# CHEM-203 Survey of Physical Chemistry

## Office hours (OM224):

## Lecture summaries for Chemical Kinetics

LMS 9.1 to 9.4, skip 9.5. do not skip 9.6 to 9.8; of 9.9 Do only Transition State theory (skip hard sphere collision theory, quantum tunneling); skip section 9.10.

Chapter 10, Intro, 10.1 to 10.5, only Enzyme Catalysis in 10.9

**Problems**

Chapter 9
Rate Constants and Order of Reaction 9.1 - 9.21
Temperature Dependence 9.25 - 9.32, 9.34, 9.36 - 9.37
Collision Theory and Transition State Theory 9.38 - 9.42, 9.44 - 9.51

Chapter 10
Composite Mechanisms and Rate Equations 10.1 - 10.8, 10.10, 10.12, 10.15
Catalysis 10.24, 10.27 - 10.34
Enzyme-Catalyzed Reactions 10.35 - 10.36, 10.39, 10.44 - 10.45

**The Final Examination will cover ONLY the parts of chapter 4 that was NOT covered in the second midterm, and all of chemical kinetics, summarized here:**

Summary of lecture 29
Summary of lecture 30
Summary of lecture 31
Summary of lecture 32
Summary of lecture 33
Summary of lecture 34
Summary of lecture 35
Summary of lecture 36
Summary of lecture 37

**Summary Lecture 29** (Top)

References: Laidler, Meiser, Sanctuary (LMS), Physical Chemistry,

Sections 9.1 to 9.4;

**The Plan and overview**

1. Obtain the rate equation for a chemical reaction: $v_A = k_A[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}...$ this separates out the concentration dependence of the rate.
2. The rate constant $k_A$ is not really a constant. It is, however, independent of concentration. It contains the details of the reaction. It is large or small or whatever because of what happens. It depends on temperature, the way molecules collide, solvents, catalysts and any other experimental conditions.
3. The temperature dependence is usually handled by the Arrhenius expression: $k(T) = A\exp\left(-\frac{E^*}{RT}\right)$ which simply says that to produce the most energetic species in the chemical reaction, you must have enough thermal energy, $RT$. The energy $E^*$ is the energy of that activated complex, as it is called. If we consider that complex to be a chemical species, then we can apply thermodynamics to it. This is called **Transition State Theory**.
4. Finally, as we get deeper into what is going on and we study the pre-exponential factor, $A$. The simplest approach is to consider the collisions are between hard spheres. The advantage is it can be solved exactly. The disadvantage is it rarely works. The most common result is to evaluate it from Transition State theory. We will not do hard spheres. We will summarize Transition State Theory.

Of course the details of molecular collisions are extremely difficult problems. The difficulty is that the actually mechanisms are usually much more complicated than single collisions. For this reason, chemical kinetics is more of an empirical or experimental science. The theory gives us insight into what goes on in simple systems.

**The Basics**

Chemical kinetics is the study of how the concentrations of reactions change over a period of time through chemical reactions. In contrast, thermodynamics tells us only what can happen, not how fast. For example, oil in the ground is thermodynamically unstable with respect to burning to mostly carbon dioxide and water. However oil sits in the ground for millions of years and does not burn. In order for it to burn, the conditions need to be right. In that case, we must supply oxygen and either some initiator, a spark, or heat.

An uncountable number of chemical reactions are going on all the time. Most of these are “fed”, which means that as the reactants are consumed and products formed, the reactants are replenished. This keeps a reaction going. If the reactants are not replenished, eventually, some equilibrium is attained, consistent with thermodynamics, and the reaction stops.

We write reactions like:

$$\text{reactants} \rightarrow \text{products} \tag{1.1}$$

This means that the reactants change to products in one direction. Sometimes there are forward and reverse, microscopic reversibility, processes going on, so we write,

$$\text{reactants} \rightleftarrows \text{products} \tag{1.2}$$

Sometimes there is a whole series of processes going on, for example,

$$\begin{aligned} &\text{reactants} \rightleftarrows \text{intermediate(1)} \rightarrow \text{product(1)} \\ &\qquad \rightarrow \text{intermediate(2)} \rightleftarrows \text{intermediate(3)} \rightarrow \text{product(2)} \\ &\text{etc.} \end{aligned} \tag{1.3}$$

Each step competes with others. Some may be slow and others fast. They can depend on conditions, like temperature, solvents, catalysts and concentrations.

More specifically, it is customary to use chemical notation and write specific reactions, for example

$$C_8H_{18}(g) + \frac{25}{2}O_2(g) \xrightarrow{\text{spark}} 8CO_2(g) + 9H_2O(g) \tag{1.4}$$

All such equations must be balanced. There is a lot going on behind this equation. All this says is that hydrocarbons burn, but does not depict how the actual process of making and breaking bonds happens. We are after understanding the mechanisms. That is the goal. In organic chemistry, for example, you have heard of elimination reactions (*E*1, *E*2), or nucleophilic substitution reactions ($S_N1$ and $S_N2$). A large number of reactions fall into these categories. There are many more. To study a certain type of reaction, we usually write them generically as, say,

$$A + 2B \rightarrow X + 3Z \tag{1.5}$$

**Experiments and theory**

Chemical kinetics is mostly an experimental science. One defines the system and conditions in a laboratory, and uses experimental techniques to follow how fast reactions take place. There are methods to follow both slow and extremely fast reactions. Once the data is obtained, it is plotted.

**Empirical**: The plots of the data are usually some function of the concentrations, (like log[A], or $[A]^2$ ): [A] is the concentration of the reactant A in mol $L^{-1}$), that when plotted against time, gives us a straight line. This “plot-person-ship” (the politically correct replacement for “plotmanship”) important in classifying reactions. As we will see, it really does not matter which of A, B, X or Z is followed as all are related and all will give the same results. Hence we choose the most convenient chemical, which is usually the easiest one to monitor.

**Mechanisms**: However the goal of chemical kinetics is not to simply get data and plot straight lines. The goal is to understand how a reaction takes place (recall science asks “How?” not “Why?”). Once we understand a mechanism, then we can intervene and try to modify it. For example, suppose we understand how a certain protein causes a reaction to proceed and this is leading to something undesirable, like a disease. Biochemists attempt to find the Achilles heel of that reaction so they can stop it happening. Another example might be the depletion of ozone or the production of greenhouse gases. The chemical kineticist tries to recreate in the laboratory what s/he believes is going on in Nature and works on discovering the mechanism for the process.

Recall, of course, that chemical kinetics is the process of breaking some bonds and forming new ones. How this happens is often complicated.

Although we certainly believe some mechanisms are correct, all they do is rationalize empirical data, not prove that the molecules actually follow that particular mechanistic pathway.

Once a mechanism has been determined, as much as possible, one of the important empirical parameters obtained is the rate constant. These rate constants depend upon the details of the reaction process for each step. Generally these are obtained from experimental data. On the other hand, the rate constants depend upon the details of the reaction mechanism, as discussed above. Chemical bonds can only be described by quantum mechanics. It is usually difficult to apply quantum mechanics to predict rate constants. The usual procedure is to obtain values from experiment and then see if we can understand those values by making assumptions about the actual process that takes place.

In summary, chemical kinetics can be generally divided into two general categories:

- The empirical determination of the reaction rates
- The theoretical understanding of the reaction mechanisms

In this course, we start with the former and then, with a foundation in that, we turn to the latter.

**Progress variable**: A chemical reaction depends upon the number and type of molecules present. Suppose we start with a certain chemical, "*i*", so at the beginning of a reaction, the number of molecules present is $N_i^o$. At a certain time later, if this is a reaction, some have changed into products and are lost, so as the reaction proceeds, there are only $N_i\left(t\right)$ molecules left after time *t*. We can then define, ξ (Greek tse) as how much is left at that time,

$$\xi_i(t) = \left(N_i(t) - N_i^o\right) \tag{1.6}$$

which describes the progress of the reaction. Since we said that "*i*" was a reactant, $\xi_i(t)$ is negative in this case.

Do not be confused by the symbol, $\xi$, it is defined by the above equation and that's all. If it bothers you, change it so something else, like $a_i(t) = \left(N_i(t) - N_i^o\right)$ (" a rose by any other name…")

Following the number of particles is not the best way to track a reaction even though that is what is happening. This is because the number of particles is an extensive variable. It is usually much easier to deal with and measure intensive variables. Since the ratio of two extensive variables in an intensive variable, we can divide the number of particles by the volume of the sample. Moreover, we can also divide by the Avogadro constant, $L$, to convert the number of particles to moles. All this gives us what we might expect,

$$\begin{aligned} \frac{\xi_i(t)}{VL} &= \frac{\left(N_i(t) - N_{0i}\right)/L}{V} = \frac{\left(n_i(t) - n_{0i}\right)}{V} = \left(n_i(t)/V - n_{0i}/V\right) \\ &\equiv \left(\lambda_i(t) - \lambda_{oi}\right) \ \text{mol l}^{-1} \end{aligned} \tag{1.7}$$

where $n_i$ is the number of moles and $\lambda_i = \left[i\right]$ is the concentration of chemical $i$ at time $t$ in moles per liter. It is called a progress variable.

Frequently concentrations are not given in molar units but rather in molality. Concentration in molality is the number of moles per kilogram of solvent. This has an advantage over molarity because volume changes in reactions, thereby changing the concentrations other than molecules being changed; also volume is temperature dependent. Neither changes the mass of the solvent, hence molality is preferable when both volume changes and temperature changes are non-negligible.

We can write the rate for any chemical in a reaction as (drop the subscript i),

$$\text{Rate}_\lambda \equiv v_\lambda = \pm \frac{\mathrm{d}\lambda}{dt} \tag{1.8}$$

where loss of concentration (reactants) has a minus sign and gain in concentration, (products) has the plus sign. The quantity, $v_\lambda$, is called the rate or velocity of the reaction with respect to $\lambda$.

