for the process? We begin with the equation

$$\frac{x_e}{a_0}\ln\left(\frac{x_e}{x_e - x}\right) = k_1 t$$

At equilibrium we have

$$0 = k_1 (a_0 - x_e) - k_{-1} x_e,$$

which can be rewritten as

$$\frac{x_e}{a_0} = \frac{k_1}{k_1 + k_{-1}}$$

Substituting this in our equation for x as a function of t yields

$$\ln\left(\frac{x_e}{x_e - x}\right) = (k_1 + k_{-1})t$$

So **the rate constant with which the system approaches equilibrium is the sum of the rate constants of the forward and reverse reactions.** This result is not necessarily intuitive. If for example, k_1 is large, and k_{-1} is small, many of us would assume that k is the average of the two. The result we've obtained tells us something very different, that adding any additional first order process, no matter how slow, to the mechanism increases the overall rate of the reaction.

This is an important result, because the opposing reactions can be viewed as parallel first order processes,

$$A \xrightarrow{k_1} Z$$

and

$$A \xleftarrow{k_{-1}} Z\ ,$$

and because we can generalize our results to any set of parallel first order processes. The rule is simply that the overall rate constant for change in concentration of a species affected by n parallel first order processes is just the sum of the rate constants of those processes,

$$k = \sum_{i=1}^{n} k_i\ ,$$

where k is the overall rate constant, and the k_n's are the rate constants of the individual parallel processes.

The significance of this is that many processes that are important in understanding the dynamics of chemical processes are intrinsically first order. For example, in photochemistry, we are interested in the rates of reactions once a molecule has been activated by absorption of a UV or visible photon,

$$A \xrightarrow{h\nu} Z\ .$$

The first step of this reaction is the creation of an excited state of the reaction,

$$A \xrightarrow{h\nu} A^*\ .$$

The yield of the reaction and rate at which it proceeds are directly tied to the concentration of A* as a function of time.

There are several different first order processes that can reduce the concentration of A*. One, of course, is reaction,

$$A^* \xrightarrow{k_1} Z\ .$$

A second is fluorescence,

$$A^* \xrightarrow{k_f} A\,.$$

A third is intersystem crossing, the conversion of a singlet excited state to a triplet excited state,

$$A^* \xrightarrow{k_{isc}} A^{triplet}\ .$$

A fourth would be thermal relaxation to the ground state,

$$A^* \xrightarrow{k_{thermal}} A\,.$$

Our rule tells us that the overall rate constant for the decay of A* is given by

$$k = k_1 + k_f + k_{isc} + k_{thermal}\,,$$

and that the decay of A* with time is given by

$$A^*(t) = A^*(0)e^{-kt}\ ,$$

where A*(t) is the population of A* at time t, and A*(0) is the initial population of A*.

A related concept to this overall rate constant is the lifetime of the species, τ . For a first order process, τ is defined as the time that it takes for the population of a species to be reduced to 1/e of its initial value. It is easy to show that for a first order reaction,

$$A \xrightarrow{k_1} Z\ ,$$

the lifetime is given by

$$\tau = \frac{1}{k_1}\,,$$

while for a pair of first order reactions approaching equilibrium,

$$\tau = \frac{1}{k} = \frac{1}{k_1 + k_{-1}}\,.$$

We see that for a set of parallel first order processes affecting the population of some species,

$$\tau = \frac{1}{k} = \frac{1}{\sum_i k_i},$$

and therefore for our photochemical process,

$$\tau = \frac{1}{k} = \frac{1}{k_1 + k_f + k_{isc} + k_{thermal}}.$$

An interesting conclusion from this discussion, as noted above, is that any time any process that affects the population of a reactant, no matter how slow, is added to a mechanism, the rate of change of that reactant is increased, and consequently, its lifetime is decreased.

An important pair of concepts related to the kinetics of chemical equilibria are the principle of microscopic reversibility, and the principle of detailed balance at equilibrium. The principle of microscopic reversibility can be expressed as follows: “In a system at equilibrium, any molecular process and the reverse of that process occur, on the average, at the same rate.” The principle of detailed balance, which is very similar, but deals with collision processes, including reactive collisions, states that in a system at equilibrium each collision has its exact counterpart in the reverse direction, and that the rate of every chemical process is exactly balanced by that of the reverse process.

These are powerful concepts, but often incorrect conclusions are drawn if they are used incorrectly. In particular, they can only be applied to processes that are both elementary and at equilibrium. For example, we concluded that for any reaction, the ratio of rate constants for forward and reverse reactions is equal to the equilibrium constant. However, rate constants are most typically measured for systems in disequilibrium, and this conclusion is not necessary correct for other than equilibrium conditions.

When we studied chemical equilibria, one of the questions that we asked was how the equilibrium constant changed when we change the temperature of our system. Now that we are studying the rates of chemical reactions we want to ask a similar question - how does temperature affect the rate of a chemical reaction?

In all of the models that we are going to consider there is one common assumption: that **all of the temperature dependence is contained in the rate constant**, i.e.,

$$v(T) = k(T)\, [A]^{\alpha}[B]^{\beta}[C]^{\gamma}....$$

Van't Hoff, who was responsible for our equation for the temperature dependence of the equilibrium constant, derived the following equation for the temperature dependence of the rate constant. He began with his equation for the temperature dependence of the equilibrium constant,

$$(\frac{\partial \ln K_{eq}}{\partial T}) = \frac{\Delta U^0}{RT^2}$$

In our discussion of the kinetics of opposing reactions, we showed that when equilibrium has been reached,

$$K_{eq} = \frac{k_1}{k_{-1}}$$

If we substitute this into the Van't Hoff equation, we get

$$\frac{\partial \ln k_1}{\partial T} - \frac{\partial \ln k_{-1}}{\partial T} = \frac{\Delta U^0}{RT^2}$$

where k_1 is the rate constant for the forward reaction and k_{-1} is the rate constant for the reverse reaction. Van't Hoff's real contribution here was to suggest that the **energy ΔU° is the difference between a characteristic forward energy and a characteristic reverse energy**, i.e.,

$$\Delta U^{\circ} = E_1 - E_{-1},$$

and that the energy of the forward reaction affected only the rate constant of the forward reaction, while the energy of the backward reaction affected only the rate constant of the backward reaction.

This means that we can separate our equation into two separate equations,

$$\frac{\partial \ln k_1}{\partial T} = \frac{E_1}{RT^2}$$

and

$$\frac{\partial \ln k_{-1}}{\partial T} = \frac{E_{-1}}{RT^2} .$$

Integrating the equation and dropping the subscripts yields

$$k = Ae^{-E/RT}$$

where A is a constant which we shall discuss shortly. This equation is commonly known as the **Arrhenius equation**, which states that the rate constant increases with increasing temperature, and that the effect of increasing the temperature depends on a preexponential factor, A, and a parameter E which we call the **activation energy**.

This is the equation that you probably used in general chemistry. It is still the most widely used equation for the analysis of the temperature dependence of reaction rates. So the big question is, why did they call this equation after Arrhenius, when Van't Hoff derived it in the late 19th century? Why isn't this called the Van't Hoff equation?

One possible answer is that there already was a Van't Hoff equation and they needed another name for this one. This explanation doesn't work though, since as any mathematician knows there are biiillions and biiillions of Euler equations. If mathematicians can handle all of these Euler equations, we chemists can handle a few measly Van't Hoff equations.

The real reason is that at the time of Van't Hoff, there were two other simple equations to explain the temperature dependence of rate constants. One of them even provides a slightly better fit to temperature data than the equation of Van't Hoff and Arrhenius. However, no one was able to come up with a physical model to explain these other two equations. Arrhenius's contribution was to provide a simple physical picture to explain Van't Hoff's equation.

In Arrhenius's picture, **the activation energy is the barrier to reaction**. In order for a reaction to occur, molecules must have energies greater than or equal to this barrier. The temperature dependence arises from the way that the percentage of molecules having energies greater than or equal to this barrier changes with temperature. This percentage is described by the Boltzmann factor, $e^{-\frac{E}{kT}}$, which describes the fraction of molecules having a given energy at a given temperature. The factor tells us that at a given energy, E, the higher the temperature, the more molecules there will be that have that energy, which explains why rates of reaction increase with temperature. It also tells us that as the required energy E increases at a given temperature, the fraction of molecules that have that required energy decreases, which explains why, at a given temperature, a molecule with a higher activation energy generally reacts more slowly than one with a lower activation energy. This is the modern view of the activation energy. It is because the Arrhenius equation is the one that gives us physical insight into the reaction process that it is the one that has survived.