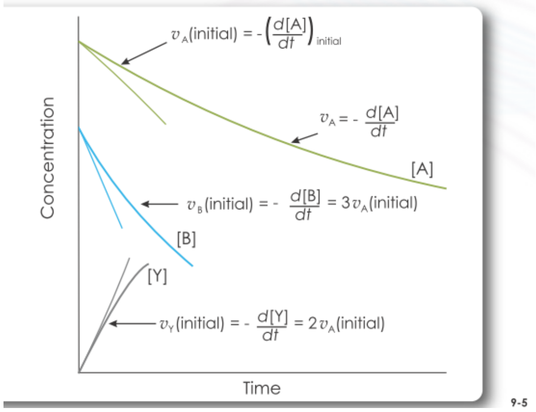
**Summary Lecture 30** (Top)

**Balance chemical equation:** It is important to always write down the balanced chemical reaction when referring to rate equations. It tells us overall what is going on. Consider the equation,

$$\mathrm{A + 3B \rightarrow 2Y} \tag{1.9}$$

See Figure 9.1 of LMS. These are typical plots. The information in the three curves is identical. Note the concentrations often vary with time in a non-linear way. Frequently, the initial rate is important to follow and this is given by the initial slope, or initial rate.

Any one of A, B or Y can be used to follow the time evolution of a reaction such as the one above. The choice of progress variable usually depends on what is the easiest chemical to monitor with time. Hence in the above reaction, $\lambda = [\mathrm{A}],\ [\mathrm{B}]$ or $[\mathrm{Y}]$ .



Let us suppose the easiest concentration to follow is A. Therefore we take λ=*A*. It follows we must have,

$$-\frac{\mathrm{d}\lambda}{dt} = -\frac{1}{1}\frac{\mathrm{d}[\mathrm{A}]}{dt} = -\frac{1}{3}\frac{\mathrm{d}[\mathrm{B}]}{dt} = +\frac{1}{2}\frac{\mathrm{d}[\mathrm{Y}]}{dt} > 0 \tag{1.10}$$

Note that in each case the integers in the denominators are the stoichiometric coefficients of the balanced chemical reaction, Eq.(1.9). We will denote such coefficients by the Greek letter *nu*, $\nu$ , so in the above, $\nu_{\mathrm{A}} = -1,\ \nu_{\mathrm{B}} = -3,\ \nu_{\mathrm{Y}} = 2.$ (do not confuse nu, $\nu$ , with velocity, *v*) and these coefficients are used when we modify the way we write chemical equations,

$$0 = -\mathrm{A} - 3\mathrm{B} + 2\mathrm{Y}$$

This simply states the rate of production of chemical B is three times faster than A is being consumed; and chemical Y is being produced at twice the rate that A is being consumed. This is consistent with the balanced chemical equation, (1.9)., and the above.

**Empirical Rate Equations**

Figure 9.1 shows plots of concentration against time generally are not straight lines (not linear). In a great many expressions, but not all, the velocity of a reaction proceeds according to an empirical equation like

$$v_A = k_A[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \tag{1.11}$$

In some cases, over a short reaction time, the rates fit to a certain order. For example, the Michaelis Menten equation is first order under some conditions and zeroth order under others.

Any rate, like Eq.(1.11), is, again, referring to the balanced chemical equation, (1.9). There is no simple relationship between the exponents of the concentration, $\alpha$ and $\beta$, and the stoichiometric coefficients (1, 3, 2) in the balanced chemical equation.

The **rate constant** is not really constant but can depend upon the temperature and **reaction coordinates** (the specific way the molecules are oriented relative to each other when they interact). The rate constant is, however, independent of the concentrations. Therefore the empirical rate equation separates out the concentration dependences from the rate constant.

Four types of reactions that follow Eq.(2.6) are:

Zeroth order:
First order: $v = k[\mathrm{A}]$
Second order (1): $v = k[\mathrm{A}]^2$
Second order (2): $v = k[\mathrm{A}][\mathrm{B}]$ initial conc. $[\mathrm{A}] \neq [\mathrm{B}]$

**Zeroth order** reactions are not common but are important in biochemistry. We will go through the metabolism of alcohol (ethanol).

**First order kinetics** is most common and leads to exponential growth or decay (*e.g.* radioactive decay). First order reactions commonly depend upon what goes on in one molecule only. That is, the rate depends only on the concentration of the reactant, such as in the ring opening of cyclopentane,

$$\Delta \longrightarrow \mathrm{CH_3\text{-}CH{=}CH_2} \qquad (1.12)$$

So the more you have, the more it produces: so the rate is proportional to the concentration.

There are many **second order reactions**. For example, the reaction:

$$\mathrm{H_2} + \mathrm{I_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\mathrm{HI} \qquad (1.13)$$

has a forward and reverse process given by

$$v_1 = -k_1[\mathrm{H_2}][\mathrm{I_2}] \text{ and } v_{-1} = k_{-1}[\mathrm{HI}]^2 \qquad (1.14)$$

The reason this is second order is it is necessary the hydrogen and iodine molecules collide. Hence the rate depends upon the probability of such a collision and such a probability depends upon the concentration of both reactants.

(Think physically: the above statement says: you need a collision between the hydrogen and iodine in order for the reaction to proceed. If conc. of hydrogen is high and iodine is low (or vice versa) then not many collisions will take place between the reactants. On the other hand, if the two concentrations are high, or equal, then collisions will take place and the reaction proceeds. That is why it is second order.

As the reaction proceeds, HI is produced. However this can collide with other HI molecules as their number increases. Hence as the concentration of HI increases, the forward reaction is inhibited.

Please try to look at the equations and think like that.)

Notice in the above example, Eq.(1.12), the mechanism is all in one step. Such a **concerted** (all in one step) reaction has the same orders as the stoichiometric coefficients.

**Concerted third order reactions** must have a triple interaction (collision). In the gas phase, such rates occur but they are rare and, in fact, third order rate laws are generally uncommon.

**Order of a reaction; non-integer rates and exceptions:** The exponents, $\alpha$ and $\beta$ are not necessarily integers and are called the **orders of the reaction**. Hence $\alpha$ is the order with respect to [A] and $\beta$ is order with respect to [B]. In this case, the overall order of the reaction is: $\alpha + \beta$.

The decomposition of acetaldehyde,

$$\mathrm{CH_3CHO \rightarrow CH_4 + CO} \qquad (1.15)$$

has the rate law with order 3/2,

$$v = k[\mathrm{CH_3CHO}]^{3/2} \qquad (1.16)$$

Some reactions do not follow an empirical rate law such as Eq.(1.11), for example Enzyme kinetics follows the **Michaelis-Menten** equation (which we will discuss later),

$$v = \frac{V[\mathrm{S}]}{K_m + [\mathrm{S}]} \qquad (1.17)$$

For a reaction:

$$\mathrm{E + S} \underset{\mathrm{k_{-1}}}{\overset{\mathrm{k_1}}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E + P} \qquad (1.18)$$

where E is an enzyme catalyst, S is the substrate, ES is the enzyme-substrate complex and P is the product. In Eq.(1.17), the maximum velocity is given by *V*. The Michaelis-Menten rate constant, $K_m$, depends upon $k_1$, $k_{-1}$ and $k_2$. When $K_m << [\mathrm{S}]$ then the substrate saturates the enzyme and the order is zeroth, $v = V$. When $K_m >> [\mathrm{S}]$ then the order is first, $v = \frac{V}{K_m}[\mathrm{S}]$.

**Mechanisms**: Equation (1.18) is an example of a mechanism. A mechanism shows the steps in the chemical reaction from start to finish. Note that in Eq.(1.14), all that is shown is a forward and reverse reaction. These are both second order. The mechanism depicts how a reaction happens and in many cases this is not simple. For example, a chain reaction has several steps:

$$H_2 + Br_2 \rightleftarrows 2HBr$$

| | | |
|---|---|---|
| $k_1$ | $Br_2 \xrightarrow{h\nu} Br\cdot + Br\cdot$ | initiation |
| $k_2$ | $Br\cdot + H_2 \rightarrow HBr + H\cdot$ | propogation |
| $k_3$ | $H\cdot + Br_2 \rightarrow HBr + Br\cdot$ | propogation |
| $k_4$ | $HBr + Br\cdot \rightarrow Br_2 + H\cdot$ | inhibition |
| $k_5$ | $Br\cdot + Br\cdot \rightarrow Br_2$ | termination |
| $k_6$ | $H\cdot + H\cdot \rightarrow H_2$ | termination |

When all these steps in this chain reaction are taken into account, the overall rate law is

$$v = \frac{k[H_2][Br_2]^{1/2}}{1 + [HBr]/\left(m[Br_2]\right)} \tag{1.19}$$

where the constants, *k* and *m* depend upon the individual rate constants, $k_i$, *i*=1,6. (Do NOT memorize this, but be ready to explain it if asked.)

**Summary**: chemical reactions follow some rate law and this is obtained empirically from experiment.

**Mechanisms** explain the step-by-step process of how a reaction follows. Usually there are several competing processes and several products. It is usual to try to understand the most abundant product and set up the experiments to by-products are minimized.

Chemical kinetics benefits from an understanding of mechanisms from theory. Primarily theory considers how molecules collide. Although the theory is well known, it is usually quite difficult to accurately calculate rate constants *a priori*. This is because it is difficult to know the forces that work between large molecules. Therefore the most common approach is to do careful experiments. From these the rate constants are obtained, often as a function of temperature and catalysts. Theory is then used to try to obtain the experimental values. If theory and experiment agree, then we believe we understand the detailed mechanisms.

**Summary Lecture 31** (Top)

**Empirical Rate Equations**

This section is all about table 9.1 in the text. You should know how to derive all those formulae in the table and understand what each entry means EXCEPT second order of the second kind (last line of table).