Since the activation energy is a positive quantity, the majority of reactions have k increasing with temperature. For some reactions, however, the rate decreases with temperature, implying a negative activation energy. A negative activation energy is physically meaningless. When a negative activation energy is obtained, what is actually occurring is that the activation energy is zero, and the preexponential factor A slowly decreases as T increases. Such reactions are generally complex, involving the formation of a weakly bound intermediate species. An example is the recombination of iodine atoms in the presence of a third body M, which proceeds via the following steps:

$$I + M \rightarrow IM$$

$$IM + I \rightarrow I_2 + M$$

The IM species is a van der Waals complex whose stability decreases with increasing temperature.

It is still possible to improve on the Arrhenius equation. In the Arrhenius equation it is assumed that the preexponential factor A is temperature independent. This is not rigorously true. In most cases, where E is substantial, the temperature dependence due to the exponential term is so large that it masks the temperature dependence of A. However, in cases where E_a is close to zero, the temperature dependence of the reaction rate will reflect both the temperature dependence of the preexponential factor and that due to the exponential term. In some cases where plots of ln k vs 1/T are not linear, better fits can be obtained with the equation

$$k = AT^m e^{-E/RT}$$

for which there is also theoretical justification.

What is the source of the temperature dependence of the pre-exponential factor, A? Remember that in adopting the Arrhenius equation, we're dividing the temperature dependence of the reaction rate into the effect of the activation process, contained in the term $e^{-\frac{E_a}{RT}}$, and the effects of all other factors, contained in the preexponential factor, A. To get a sense of the reason for the temperature dependence of A we'll consider two factors that contribute to the value of A for a given reaction – the collision frequency, and the steric factor.

It should be fairly obvious that collision frequency will affect the rate at which a reaction occurs. The Arrhenius factor only shows the effect of energy on a reaction once the reactants have met. The rate at which they meet, which is described by the collision frequency, is also a critical factor in determining reaction rates. It should also be clear that the rate of collisions increases as temperature increases, since the average speed of a molecule at a given temperature is given by

$$\langle \mathrm{v} \rangle = \left(\frac{3kT}{m} \right)^{1/2} .$$

While this makes it apparent that collision rates are important in determining the rates of reactions such as bimolecular and termolecular reactions, in which more than one reactant has to meet, it turns out that collision rates are critical for determining the rates of unimolecular reactions as well. The reason for this is that collisions between molecules are the main mechanism for providing a molecule with sufficient energy to overcome the activation barrier.

The other critical factor in the pre-exponential factor is the steric factor. The steric factor recognizes that for a reaction to occur, it is usually not just necessary for two species to collide, but for the right parts of the two molecules to strike each other. For example in the reaction

$$K + CH_3I \rightarrow KI + CH_3 ,$$

it is necessary for the potassium atom to collide with the iodine atom for the reaction to proceed. However, if the potassium collides with the methyl group, no matter how high the collision energy is, the reaction will not proceed. So we can see from this that there will be orientations of the potassium relative to the methyl iodide at which no collision will result in a reaction.

Why does this lead to temperature dependence? We need to be aware that the orientations of the reactant molecules relative to each other are not static. Vibrations and especially rotations of the molecules have the effect of presenting different parts of the reacting molecules to each other, even in the course of an individual collision. Of course, the higher the temperature is, the greater the degree of rotation, and the greater the degree of vibration, and these temperature dependences appear in the temperature dependence of the preexponential factor. Once again, it needs to be emphasized that the temperature dependence of the preexponential factor is typically smaller than that of the Arrhenius factor, and that therefore, unless activations energies are small, or rate data extremely precise, it is typically not observed.

To summarize, our equation of first resort is the Arrhenius equation,

$$k = Ae^{-E/RT}$$

From it we extract the activation energy, which we formally define as

$$E_a = -R\frac{\partial \ln k}{\partial(1/T)}.$$

This definition is important because it means that the activation energy is defined even if the plot of ln k vs 1/T is not linear. Let’s see what this means. This is a somewhat exaggerated example of a nonlinear ln k vs 1/T plot. The activation energy is the slope of this plot. If the plot is curved it means that the activation energy is temperature dependent.

But it also means something else. Remember that

$$k = Ae^{-E_a/RT}$$

So the intercept of the ln k vs 1/T line is the ln of the preexponential factor. Note that when the plot is curved and the activation energy is temperature dependent that the preexponential factor is temperature dependent as well.

Now if our plot of ln k vs 1/T had been linear, we would have determined E_a from the slope, and A from the intercept, and we would have been done. However, current practice is to fit kinetic data that does not yield a straight line to

$$k = AT^m e^{-E_0/RT}.$$

Note that the energy in this equation is labeled E_0 rather than E_a. What is the relationship between these two quantities? We can determine this by taking the log of the above equation to obtain

$$\ln k = \ln A + m \ln T - \frac{E_0}{RT}$$

and then applying our definition of E_a,

$$E_a = -R\frac{\partial \ln K}{\partial(1/T)}$$

This yields

$$E_a = E_0 + mRT.$$

This gives a simple physical interpretation to E_0. It is the activation energy the reaction would have if it could be run at absolute zero. Note that for a reaction where the plot of ln k vs 1/T is linear, E_a and E_0 are identical.

Lecture 35

So far in determining the rate equations for chemical reactions we have limited ourselves to integrating simple rate laws. I'd like to return to complex reactions, and the relationships between their mechanisms and their rate laws. As noted earlier, most chemical processes are not elementary, but are composed of a sequence of elementary reactions. A reaction that takes place through more than one elementary reaction is called a composite reaction, and the sequence of elementary reactions by which the composite reaction takes place is called the reaction mechanism.

How do we tell experimentally whether a reaction is elementary or composite? As we noted earlier, this can be extraordinarily difficult. However, there is one clear distinction between elementary and composite reactions. That is that the rate law for an elementary reaction can be deduced from the balanced equation for the reaction. For an elementary reaction of the form,

$$aA + bB \rightarrow cC + dD,$$

the rate law is

$$v = k[A]^a[B]^b,$$

where the partial orders of the reactants A and B are the same as the stoichiometric coefficients for the reaction. Thus if we determine a rate law for a reaction, and the partial orders are different than the stoichiometric factors, the reaction is composite. However, the converse is not necessarily true - if the partial orders are the same as the stoichiometric factors, the reaction is not necessarily elementary, since a composite reaction may have a mechanism that yields a rate law that appears to be that of an elementary reaction. Thus while comparison of partial orders and stoichiometric coefficients can conclusively tell us that a reaction is composite, it can only suggest that a reaction may be elementary.

As an example, the gas phase reaction between nitric oxide and hydrogen has the balanced equation

$$2NO + 2\ H_2 \rightarrow N_2 + 2H_2O.$$

If this reaction were elementary, the reaction would be fourth order with a rate law

$$v = k[NO]^2[H_2]^2.$$

However, the experimentally determined rate law for the reaction is

$$v = k[NO]^2[H_2],$$

and the reaction is third order. Therefore the reaction is composite.

One of the reasons that reactions involving many reactants are usually composite reactions is that collisions involving large numbers of reactants are very improbable. Thus collisions involving three reactants are less likely than collisions involving two reactants, and collisions involving four or more reactants are even less likely. Thus reactions involving more than three reactants will proceed more efficiently as a series of unimolecular, bimolecular or trimolecular reactions in a composite reaction.

Composite reactions can be made up from elementary reactions in a number of ways. One is when two or more reactions occur in parallel, known as simultaneous reactions. An example of two simultaneous reactions would be

$$A \rightarrow Y$$

$$A \rightarrow Z,$$

where reactant A can form two different products. Sometimes the simultaneous reactions result in competition for a reactant such as the case

$$A + B \rightarrow Y$$

$$A + C \rightarrow Z$$

where B and C compete with one another for A.

Reactions that occur in forward and reverse directions are called opposing reactions, i.e.

$$A + B \rightleftharpoons Z,$$

where the reactions $A + B \rightarrow Z$ and $Z \rightarrow A + B$ are opposing.

Reactions occurring in sequence such as

$$A \rightarrow X \rightarrow Y \rightarrow Z$$

are known as consecutive reactions and the overall process is said to occur by consecutive steps. Reactions are said to exhibit feedback if a substance formed in one step affects the rate of a previous step. For example in the scheme

$$A \xrightarrow{1} X \xrightarrow{2} Y \xrightarrow{3} Z$$

the intermediate Y may catalyze reaction 1 (positive feedback) or inhibit reaction 1 (negative feedback). Positive feedback is also known as autocatalysis. Negative feedback is also known as inhibition.