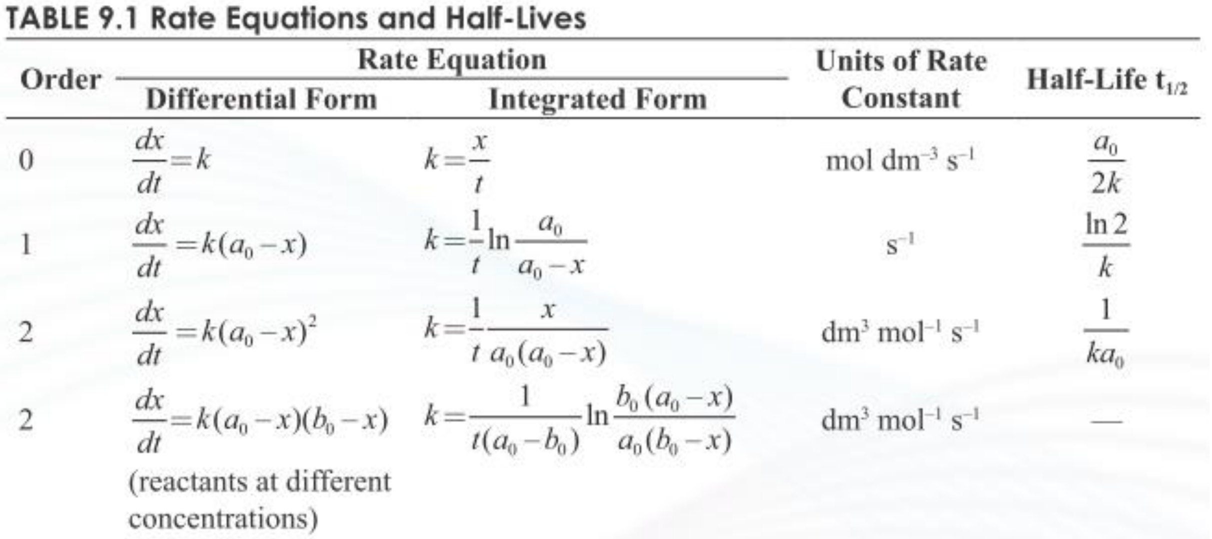


**TABLE 9.1 Rate Equations and Half-Lives**

| Order | Rate Equation: Differential Form | Rate Equation: Integrated Form | Units of Rate Constant | Half-Life $t_{1/2}$ |
|---|---|---|---|---|
| 0 | $\frac{dx}{dt}=k$ | $k=\frac{x}{t}$ | mol dm$^{-3}$ s$^{-1}$ | $\frac{a_0}{2k}$ |
| 1 | $\frac{dx}{dt}=k(a_0-x)$ | $k=\frac{1}{t}\ln\frac{a_0}{a_0-x}$ | s$^{-1}$ | $\frac{\ln 2}{k}$ |
| 2 | $\frac{dx}{dt}=k(a_0-x)^2$ | $k=\frac{1}{t}\frac{x}{a_0(a_0-x)}$ | dm$^3$ mol$^{-1}$ s$^{-1}$ | $\frac{1}{ka_0}$ |
| 2 | $\frac{dx}{dt}=k(a_0-x)(b_0-x)$<br>(reactants at different concentrations) | $k=\frac{1}{t(a_0-b_0)}\ln\frac{b_0(a_0-x)}{a_0(b_0-x)}$ | dm$^3$ mol$^{-1}$ s$^{-1}$ | — |

Experimental chemical kinetic data can be studied in two general ways. Consider the equation:

$$\mathrm{A} \rightarrow \mathrm{Z}$$

The rate law is found in **differential form**:

$$\frac{d[\mathrm{A}]}{\mathrm{d}t}=-k[\mathrm{A}]^{\alpha} \qquad (1.20)$$

This equation is found experimentally by taking the slopes of a plot of the concentration, [A](*t*) *vs*. time.

The second way of studying reaction rates is by the **method of integration**:

$$\int_{[\mathrm{A}]_o}^{[\mathrm{A}](t)}\frac{d[\mathrm{A}]}{[\mathrm{A}]^{\alpha}}=-k\int_o^t dt \qquad (1.21)$$

This gives the area under the curve of a rate law between two different times.

**Zeroth order** reaction:

$$\int_{[\mathrm{A}]_o}^{[\mathrm{A}](t)}d[\mathrm{A}]=-k\int_o^t dt \rightarrow \boxed{[\mathrm{A}](t)-[\mathrm{A}]_o=-kt}$$

Differential form: $\frac{d[\mathrm{A}]}{\mathrm{d}t}=-k$ the slopes of a plot of [A](*t*) *vs*. time (1.22)

Integrated form: (1.23)

Define $x = [\mathrm{A}]_o - [\mathrm{A}](t)$ so that we get the same form as in table 9.1 of text,

$$x = kt \quad \text{or } k = \frac{x}{t} \tag{1.24}$$

Since the units of concentration are moles $l^{-1}$, (moles dm$^{-1}$) then the rate constant must have the units of moles dm$^{-1}$ s$^{-1}$.

From Eq.(1.23), we can write,

$$[\mathrm{A}](t) = -kt + [\mathrm{A}]_o \tag{1.25}$$

which is the equation of a straight line if we plot $[\mathrm{A}](t)$ *vs. t*. This has a negative slope which gives the rate constant, *k*, and the intercept is the initial concentration, $[\mathrm{A}]_o$. It is plotted on the previous page.

**Half-life**: It is often useful to express a chemical reaction in terms of the time it takes for the initial concentration to drop to one half its original value,

$$[\mathrm{A}](t_{1/2}) = [\mathrm{A}]_o / 2 \tag{1.26}$$

From Eq.(1.23), we can write,

$$[\mathrm{A}]_o / 2 - [\mathrm{A}]_o = -kt_{1/2} \tag{1.27}$$

This tells us that the half-life for a zeroth order reaction is:

$$\boxed{t_{1/2} = \frac{[\mathrm{A}]_o}{2k}} \tag{1.28}$$

which is also found on table 9.1. It tells us that the half-life of a zeroth order rate is proportional to the initial concentration. Therefore, the time it takes to drop to one-half the original concentration depends on how large the initial concentration is.

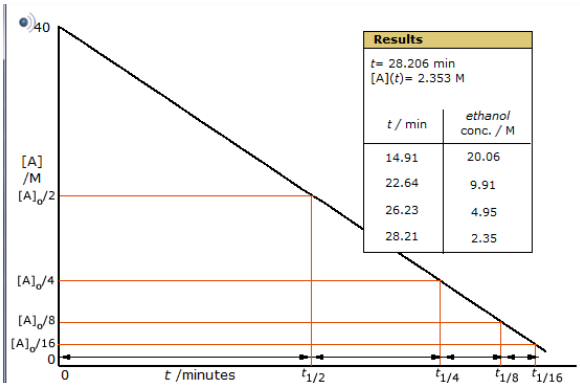
The metabolism of ethanol by the liver, discussed in class, is an important example of a zeroth order reaction,

$$\mathrm{CH_3CH_2OH} + \mathrm{NAD^+} \xrightarrow{\mathrm{LADH}} \mathrm{CH_3CHO} + \mathrm{NADH} + \mathrm{H^+} \tag{1.29}$$

where $NAD^+$ is the nicotinamide adenine dinucleotide ion which is catalyzed by LADH, Liver Alcohol Dehydrogenase. This forms a complex with $NaD^+$. (You do not have to remember these names). The rate law is

$$\frac{d\left[\mathrm{CH_3CH_2OH}\right]}{\mathrm{d}t}=-\frac{d\left[\mathrm{CH_3CHO}\right]}{\mathrm{d}t}=-k \qquad (1.30)$$

Suppose that one drink has a half-life of 30 minutes. Therefore, after 30 minutes, you liver has removed 50% of the ethanol from that one drink. Suppose this is the legal driving limit. How long do you have to wait if you drink more than one beer? Does 2 beer take one hour, 4 beers 2 hours? No, much longer.



**Results**

$t$= 28.206 min
$[A](t)$= 2.353 M

| $t$ / min | *ethanol* conc. / M |
|---|---|
| 14.91 | 20.06 |
| 22.64 | 9.91 |
| 26.23 | 4.95 |
| 28.21 | 2.35 |

Suppose you have two quick drinks. Now it takes 60 minutes to go from two drinks to one drink. It then takes another 30 minutes to go from one drink to half a drink. Therefore, if you drink two drinks it take 90 minutes to get to half a drink which is three times longer than it takes to metabolize one drink to half a drink.

If you have four fast drinks, it takes three and one half hours for this amount to drop to the level of half a drink in your body. That is, it takes seven times longer to metabolize four drinks to the same level as it takes you to metabolize one drink. (4 drinks to 2 drinks (two hours); 2 drinks to one drink (one hour) and one drink to half a drink (30 minutes) for a total of 3.5 hours.

You can rationalize this from Eq. (1.28).

For other reactions with different orders, we do the same: differential rate law, integrated rate law, half-life and plot that gives a straight line.

**First order rates**:

Differential form: $\frac{d\left[\mathrm{A}\right]}{\mathrm{d}t}=-k\left[\mathrm{A}\right]$ the slopes of a plot of $[A](t)$ *vs*. time (1.31)

Integrated form: $\int_{[\mathrm{A}]_o}^{[\mathrm{A}](t)}\frac{d\left[\mathrm{A}\right]}{\left[\mathrm{A}\right]}=-k\int_o^t dt \rightarrow \boxed{\ln\left(\left[\mathrm{A}\right](t)/\left[\mathrm{A}\right]_o\right)=-kt}$ (1.32)

Define $x=\left[\mathrm{A}\right]_o-\left[\mathrm{A}\right](t)$ so that we get the same form as in table 9.1 of text,

$$\ln\left\{\left[\mathrm{A}\right]_o/\left(\left[\mathrm{A}\right]_o-x\right)\right\}=kt \qquad (1.33)$$

The rate constant must have the units of moles $s^{-1}$ . This is exponential decay

$$[\mathrm{A}](t) = [\mathrm{A}]_o \exp(-kt) \tag{1.34}$$

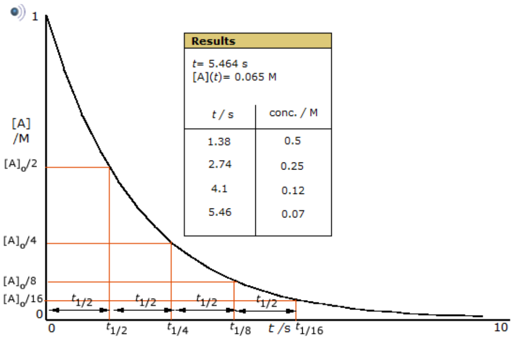
**Half-life**: from the definition of half-life,

$$[\mathrm{A}](t_{1/2}) = [\mathrm{A}]_o / 2 \tag{1.35}$$

and Eq.(1.32), we can write,

$$\ln\left(2[\mathrm{A}]_o / [\mathrm{A}]_o\right) = kt_{1/2} \text{ or } t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \tag{1.36}$$

which is also found on table 9.1. It tells us that the half-life of a first order rate is independent of concentration. Therefore, the time it takes to drop to one-half the original concentration is always the same, no matter what the concentration.