Now suppose we have some composite reaction,

$$2A + B + C \rightarrow Y + Z.$$

We propose a mechanism, or a sequence of elementary reactions, for this composite reaction. How do we know if this mechanism is reasonable? The simplest answer is that we measure the empirical concentration behavior of the reactants and products and compare this to the behavior predicted by the mechanism. What this implies is that we must develop tools for working out rate equations for composite reactions.

Let's look at a simple example, the sequence

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$$

$$X \xrightarrow{k_2} Z$$

In the first step of the mechanism we have opposing reactions in which A reacts to form an intermediate X and X reacts to form A. In the second step, X reacts to form Z.

The most basic form of the rate equation is the differential rate equation. It is extremely useful because, as we will soon find out, finding integrated rate equations for even relatively simple composite mechanisms gets difficult very quickly and is often impossible, but even for complex mechanisms it is relatively easy to work out the differential rate equations. This differential rate law can then be tested by measuring concentration vs time and then either calculating the slopes of the curves or by numerically integrating the rate law on a computer.

In our simple example we want to write rate laws for three species, A, X and Z. Let's begin with A. There are two reactions that affect the concentration of A, reaction 1, which consumes A and reaction –1, which produces A. The rate of reaction, $-\frac{d[A]}{dt}$, is the difference between the rate of consumption of A in reaction 1, given by $k_1[A]$ and the rate of production, given by $k_{-1}[X]$, i.e.,

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X]$$

For X, the rate of formation is the difference between the rate at which X is formed and the rate at which it is destroyed. All three reactions affect the concentration of X, with two, reactions -1 and 2, consuming it and one, reaction 1, forming it. The rate of formation of X is given by

$$\frac{d[X]}{dt} = k_1[A] - k_{-1}[X] - k_2[X] = k_1[A] - (k_{-1} + k_2)[X]$$

Finally, the rate law for Z is trivial, involving only one elementary reaction, and is given by

$$\frac{d[Z]}{dt} = k_2[X].$$

It is easy to see how this procedure for generating differential rate equations for each species could be generalized to very complex reactions.

It is possible to come up with integrated rate laws for the simplest of complex reactions. Consider, for example, the two step sequential reaction,

$$A \xrightarrow{k_1} X$$

$$X \xrightarrow{k_2} Z$$

We can write rate laws for each of the three species. We've already shown that the integrated rate law for A is

$$[A] = [A]_0 e^{-k_1 t}$$

To find the integrated rate law for [X] we need to begin by writing out the differential rate law for X. WHAT IS THE DIFFERENTIAL RATE LAW FOR X?

$$\frac{d[X]}{dt} = k_1[A] - k_2[X].$$

If we substitute our equation for [A] in this equation it becomes,

$$\frac{d[X]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[X].$$

Using techniques of differential equations, this equation can be integrated to obtain,

$$[X] = \frac{[A]_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

To find [Z] as a function of time, we need to turn to a concept called **material balance**. The concept is simply that the amount of matter in the system has to stay constant throughout the reaction. Remember that at time zero, all of the matter in the system is in the form of A. Therefore, because of the stoichiometry, the total number of molecules in the system at any time must equal $[A]_0$ as well, i.e.,

$$[A] + [X] + [Z] = [A]_0, \text{ or}$$

$$[Z] = [A]_0 - [A] - [X].$$

Finally substituting our equations for [A] and [X] and simplifying yields

$$[Z] = \frac{[A]_0}{k_2 - k_1}(k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t}))\ .$$

It should be noted that for reactions with more complex stoichiometry, the materials balance equation would be more complicated.

If we look at the time dependence of the concentration of each of the species, we see that [A] decays exponentially as shown earlier. [X] shows a more complex behavior, growing in exponentially and then decaying as the rate of reaction 2 increases relative to reaction 1. Finally, we have [Z] growing with a sigmoidal growth curve, with zero initial slope. Note that since formation of X is necessary for formation of Z, the onset of Z formation is delayed.

Obtaining integrated rate equations even for this simple composite reaction was involved.

It would be useful to develop some tools that allow us to simplify the process of determining rate laws for complex equations. One particularly important tool is the **steady state approximation**. It is applicable when a slow elementary reaction is immediately followed by a fast one. For the sequential reaction we just studied, it would be useful for those cases where $k_2 >> k_1$.