Results

$t$= 5.464 s
$[\mathrm{A}](t)$= 0.065 M

| $t$ / s | conc. / M |
|---|---|
| 1.38 | 0.5 |
| 2.74 | 0.25 |
| 4.1 | 0.12 |
| 5.46 | 0.07 |

**Double your money**: How long does it take your money to double if your interest rate is $k$? There is a rule in the investment industry: *"the time it takes your money to double is 70 divided by the interest rate in percentage*." (Actually th $\text{Double your money}=\dfrac{70}{\text{interest rate\%}}$ e correct answer is 69.3, not 70, so rounded off.)

You can see where this comes from. If money is compounded, say daily, it is almost **exponential growth**. (I did it in class),

$$[\mathrm{A}](t) = [\mathrm{A}]_o \exp(kt) \tag{1.37}$$

Therefore, for exponential growth, the time it takes for the initial investment, $[\mathrm{A}]_o$ to get to $2[\mathrm{A}]_o$ is $t_{1/2}$ .

An investment at 10% doubles every 7 years. Think of this in terms of, say, a pension. If you work for 35 years, a \$1,000 in your pension at the beginning of your career becomes \$32,000 at retirement 35 years later, doubles 5 times. (so the two truths about investing are: “*in the long run we will all be rich but in the long run we will all be dead*.” And the second is “*pigs get slaughtered*”.)

If the population of the Earth is 7 billion today and the population is growing at a rate of 1% a year, then the population will double about every 70 years (your life time), , the population of the Earth will be about 14 billion and in 2152 it will be 28 billion. That assumes that the growth is constant. However it is not and this will not happen because the Baby Boomers will kick the bucket and the population growth rate will decrease as education increases. It is expected that the Earth’s population will stabilize at about 10 Billion.

**Plot-person-ship**: From Eq.(1.33) we can plot, $\ln\left\{[\mathrm{A}]_o/\left([\mathrm{A}]_o-x\right)\right\}$ *vs. t* to get a straight line. The intercept gives us the first order rate constant. We can also write,

$$\ln\left([\mathrm{A}]_o-x\right)=-kt+\ln\left([\mathrm{A}]_o\right) \tag{1.38}$$

which gives a straight line when $\ln\left([\mathrm{A}]_o-x\right)$ is plotted against *t*. The slope is –*k* and the intercept is $\ln\left([\mathrm{A}]_o\right)$, See figure 9.2 of text.

**Summary Lecture 32** (Top)

**Second order rates**: By now you should see what is going on. For second order type (1) the equations are:

Differential rate law:

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}]^2 \tag{1.39}$$

Integrated rate law:

$$\int_{[\mathrm{A}]_o}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k\int_0^t dt \rightarrow \boxed{\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_o} = kt} \tag{1.40}$$

Half-life:

$$t_{1/2} = \frac{1}{k\left[\mathrm{A}\right]_o} \tag{1.41}$$

Equation of a straight line,

$$\frac{1}{[\mathrm{A}]} = kt + \frac{1}{[\mathrm{A}]_o} \tag{1.42}$$

So a plot of $\frac{1}{[\mathrm{A}]}$ vs. *t* gives a positive slope of *k* and an intercept of $\frac{1}{[\mathrm{A}]_o}$ .

Note that

- Zeroth order half-live are proportional to the initial concentration;
- First order half-lives are independent of initial concentration;
- Second order (type 1) half-lives are inversely proportional to the initial concentration.

Type (2) second order kinetics has a more complicated integrated form. I will just do the mathematics here (you do not have to reproduce it, but read the story and understand the words):

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}][\mathrm{B}] \tag{1.43}$$

Let $a_o = \left[\mathrm{A}\right]_\mathrm{o}$ and $b_o = \left[\mathrm{B}\right]_\mathrm{o}$, so at time *t*,

$$[\mathrm{A}](t) = a_o - x \text{ and } [\mathrm{B}](t) = b_o - x \tag{1.44}$$

Hence the differential rate law becomes,

$$\frac{dx}{dt} = k\left(a_o - x\right)\left(b_o - x\right) \tag{1.45}$$

Integrate

$$\int_0^x \frac{dx}{\left(a_o - x\right)\left(b_o - x\right)} = k\int_0^t dt = kt \tag{1.46}$$

If an integral exists then, if you cannot do it on your own, look it up in tables, if not found, use a computer. Integrals can always be evaluated. I will NOT ask you to do integrals more complicated than Eq.(1.40). The result from tables is,

$$\frac{1}{\left(a_o - b_o\right)} \ln \frac{\left(a_o - x\right)}{\left(b_o - x\right)} \Big|_0^x = kt \tag{1.47}$$

$$\frac{1}{\left(a_o - b_o\right)} \left[ \ln \frac{\left(a_o - x\right)}{\left(b_o - x\right)} - \ln \frac{a_o}{b_o} \right] = kt \tag{1.48}$$

$$\boxed{\frac{1}{\left(a_o - b_o\right)} \ln \frac{b_o\left(a_o - x\right)}{a_o\left(b_o - x\right)} = kt} \tag{1.49}$$

So you can see that it is necessary that the initial concentrations of the two species are different, $a_o \neq b_o$ . If they are equal, the type (2) reduces to type (1) second order chemical kinetics.

Using the definition of $x$ above, you should be able to obtain all the equations in table 9.1. The approaches used here are applied to all types of rate laws.

From the plots we can determine the rate law, at least over a certain time interval, and the rate constants.

In class I did not do the following examples. I do them here (typical exam questions).

I did three examples of using rate equations.

1. The unimolecular decay of $N_2O_5$
2. Carbon-14 dating
3. Second order rates for ozone depletion using 2nd order reactions.

1. At a certain temperature, the rate constant for the unimolecular decomposion of $N_2O_5$ is $10^{-5}$ $s^{-1}$.
    a. What is the rate if the conc. is a. 0.25 nd b. 0.50 mol $l^{-1}$?

**Solution**: since this is unimolecular, the process follows first order kinetics, so the rate is

$$\text{Rate}([\text{N}_2\text{O}_5]) - \frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

Therefore the initial rates are:

a. $\text{Rate}(0.50) = -10^{-5}\text{s}^{-1} \times 0.0 = -5\times10^{-6}\ \text{mol l}^{-1}\text{s}^{-1}$

b. $\text{Rate}(0.25) = -10^{-5}\text{s}^{-1} \times 0.25 = -2.5\times10^{-6}\ \text{mol l}^{-1}\text{s}^{-1}$

b. If the initial conc is 0.50 mol $\text{l}^{-1}$ what is the conc. after 100 hours.

Use the integrated rate law for first order kinetics:

$$\ln\left(\frac{[\text{N}_2\text{O}_5]_o}{[\text{N}_2\text{O}_5](t)}\right) = k\text{t}$$

$$\ln\left(\frac{0.5}{\text{x}(t)}\right) = 10^{-5}\,\text{t}$$

Solve for *x*

$$\ln(\text{x}(t)) = \ln(0.5) - k\text{t}$$

$$\ln(\text{x}(t)) = \ln(0.5) - 10^{-5}\text{s}^{-1} \times 100\ \text{hr} \times 60\frac{\text{min}}{\text{hr}} \times 60\frac{\text{s}}{\text{min}}$$

$$\boxed{\text{x}(t) = 1.37\times10^{-3}\ \text{mol l}^{-1}}$$

---

2. Carbon-14 dating: Assume the percentage of $^{14}{}_6$ c in a dead sample of wook is 54.9% that of the atmosphere. When did the tree die? Half-life of carbon-14 is 5770 years.

$$\ln\left(\frac{[{}^{14}_{6}\text{C}]}{[{}^{14}_{6}\text{C}]_o}\right) = \ln(0.549) = -kt = \frac{0.693}{t_{1/2}}t = -\frac{0.693}{5770}t$$

Solve for *t* $\boxed{t = \frac{5770}{0.693}\ln(0.549) = 4990\ \text{years}}$

3. The rate constant for the depletion of ozone is $k$=1.2 x $10^{10}$ $cm^3$ $mol^{-1}$ $s^{-1}$ for

$$NO+O_3 \rightarrow NO_2+O_2$$

   a. Suppose $[NO]_o = [O_3]_o$=0.10
   b. Suppose $[NO]_o = [O_3]_o$= 1 g $l^{-1}$,

   This is a biomolecular process. NO and $O_3$ must collide in order to react. How much ozone is left after $10^{-5}$ sec second?

a.

$$\frac{1}{[A]}-\frac{1}{[A]_0}=kt \rightarrow \frac{1}{[O_3]}=kt+\frac{1}{[O_3]_0}=\frac{1.2\times10^{10}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{1.000\ \text{cm}^3\ \text{l}^{-1}}\times1.0\times10^{-5}s+\frac{1}{0.1}\ \text{l mol}^{-1}$$

$$\frac{1}{[A]}-\frac{1}{[A]_0}=kt \rightarrow \frac{1}{[O_3]}=kt+\frac{1}{[O_3]_0}=\frac{1.2\times10^{10}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{1.000\ \text{cm}^3\ \text{l}^{-1}}\times10^{-5}\ \text{s}+\frac{1}{0.1}\ \text{l mol}^{-1}=1.20\times10^2+10$$
$$=130\ \text{l mol}^{-1}$$
$$[O_3](1.0\ \text{s})=0.1-0.0333=0.0667\ \text{mol l}^{-1}$$

NO is effective at removing ozone because the rate constant is so large.

b. $NO]_o = [O_3]_o$= 1 g $l^{-1}$, means that the two concentrations are different and must use the second order rate equation of the second kind:

$$\boxed{\frac{1}{(a_o-b_o)}\ln\frac{b_o(a_o-x)}{a_o(b_o-x)}=kt}$$

$[NO]_o = [O_3]_o$= 1 g $l^{-1}$,

$$[\text{NO}]_o = [\text{O}_3]_o = 1\ \text{g l}^{-1},$$
$$[\text{NO}]_o=\frac{1\ \text{g l}^{-1}}{30\ \text{g mole}^{-1}}=0.033\ \text{mol l}^{-1}$$
$$[\text{NO}]_o=\frac{1\ \text{g l}^{-1}}{48\ \text{g mole}^{-1}}=0.021\ \text{mol l}^{-1}$$

$$\frac{1}{\left(a_o-b_o\right)\ \text{mol l}^{-1}}\ln\frac{b_o\left(a_o-x\right)}{a_o\left(b_o-x\right)}=kt\rightarrow\frac{1}{\left([\text{O}_3]_0-[\text{NO}]_0\right)}\ln\frac{[\text{NO}]_0\left([\text{O}_3]_0-x\right)}{[\text{O}_3]_0\left([\text{NO}]_0-x\right)}=$$

$$=\frac{1}{(0.021-0.033)}\ln\frac{0.033(0.021-x)}{0.021(0.033-x)}=kt=1.2\times10^{10}\,\text{cm}^3\text{mol}^{-1}\text{s}^{-1}\times10^{-5}\ \text{s}$$

$$=\frac{1}{-0.012}\ln\frac{0.033(0.021-x)}{0.021(0.033-x)}\text{l mol}^{-1}=\frac{1.2\times10^5\ \cancel{\text{cm}^3}\,\text{mol}^{-1}\,\cancel{\text{s}^{-1}}}{10^3\ \cancel{\text{cm}^3}\,\text{l}^{-1}}=1.2\times10^2\ \text{l mol}^{-1}$$

$$\ln\frac{0.033(0.021-x)}{0.021(0.033-x)}=-1.444\ \text{dimensionless}$$

$$\frac{0.033(0.021-x)}{0.021(0.033-x)}=\exp(-1.44)=0.237$$

$$\frac{0.033}{0.021}(0.021-x)=(0.033-x)\times0.237$$

$$0.033-1.57143x=0.007821-x\times0.237$$

$$0.033-0.007821=+(1.57143-0.237)x$$

$$x=\frac{0.25179}{1.33443}=0.01889$$

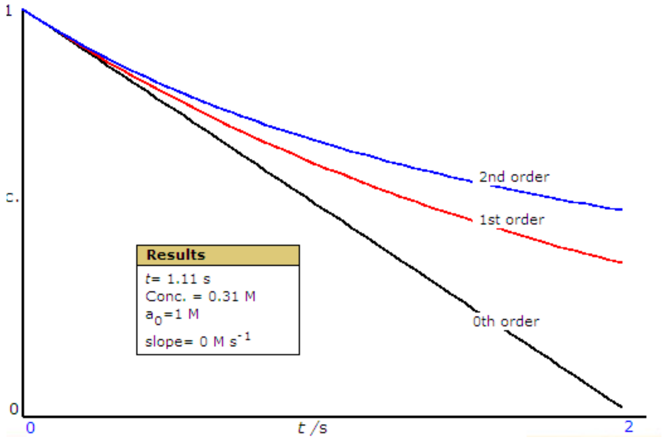
Solve for x, then at time *t*,

$$[\text{NO}](t)=(0.033-x)=(0.033-0.01889)=0.0141\ \text{mol l}^{-1}$$

$$[\text{O}_3](t)=(0.021-x)=(0.021-0.01889)=0.0021\ \text{mol l}^{-1}$$

## Summary Lecture 33 (Top)

Here is a plot of zeroth, first and second order rates with all having the same rate constant (see multimedia empirical rate equations in the kinetics chapter),



Although this plot is labeled 0th, 1st and 2nd, it is quite difficult to distinguish one from the other at short times. Also, at longer times, it is difficult to distinguish 1st from 2nd. Moreover, spread and scatter of data points also adds to the confusion. Finally, determining the order of a reaction with respect to different chemicals, (say with respect to [A] or [B] in a second order) can be difficult to untangle.

**The Plot-person-ship method**: Take the experimental data and use the integrated rate equations to plot it in order to get a straight line. We then know the overall order of the reaction and the rate constant.

If we have a set of data points, we have already seen that plotting in different ways allows us to get straight lines. *A priori*, however, we do not know the order and it would make things easier if we knew the order before we plot the data.

Here a few methods are discussed that help in obtaining the order of reactions.

**Differential rate method**: From the general expression for a rate,

$$-\frac{da}{dt} = v = ka^n \tag{1.50}$$

simply take the logarithm,

$$\ln v = n \ln a + \ln k \tag{1.51}$$

which gives a straight line if $\ln v$ is plotted against $n \ln a$. The slope gives the order, *n*, and the intercept gives the rate constant.

**Ratio of rates method**: This is exemplified by problems 9.2 and 9.3. The differential rate is determined at various concentrations of the reactants and products. Using the ratio of the rates, we can determine the order with respect to each chemical,

$$\frac{v_1}{v_2}=\frac{\cancel{k}\left[\mathrm{A}_1\right]^{\alpha}\left[\mathrm{B}_1\right]^{\beta}}{\cancel{k}\left[\mathrm{A}_2\right]^{\alpha}\left[\mathrm{B}_2\right]^{\beta}}=\left(\frac{\left[\mathrm{A}_1\right]}{\left[\mathrm{A}_2\right]}\right)^{\alpha}\left(\frac{\left[\mathrm{B}_1\right]}{\left[\mathrm{B}_2\right]}\right)^{\beta} \tag{1.52}$$

So, for example, if we double the concentration of B and keep A fixed, and we notice the rate increases by a factor of four, $v_2=4v_1$, then it follows that $\beta$ must equal 2,

$$\frac{v_1}{v_2}=\frac{1}{4}=\left(\frac{\left[\mathrm{A}_1\right]}{\left[\mathrm{A}_1\right]}\right)^{\alpha}\left(\frac{\left[\mathrm{B}_1\right]}{2\left[\mathrm{B}_1\right]}\right)^{\beta}=\left(\frac{1}{2}\right)^{\beta} \tag{1.53}$$

Now do the same for the other chemicals, *e.g.* A.

**The half-life method:** For all rates found in Table 9.1 (except first order), we can express the half-life as:

$$t_{1/2}=\frac{2^{n-1}-1}{k\left(n-1\right)a_o^{n-1}} \tag{1.54}$$

Simply use two different initial conditions for the same reaction and take the ratio,

$$\frac{t_{1/2}\left(a_1\right)}{t_{1/2}\left(a_2\right)}=\left(\frac{a_1}{a_2}\right)^{n-1} \tag{1.55}$$

Now take the logarithm of both sides,

$$n=1+\frac{\log\left(t_{1/2}\left(a_1\right)/t_{1/2}\left(a_2\right)\right)}{\log\left(a_1/a_2\right)} \tag{1.56}$$

This gives *n* from knowledge of the half-lives at two different concentrations.

**Pseudo rate law method**: Consider the rate law

$$v=k\left[\mathrm{A}\right]^{\alpha}\left[\mathrm{B}\right]^{\beta} \tag{1.57}$$

Now set up an experiment such that the concentration of one of the chemicals is very large. This is done so that over the course of the reaction, this large concentration does not change much and so remains virtually constant. Hence we can write,

$$v=\left(k\left[\mathrm{A}\right]^{\alpha}\right)\left[\mathrm{B}\right]^{\beta}=k'\left[\mathrm{B}\right]^{\beta}\quad\text{for}\quad\left[\mathrm{A}\right]>>\left[\mathrm{B}\right] \tag{1.58}$$

That is, the almost-constant concentration of [A] can be absorbed into the rate constant so that, although not a true rate constant, $k'$ is almost a constant. We therefore study the rate of this equation by one of the above methods to obtain the order with respect to B. Following this, we can set up another experiment with the opposite conditions $[\mathrm{A}] << [\mathrm{B}]$ and find the order with respect to A.

Since a catalyst does is not consumed in a reaction, we put the concentration of it into the rate constant,

$$v = \left(k[\mathrm{cat}]\right)[\mathrm{B}]^{\beta} = k'[\mathrm{B}]^{\beta}$$

Then we study the rate as a function of catalyst concentration and can find the effect of the catalyst on the rate.

Once the order of a reaction is known, attention is changed to determining the mechanism, or steps, that take a reaction from its reactants to its products. We will find it useful to consider the various possible steps one by one. Later we can combine these to get the overall rate equation. This must be consistent with the experimental data and therefore, once we think we have sussed out a mechanism, we obtain the various rate constants for each step. Some are large: so fast; some are small: so slow. Sometimes there is a bottleneck, or rate determining step; sometimes reactions go so fast it is difficult to follow them. Finally we try to calculate the rate constants and from these we get an understanding of the reasons why a reaction takes place.

I did opposing reactions, (see end of section 9.4) and you should know elementary or concerted reactions; composite reactions (def.), molecularity; relation between order and molecularity; effect of a large concentration of solvent and how catalysts effect the rate constants.

Next stop, temperature dependence and the Arrhenius Law. Then we talk about the pre-exponential factor, *A*, (transition state theory, hot hard sphere collisions) and finally in chapter 9 potential energy diagrams.

**Summary Lecture 34** (Top)

**Opposing Reactions**: Pages 9-23 to 9-25. The relationship between the rate constants and the equilibrium constant for an opposing reaction is presented. Consider unimolecular opposing reactions,

$$\begin{array}{lll} & \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} & Z \\ \text{initial amounts:} & a_o & 0 \\ \text{at time } t: & a_o - x & x \\ \text{at equilibrium:} & a_o - x_{\text{equil}} & x_{\text{equil}} \end{array} \tag{1.59}$$

From Eq.(9-45) we have

$$\frac{dx}{dt} = k_1\left(a_o - x\right) - k_{-1}x \tag{1.60}$$

but at equilibrium, there is no change in the concentration so the rate is zero. That is, the forward and reverse reactions have balanced giving,

$$\frac{dx_{\text{equil}}}{dt} = 0 = k_1\left(a_o - x_{\text{equil}}\right) - k_{-1}x_{\text{equil}} \tag{1.61}$$

and rearranging this result leads to

$$K_{\text{equil}} \equiv \frac{[\mathrm{Z}]}{[\mathrm{A}]} = \frac{k_1}{k_{-1}} = \frac{x_{\text{equil}}}{\left(a_o - x_{\text{equil}}\right)} \tag{1.62}$$

This means that the equilibrium constant for a chemical reaction can be related to the rate constants as seen from Eq.(1.62). If the forward rate constant is much larger than the reverse rate constant, $k_1 >> k_{-1}$ , then the equilibrium constant is large and the reaction produces a large concentration of Z. For the opposite condition, $k_1 << k_{-1}$, the reaction does not proceed far so not much product is formed.