Let's look at the evolution of the [X] under these circumstances. When $k_2 >> k_1$, the second reaction, which consumes X, is much faster than the first, which produces it. As a result, the [X] does not rise very far before it drops down again. After a short time the [X] settles down to a small approximately constant level. This is what we mean when we refer to the steady state. A wealth of experimental results has led to the following generalization: "The rate of change of an intermediate can be approximately set to zero whenever it is formed slowly and consumed rapidly."

To see the power of the steady state approximation, let's return to the mechanism,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$$

$$X \xrightarrow{k_2} Z$$

Our differential rate laws were

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[X]$$

$$\frac{d[X]}{dt} = k_1[A] - (k_{-1} + k_2)[X]$$

$$\frac{d[Z]}{dt} = k_2[X].$$

It is often useful to eliminate [X] from our equation for [Z], since the concentrations of intermediates often cannot be determined reliably, and since we wish to understand the effect of reactant A, which we can control, on the rate of formation of Z. We can eliminate [X] by using the steady state approximation. In this case, if $k_{-1} + k_2 >> k_1, \frac{d[X]}{dt} \approx 0$. The significance of this result is that under these conditions, we can easily express the [X] in terms of the [A], i.e.,

$$k_1[A] = (k_{-1} + k_2)[X]$$

and

$$[X] = \frac{k_1[A]}{k_{-1} + k_2}.$$

If we substitute this in our equations for [Z] and [A] we get,

$$\frac{d[Z]}{dt} = \frac{k_2 k_1}{k_{-1} + k_2}[A] \text{ and } -\frac{d[A]}{dt} = k_1\left(1 - \frac{k_{-1}}{k_{-1} + k_2}\right)[A].$$

THE STEADY STATE APPROXIMATION IS APPLIED ONLY TO INTERMEDIATES AND NOT REACTANTS OR PRODUCTS. WHY?

The steady state approximation is only one way of simplifying the job of writing rate laws of composite reactions. Another reasonable question to ask, especially in a lengthy mechanism, is whether we need to consider all of the steps in a mechanism in working out the rate law.

Consider the following case. In the reaction,

$$H_2(g) + Br_2(g) \leftrightarrow 2HBr(g)$$

The mechanism of the reaction has been proposed to be

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 2Br + M \quad \textit{fast equilibrium}$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \quad \textit{slow}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \quad fast$$

In the second step of this sequence bromine atoms and H_2 react slowly to form H atoms that are quickly consumed in the third step. It should be apparent that the third step can't proceed until the second step produces the H atoms, and that therefore the overall reaction can proceed no faster than reaction 2. In such a case we call reaction 2 the **rate-determining step**, and the overall rate of the reaction is equal to the rate of step 2,

$$v = k_2[Br][H_2].$$

As before we wish to express this rate law in terms only of reactants and products, and therefore we wish to eliminate [Br] from this equation. This becomes easy because of the slowness of reaction two. Since this implies that $k_2 << k_{-1}$, the opposing reactions come quickly to equilibrium, and [Br] is essentially independent of reaction 2. Since the opposing reactions come quickly to equilibrium we can solve easily for [Br] in terms of $[Br_2]$ by writing an equilibrium expression for the opposing reactions, i.e.,

$$K_c = \frac{k_1}{k_{-1}} = \frac{[Br]^2[M]}{[Br_2][M]}$$

which implies in turn that

$$[Br] = (\frac{k_1}{k_{-1}}[Br_2])^{1/2}$$

and the overall reaction rate is given by

$$v = \frac{1}{2}\frac{d[HBr]}{dt} = k_2(\frac{k_1}{k_{-1}})^{1/2}[Br_2]^{1/2}[H_2]\,.$$

So we see that a number of useful tools exist to simplify the process of determining rate laws for complex mechanisms.

It is important to realize that the both the rate determining step and the steady state approximation are most typically used to help in the process of deducing the mechanism of a complex reaction from experimental kinetic measurements. In most cases the way that the approximations are used is to suggest a mechanism based on all available information about the reaction, and then to use the approximations to see if the mechanism can correctly explain the experimental observations. A good match between the observations and the predicted rate behavior validates the approximations, although in the case of the steady state approximation, direct detection of the intermediate is the best validation.