Since the equilibrium constant is related to the rate constants, we can eliminate one using

$$k_{-1} = \frac{k_1}{K_{\text{equil}}} = \frac{k_1\left(a_o - x_{\text{equil}}\right)}{x_{\text{equil}}} \tag{1.63}$$

Substitution into Eq.(1.60) gives the differential rate law for opposing first order reactions,

$$\frac{dx}{dt} = \frac{a_o k_1}{x_{\text{equil}}}\left(x_{\text{equil}} - x\right) \tag{1.64}$$

The integrated rate law is

$$
\begin{aligned}
\int_0^x \frac{dx}{\left(x_{\text{equil}} - x\right)} &= \frac{a_o k_1}{x_{\text{equil}}} \int_0^t dt \\
\ln \frac{x_{\text{equil}}}{\left(x_{\text{equil}} - x\right)} &= \frac{a_o k_1}{x_{\text{equil}}} t
\end{aligned}
\tag{1.65}
$$

Therefore a plot of $\ln \frac{x_{\text{equil}}}{\left(x_{\text{equil}} - x\right)}$ *vs. t* gives a straight line with slope $\frac{a_o k_1}{x_{\text{equil}}}$.

(Note that figure 9.4, stating the slope is $k_1$ is incorrect for the LHS (Left Hand Side) and should be $\frac{a_o k_1}{x_{\text{equil}}}$. Look on the multimedia under chemical kinetics and opposing reactions. Choose different rate constants and show that equilibrium attained is consistent with the equations in this section. Follow the suggestions to see what happens when the two rate constants are the same; also when the initial concentrations are the same.)

For opposing second order reactions,

$$\mathrm{A} + \mathrm{B} \underset{\mathrm{k}_{-1}}{\overset{\mathrm{k}_1}{\rightleftarrows}} Y + \mathrm{Z} \tag{1.66}$$

the relationship to equilibrium is the same as first order opposing reactions,

$$K_{\text{equil}} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{Z}][\mathrm{Y}]}{[\mathrm{A}][\mathrm{B}]} \tag{1.67}$$

However, as might be expected, the differential and integrated rate equations differ from Eqs.(1.64) and (1.65), (not given here).

**Rate constants**: We have seen that the rates of chemical reactions often fit into an overall rate equation of the form,

$$v = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}[\mathrm{C}]^{\chi}\ldots \tag{1.68}$$

We have also seen that composite chemical reactions can be broken up into elementary steps. These steps are usually deduced from knowledge concerning the chemical reaction but they have to be tested to make sure the mechanism is correct. Recall that one of the main advantages of knowing the mechanism is that we can follow all the steps logically and, if necessary, intervene by introducing inhibitors, other chemicals and catalysts. Inhibitors and catalysts are not consumed in chemical reactions. They do not affect the final products nor do they affect the equilibrium. Rather they affect the magnitude of the rate constants. Let us write the effect of a catalyst as,

$$\mathrm{A} + 2\mathrm{B} + \mathrm{cat} \rightarrow \mathrm{Y} + 3\mathrm{Z} + \mathrm{cat} \tag{1.69}$$

From Eq.(1.62) it is clear that the catalyst has no effect on the equilibrium state,

$$K_{\text{equil}} = \frac{[\text{Y}]_{\text{equil}}[\text{Z}]^3_{\text{equil}}\cancel{[\text{cat}]}}{[\text{A}]_{\text{equil}}[\text{B}]^2_{\text{equil}}\cancel{[\text{cat}]}} = \frac{[\text{Y}]_{\text{equil}}[\text{Z}]^3_{\text{equil}}}{[\text{A}]_{\text{equil}}[\text{B}]^2_{\text{equil}}} \tag{1.70}$$

Every one of the elementary steps involves a rate constant and the overall rate constant for the composite reaction is a function of the rate constants for the elementary steps. In all cases the rate constants are independent of concentration but they do depend upon the temperature, molecular interactions and collisions.

## Summary Lecture 35 (Top)

**The Arrhenius Equation**: Certain external conditions are usually imposed on chemical reactions. Recall from thermodynamics that we can keep the temperature and pressure fixed. This is usually a "bench top" experiment. From thermo, this case has the minimum energy given by the Gibbs (free) energy. If the temperature and volume are fixed, like in a bomb calorimeter experiment, the minimum energy is given by the Helmholtz (free) energy.

Let us consider that the temperature is fixed for a reaction which is exothermic, such as burning methane gas is a boiler to heat your house,

$$\overbrace{\mathrm{CH_4} + \mathrm{O_2}}^{\mathrm{T = 25\,C}} \rightarrow \overbrace{\mathrm{CO_2} + \mathrm{H_2O}}^{\mathrm{T = 25\,C}} + \text{heat.} \tag{1.71}$$

It is often confusing for such exothermic reactions because why does the heat produced not raise the temperature of the products? The answer is the same as how you heat a house: there is a heat exchanger which carries off the heat and distributes it throughout the house. If the heat exchange was 100% efficient, then all the heat would be carried away and the products would be the same temperature as the reactants. We will assume that all the heat is taken away, so this justifies why reactants and products are at the same temperature.

Now let us consider that the external temperature is given by *T*. This is maintained throughout the reaction. Generally we know that for most chemical reactions, the rate increases with temperature, but how? Reactions need energy to proceed. They need enough kinetic energy, for example, so that collisions are energetic enough to push a reaction over some barrier, through some intermediate short-lived complex, and finally to the products. Let us suppose that the amount of energy needed per mole of reactants is *E*. Where does this energy come from? It comes from the **thermal energy** of the surroundings: the heat that is found at temperature *T*. Recall that temperature is not heat. However the thermal energy is given by *RT*, where *R* is the gas constant. If the thermal energy is high enough relative to *E*, then the reaction has enough energy to proceed, and the rate constant is large. If the temperature is too low, then the rate constant is not large enough and so the rate is slow.

In thermodynamics you learned that the Boltzmann distribution is one that gives the relationship between energy needed and thermal energy available, $\exp\left(-E/RT\right)$. It is found for a large number of reactions that the rate constant has the form,

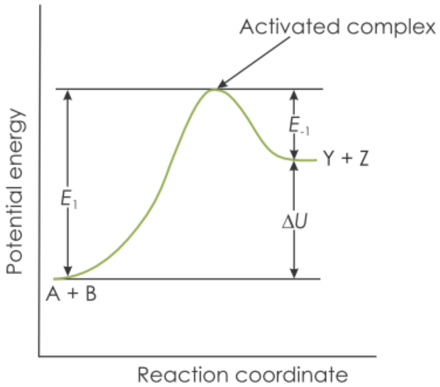
$$k(T) = A\exp\left[-\frac{E}{RT}\right] \tag{1.72}$$

This is called the **Arrhenius equation**. It is satisfied by a large number of rate constants. It simply states that there has to be enough energy for an elementary step in a reaction to take place. The quantity *A* is called the **pre-exponential factor**. It depends, as we will see, on how the particles collide or on now internal motions of bonds lead to them to break and to form new ones. We will discuss *A* in more detail later.

For opposing reactions, there is a relationship between the equilibrium constant and the forward and reverse rate constants, Eqs.(1.66) and (1.67). We know, however, from thermodynamics that there is a relationship between the internal energy change of a reaction under standard conditions, $\Delta U^o$, and the equilibrium constant. The temperature dependence of the equilibrium constant is found by taking the derivative *wrt* temperature. Note here that we start at equilibrium, at constant pressure and temperature and then, with the pressure fixed, see how the Gibbs energy changes with temperature,

$$\begin{aligned}
&\Delta G^0 = -RT\ln K_{\text{equil}} \\
&-\frac{\Delta G^0}{RT} = -\left[\frac{\left(\Delta U^0 + P\Delta V - T\Delta S^0\right)}{RT}\right] = \ln K_{\text{equil}} \\
&-\frac{d}{dT}\left[\frac{\left(\Delta U^0 + P\Delta V - T\Delta S^0\right)}{RT}\right] = \frac{d\ln K_{\text{equil}}}{\text{dT}} \\
&-\frac{d}{dT}\left[\left(\frac{\Delta U^0}{RT} + \underbrace{\frac{\overbrace{P\Delta(V)}^{\Delta nRT}}{RT} - \frac{\Delta S^0}{R}}_{\text{derivative of constant is zero}}\right)\right] = \frac{d\ln K_{\text{equil}}}{\text{dT}} \\
&-\left[\left(-\frac{\Delta U^0}{RT^2} + 0 - 0\right)\right] = \frac{d\ln K_{\text{equil}}}{\text{dT}} \\
&\boxed{\frac{d\ln K_{\text{equil}}}{\text{dT}} = \frac{\Delta U^o}{RT^2}}
\end{aligned} \tag{1.73}$$

The trick of taking the derivative gets rid of constant terms and is less cluttered. Later on we can integrate and put back the constant terms. Here we are assuming that the internal energy and entropy do not change much with temperature.



But we know the relationship between the rate constants and the equilibrium constant, Eq.(1.67), so substitution gives, $K = \frac{k_1}{k_{-1}}$

$$\frac{d\ln k_1}{\text{dT}} - \frac{d\ln k_{-1}}{\text{dT}} = \frac{\Delta U^o}{RT^2} \tag{1.74}$$

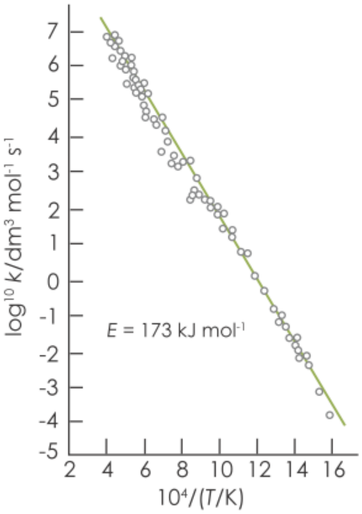
Now let us look at the internal energy, $\Delta U^o$. This is the difference between internal energy of the reactants and products. Let us suppose that the reactants have internal energy $E_1$ and the products $E_{-1}$ so that $\Delta U^o = E_1 - E_{-1}$ (see figure 9.11). Then we can write,

$$\frac{d\ln k_1}{\mathrm{dT}} - \frac{d\ln k_{-1}}{\mathrm{dT}} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2} \tag{1.75}$$

or for each,

$$\begin{aligned} \frac{d\ln k_1}{\mathrm{dT}} &= \text{constant} + \frac{E_1}{RT^2} \\ \frac{d\ln k_{-1}}{\mathrm{dT}} &= \text{constant} + \frac{E_{-1}}{RT^2} \end{aligned} \tag{1.76}$$

Finally we have justified the Arrhenius equation, (1.72) by integrating Eq.(1.76),



$$\begin{gathered} \Delta G^0 = -RT\ln K_{\text{equil}} \\ -\frac{\Delta G^0}{RT} = \left[\frac{\left(\Delta U^0 + P\Delta V - T\Delta S^0\right)}{RT}\right] = \ln K_{\text{equil}} \\ -\frac{d}{dT}\left[\frac{\left(\Delta U^0 + P\Delta V - T\Delta S^0\right)}{RT}\right] = \frac{d\ln K_{\text{equil}}}{\mathrm{dT}} \\ -\frac{d}{dT}\left[\left(\frac{\Delta U^0}{RT} + \frac{\overbrace{P\Delta(V)}^{\Delta nRT}}{RT} - \frac{\Delta S^0}{R}\right)\right] = \frac{d\ln K_{\text{equil}}}{\mathrm{dT}} \\ -\left[\left(-\frac{\Delta U^0}{RT^2} + 0 - \overset{0}{\frac{\Delta S^0}{R}}\right)\right] = \frac{d\ln K_{\text{equil}}}{\mathrm{dT}} \\ \boxed{\frac{d\ln K_{\text{equil}}}{\mathrm{dT}} = \frac{\Delta U^o}{RT^2}} \end{gathered} \tag{1.77}$$

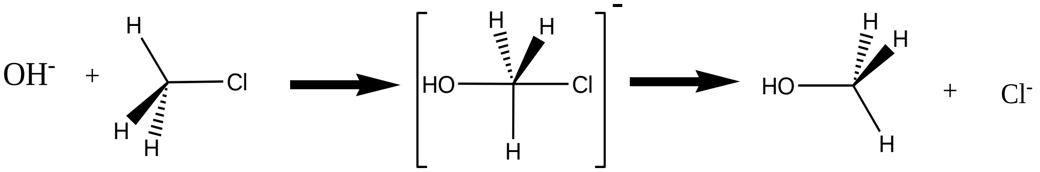
The pre-exponential factor and the energy, *E*, can be obtained from a plot of $\ln k$ *vs.* $1/T$

$$\ln k = -E/RT + \ln A \tag{1.78}$$

The intercept gives $\ln A$ and the slope is $-E/R$.

Looking again at Figure 9.11, the relationship between the internal energy change of the reaction, $\Delta U^o$, and the two energies, $E_{\pm 1}$, is given. Note that the reactants have to have enough energy, $E_{+1}$, to mount the barrier in the forward direction and enough energy $E_{-1}$ for the reverse. At the top of the barrier is the intermediate compound called the **activated complex**. Relative to the reactants, they must have enough energy to form such a complex. Therefore, relative to reactants, we say the activated complex has **activation energy** of $E_{+1}$, while relative to the products, the activated complex has energy $E_{-1}$.

Figure 9.11 in plotted against **reaction coordinates**. Reaction coordinates specify the relative orientation of reactants and products. If this alignment of molecules favours a reaction, then the barrier height is lower than if the alignment did not favour the reaction, for example,

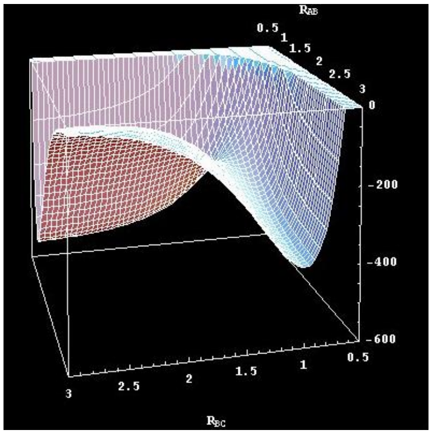


(1.79)

Clearly this is a bimolecular reaction which favours backside attack from the hydroxide ion. This is a specific **reaction coordinate** that has the lowest **activation energy**. If the hydroxide ion attacks from any other direction, then the activated complex is more difficult to form. Consequently the activation energy for those unfavourable reaction coordinates is higher. The specific way that molecules are oriented when they interact is their reaction coordinate.

The activated complex is not a molecule you can find in a bottle. It is energetically unstable and quickly decomposes by either falling into the products (successful reaction) or falling back to the starting reactants (unsuccessful reaction). See multimedia, Chemical Kinetics 1, section 9.7 Arrhenius equation.

**Potential energy surfaces**: (see multimedia, Chemical Kinetics 1, section 9.8 Potential energy surfaces.) If we think of two molecules that can collide, like in Eq.(1.79), let's call them A and B, then as they come together, they start to feel each other's presence. When they are far apart, the electrostatic forces between them must be zero. Since they are stable molecules, they have a minimum energy. As they come together, there develops a potential energy between them. Let us consider mapping out the potential energy between two molecules before, during and after they react. There are many reaction coordinates and when all are considered, we find a trough or channel through which the molecules pass most easily as they



change from reactants to products. See the diagram and imagine that the two reactant molecules are coming in from the left. The minimum energy from reactants to products is along the bottom of the trough. Along this trough of minimum energy, the molecules start to react and form the activated complex. That unstable molecule is located in the middle of the trough near the bend. Notice the energy is higher at that point. It is the barrier over which the molecules must pass in order to form the products, which exit on the right hand side of the trough.

A potential energy diagram plots reaction coordinates on one side for the reactants, and on the other side, the reaction coordinates for the products. These diagrams depend upon detailed knowledge of the potential energy between the molecules. The calculations are done using quantum mechanics. The surface is extremely sensitive to small changes in interactions between the molecules that lead to large changes in the potential energy surface. The calculations are difficult and time consuming. They do, however, give a clear picture of what is happening in a reaction.

## Summary Lecture 36 (Top)

### The Pre-exponential Factor

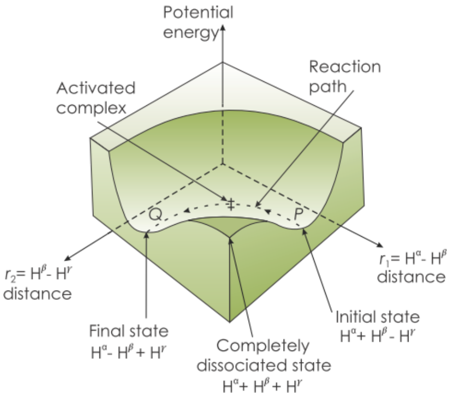
General Summary to date:

Empirical rate law: $Rate = v_{\lambda} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}[\mathrm{C}]^{\gamma}...$ separates out concentration from the rate constant. The order is the sum of the exponents but not all rates can be put in this form. We find empirical rate laws from experiment and recognize the differential, integrated and half-life forms, table 9.1. The most common chemical reactions are unimolecular (first order) and bimolecular (second order). Generally a chemical rate law is the result of many elementary steps that compose a composite reaction. If we can find, guess or deduce the elementary steps, we are getting close to the mechanism in terms of how different molecules react. This is called **molecularity** and an individual rate equation including gain and loss for each step can be written down. We then need to solve the coupled set of differential equations in order to get the overall rate law. From each elementary step, we extract a rate constant.

**Mechanisms**: How reactions take place, *i.e.* the mechanistic pathways from reactants to products through the intermediates. I will discuss this in the next lectures.

**The temperature dependence**: Generally we find that the temperature dependence of a reaction follows the **Arrhenius equation**: $k(T) = A\exp(-E_a / RT)$. This equation basically is saying that for a reaction to take place, there must be enough **thermal energy** in the surroundings, $RT$, in order for the system of interacting molecules to mount a barrier that exists between reactants and products. We consider $E$ to be the minimum energy for a reaction to proceed. That is, $E_a$ is the activated energy needed to form the intermediate, **transition state complex**. The theory treats the activated complexes in a procedure called **transition state theory**.

**Potential energy diagrams**: Molecules separated by large distances have no potential energy between them. As they come together, and react, electrons are usually transferred and new bonds are formed as old bonds are broken. The efficacy of this process is dependent upon the orientation of the molecules. The orientations can be favourable or unfavourable. Such orientations are called **reaction coordinates**. Catalysts, inhibitors and solvents affect reaction coordinates. These surfaces are usually calculated from quantum mechanics and are not easy to get right because of the complexity of molecular collisions.



**The Pre-exponential factor**: Since concentration and temperature effects have been removed from a rate law, we are left with the pre-exponential factor. We discuss this in terms of two treatments. The first, **classical**, treatment gives insight but is not adequate in general. However, the classical treatment of collisions generally accounts for bimolecular processes that can occur as a result of collisions between hard spheres. This treatment is also consistent with the approach that uses collisions to understand the ideal gas law and some non-equilibrium transport properties in thermodynamics. The second approach is **Transition State Theory**.

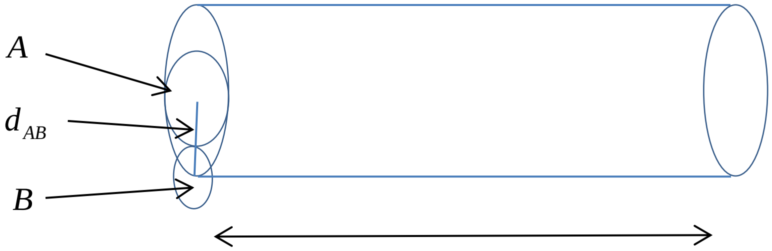
If we assume hard sphere elastic collisions, the rate equation for a bimolecular process depends upon the collision frequency, $Z_{\mathrm{AB}}$,

$$v_{\mathrm{AB}} = Z_{\mathrm{AB}} \exp\left[-\frac{E_a}{RT}\right][\mathrm{A}][\mathrm{B}] \tag{1.80}$$

The collision frequency is the number of collisions between particles $A$ and $B$. Since they are hard spheres, collisions only occur if the two particles lie in the tube below. Consider particle $A$ at the center of that tube. Any particles $B$ within that tube will collide with $A$. Hence the first term says that the area $\pi d_{AB}^2$ is the cross section and any particles that lie within will collide and without, will not collide. That radius, $d_{AB}$, is the value when particles $A$ and $B$ just "kiss" (pool term for "just touch").