Detailed balance and microscopic reversibility, which we discussed earlier, have consequences for complex reactions. As noted earlier, for an elementary reaction, the equilibrium constant must be the ratio of the rate constants in the forward and reverse directions. Thus, consider the process

$$A + B \rightleftharpoons Y + Z$$

in which the reactions in the forward and reverse directions are elementary. The rates in the two directions are

$$v_1 = k_1[A][B]$$

and

$$v_{-1} = k_{-1}[Y][Z].$$

If the system is at equilibrium, these rates are equal; hence,

$$\frac{k_1}{k_{-1}} = \left(\frac{[Y][Z]}{[A][B]}\right)_{eq} = K_c$$

where K_c is the equilibrium constant.

This argument can be extended to a reaction that occurs in two or more stages. Consider, for example the reaction

$$H_2 + 2ICl \rightleftharpoons I_2 + 2HCl\,,$$

which occurs in two steps. At equilibrium the processes are occurring at equal rates in the forward and reverse directions:

$$(1)\quad H_2 + ICl \rightleftharpoons HI + HCl$$

$$(2)\quad HI + ICl \rightleftharpoons HCl + I_2$$

Thus at equilibrium,

$$k_1[H_2][ICl] = k_{-1}[HI][HCl]$$

$$k_2[HI][ICl] = k_{-2}[HCl][I_2]\,.$$

The equilibrium constant for each reaction is thus

$$K_1 = \frac{k_1}{k_{-1}} = \left(\frac{[HI][HCl]}{[H_2][ICl]}\right)_{eq}$$

$$K_2 = \frac{k_2}{k_{-2}} = \left(\frac{[HCl][I_2]}{[HI][ICl]}\right)_{eq}$$

The product of these two equilibrium constants is

$$K_1K_2 = \frac{k_1k_2}{k_{-1}k_{-2}} = \left(\frac{[I_2][HCl]^2}{[H_2][ICl]^2}\right)_{eq} = K_c$$

where K_c is the equilibrium constant for the overall reaction. For any mechanism, involving any number of elementary and consecutive steps, the overall equilibrium constant is the product of the equilibrium constants for the individual steps, and is the product of the rate constants for the reactions in the forward direction divided by the product of those for the reverse reactions:

$$K_c = K_1 K_2 K_3 \bullet\bullet\bullet = \frac{k_1 k_2 k_3 \bullet\bullet\bullet}{k_{-1} k_{-2} k_{-3} \bullet\bullet\bullet}$$

If a reaction occurs by a complex mechanism, and we measure a rate coefficient k_1 for the overall reaction from left to right and also measure a rate coefficient k_{-1} for the overall reaction from right to left, at the same temperature, the ratio k_1/k_{-1} is not necessarily the equilibrium constant for the overall reaction. The reason is that the rate laws for composite reactions change with the experimental conditions, such as reactant concentrations, and the rate coefficients also change. The ratio of the rate coefficients k_1 and k_{-1} that apply when the system is at equilibrium is equal to the equilibrium constant, but rate coefficients determined away from equilibrium are not necessarily the same as those at equilibrium, and their ratio is not necessarily equal to K_c. Therefore, great caution should be used in deducing rate coefficients and rate laws for reactions from the equilibrium constant and the rate coefficient for the reverse reaction.

As an example of a situation where the ratio of the rate constants is not the equilibrium constant, consider the reaction system

$$A \underset{-1}{\overset{1}{\rightleftharpoons}} X \underset{-2}{\overset{2}{\rightleftharpoons}} Z$$

If the system is at complete equilibrium,

$$\left(\frac{[X]}{[A]}\right)_{eq} = \frac{k_1}{k_{-1}},$$

$$\left(\frac{[Z]}{[X]}\right)_{eq} = \frac{k_2}{k_{-2}}$$

and

$$\left(\frac{[Z]}{[A]}\right)_{eq} = \frac{k_1 k_2}{k_{-1} k_{-2}} = K_c$$

If one makes measurements of the rate of consumption of A at the very beginning of the reaction, before any X and Z have accumulated,

$$-\frac{d[A]}{dt} = k_1[A]$$

and the first-order rate constant is k_1. Similarly, if one starts with pur Z and measures initial rates of consumption of Z, the rate constant obtained is k_{-2}. In general, the ratio k_1/k_{-2} is not equal to the equilibrium constant K_c.