The second term is the velocity: this says that the faster the particles are moving relative to each other, the more collisions are possible and the greater $Z_{\mathrm{AB}}$.

$$\text{where } Z_{AB} \sim \overbrace{\left(\pi d_{AB}^2\right)}^{\text{cross sectional area}} \overbrace{\left(\frac{8\pi RT}{\mu_{AB}}\right)^{1/2}}^{\text{average velocity}}$$



Relative speed draws out the collision cylinder

However this means that every collision is successful if the temperature is high enough. This is not right. Catalysts, solvents and steric effects play a role.

There is an unsatisfactory way to take into account the fact that all binary collisions are not successful due to orientation. Recall these are hard spheres and have no structure that could include steric effects. This is simply fudged by multiplying the rate constant by a factor, $P$, which is called a steric factor. This takes into account that different orientations can be unfavourable, introducing a steric effect,

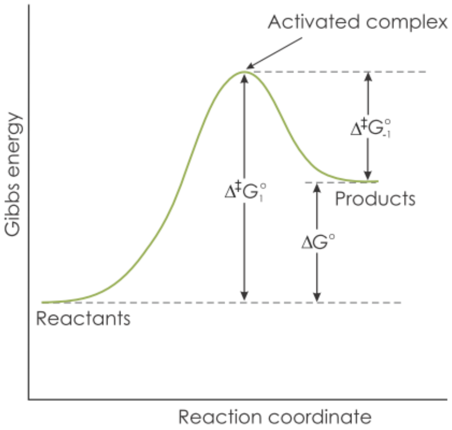
$$k = PA\exp\left[-\frac{E}{RT}\right] \tag{1.81}$$

where $0 < P \leq 1$ and this is adjusted so the rate constant agrees with the experimental value.

It is possible to move away from hard spheres and do more realistic collisions. Although useful in understanding the role of binary collisions on the rate constant, the steric factor is clearly unsatisfactory.

**Transition State Theory:** Full appreciation of this approach can only be complete after a course in equilibrium statistical mechanics. However we can write down the equations and state some results without proof. Transition state theory is really what the name implies, it is thermodynamics applied to the **activated complex** that is formed at the transition state between reactants and products.

The advantage over the collision model above is that the entropy comes into the picture and accounts for steric effects. Recall that entropy is a measure of randomness (large entropy) and order (small entropy).



The treatment (logical story you should follow, but not memorize) here is similar to what we saw for obtaining the Arrhenius equation. Rather than using the internal energy, however, the Gibb's energy is used,

$$\ln K = -\frac{\Delta G^o}{RT} = \ln \frac{k_1}{k_{-1}} \tag{1.82}$$

so we easily get, see Figure 9.16, above,

$$\begin{aligned} \ln k_{+1} &= \ln \nu - \frac{\Delta^{\pm} G^o_{+1}}{RT} \\ \ln k_{-1} &= \ln \nu - \frac{\Delta^{\pm} G^o_{-1}}{RT} \end{aligned} \tag{1.83}$$

The constant, $\ln \nu$ cancels in Eq.(1.82) and is arbitrary, so we make a convenient choice. It is important to note the difference between in Eq.(1.83) and the Arrhenius equation, Eq(1.76). Here we consider the activated complex that is formed at the top of the barrier as a real compound that obeys thermodynamics. Hence the activated complex is described by such quantities as $\Delta^{\pm}G^o$ ,$\Delta^{\pm}H^o$ , $\Delta^{\pm}V^o$ and $\Delta^{\pm}S^o$.

Recalling that $\Delta G = \Delta H - T\Delta S$ we can write,

$$k_1 = \nu \exp\left(\frac{\Delta^{\pm} S^o_1}{R}\right) \exp\left(-\frac{\Delta^{\pm} H^o_1}{RT}\right) \tag{1.84}$$

In the following the goal is to relate $\Delta^{\pm}H_1^o$ to the activation energy, $E_a$. You are not responsible for the derivation below:

In other words, by making this change, we have the forward and reverse rate constants in terms of the enthalpy and entropy of the activated complex. Without Statistical Mechanics, we cannot derive the pre-factor, but it is equal to $\nu = \frac{k_B T}{h}$ where *h* is Planck's constant, so we just accept this for now,

$$k_1 = \frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right)\exp\left(-\frac{\Delta^{\pm}H_1^o}{RT}\right) = \frac{k_B T}{h}K^{\pm} \qquad (1.85)$$

We can go back to the Arrhenius treatment and replace the internal energies, $E_1$ and $E_{-1}$ by the internal energy of the activated complex $\Delta^{\pm}U^o = E_1 - E_{-1}$,

$$\frac{d\ln K^{\pm}}{dT} = \frac{\Delta^{\pm}U^o}{RT^2} \qquad (1.86)$$

To find the relationship between Eq.(1.86) and the activation energy, take the ln of Eq.(1.85) and differentiate with respect to the temperature,

$$\frac{d\ln k_1}{dT} = \frac{1}{T} + \frac{d\ln K^{\pm}}{dT} \qquad (1.87)$$

Now substitute Eq.(1.86) to get,

$$\frac{d\ln k_1}{dT} = \frac{1}{T} + \frac{\Delta^{\pm}U^o}{RT^2} = \frac{RT + \Delta^{\pm}U^o}{RT^2} \qquad (1.88)$$

By comparison with Eq. (1.77), we can identify the activation energy,

$$E_a = \Delta^{\pm}U^o + RT = \Delta^{\pm}H^o - P\Delta^{\pm}V^o + RT \qquad (1.89)$$

For unimolecular reactions, there is no molar change from reactants to activated complex, $P\Delta^{\pm}V^o = \Delta nRT = 0$,

$$\mathrm{A} \rightarrow \mathrm{X}^{\dagger\dagger}$$

so and from Eqs.(1.85) and (1.89) we get,

$$\begin{aligned}
k_1 &= \frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right)\exp\left(-\frac{\Delta^{\pm}H_1^o}{RT}\right) \\
&= \frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right)\exp\left(-\frac{(E_a - RT)}{RT}\right) \\
&= \frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right)\exp\left(-\frac{E_a}{RT}\right)\exp\left(\frac{RT}{RT}\right) \\
&= e\frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right)\exp\left(-\frac{E_a}{RT}\right)
\end{aligned} \qquad (1.90)$$

That is, (compare with Eq.(1.84)—very similar)

$$k_1 = e\frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right)\exp\left(-\frac{E_a}{RT}\right) \tag{1.91}$$

from which we can deduce the pre-exponential factor,

$$A = e\frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right) \tag{1.92}$$

This is quite different from the expression from hard sphere collisions, Eq.(1.80) and does not require the steric factor $P$, in Eq.(1.81), to take into account the orientation of the particles. Entropy naturally arises in Transition State Theory. If every possible orientation is possible, then the entropy is large, so all collisions are effective. In this case, the pre-exponential factor is large. If, on the other hand, only a specific, or highly ordered collision will be successful, then the system must be ordered for the reaction to occur, and so the entropy is low and the pre-exponential factor small.

To treat more than unimolecular processes, we consider the change in stoichiometry for gas phase reactions from reactants to products. In this case the volume change follows the ideal gas law,

$$P\Delta^{\pm}V^o = \sum \nu RT \tag{1.93}$$

where $\nu$ is the change in stoichiometry between reactants and products. For a biomolecular process

$$\mathrm{A+B} \rightarrow \mathrm{X}^{\dagger\dagger}$$

where two molecules collide to give the activated comples, the change is $\Delta n = -1$ which, on substitution into Eq.(1.89) and following through Eq.(1.90), leads to,

$$A = e^2\frac{k_B T}{h}\exp\left(\frac{\Delta^{\pm}S_1^o}{R}\right) \tag{1.94}$$

The thermodynamic properties we have studied get their values by averaging over a huge number of microscopic events. A rate constant is governed by many interactions and reflects what is happening at the microscopic level. The entropy taking into account steric effects is a measure of the effects of orientation on reaction rate. From Eq.(1.94) the entropy of the activated complex can be found.

Skip the section on **Tunneling**: Quantum mechanical tunneling is the phenomenon that particles can pass through barriers because they act as waves. Electromagnetic waves can pass through walls. When you drive into a tunnel, for example, the radio volume decreases because the radio waves are attenuated by the thickness of the walls. For similar reasons, particles can tunnel into regions that are unavailable to classical particles because particles have wave properties.

**Summary Lecture 37** (Top)

**The Composite Reactions**

Most reactions are composite, meaning that they are composed of elementary steps. These complex reactions can often be decomposed into their elementary steps to reveal the mechanism.

In Section 10.6, for example, the mechanism for the chain reaction to form HBr was written down. It is really never possible to be sure that a mechanism is correct. We can write down mechanisms and agree with the data, but they still might be wrong. However, if we think we have a mechanism, we can disprove it using the experimental kinetic data, but not generally confirm it.

See example sections 10.1-3 for ways of deducing the steps in a mechanism. Notice that these deductions are empirical, or guesses, which are consistent with observations. We do not really know if they are correct.

Frequently a reaction rate is determined by a slow step or a step that depends upon the value of a particular rate constant, whether large or small. This is called the rate determining step. Also in many cases the composite rate does not follow the form we have been using, $Rate = v_\lambda = k\left[\mathrm{A}\right]^\alpha\left[\mathrm{B}\right]^\beta\left[\mathrm{C}\right]^\gamma\ldots$ but have forms such as for the formation of HBr in the gas phase,

$$\mathrm{H_2} + \mathrm{Br_2} \rightarrow 2\mathrm{HBr} \tag{1.95}$$

with observed rate law,

$$v = \frac{k\left[\mathrm{H_2}\right]\left[\mathrm{Br_2}\right]^{1/2}}{1+\left[\mathrm{HBr}\right]/m\left[\mathrm{Br_2}\right]} \tag{1.96}$$

The types of composite reactions have already been discussed in Section 5,

**Unimolecular irreversible:**

$$\mathrm{A} \xrightarrow{\mathrm{k}} \mathrm{B} + \mathrm{C}\ etc.\ \ \text{then}\ \frac{\mathrm{d[A]}}{\mathrm{dt}} = -k[\mathrm{A}] \tag{1.97}$$

**Bimolecular irreversible:**

$$\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k}} \mathrm{C} + \mathrm{D}\ etc.\quad \text{then}\ \frac{\mathrm{d[A]}}{\mathrm{dt}} = -k[\mathrm{A}][\mathrm{B}] \tag{1.98}$$

**Trimolecular irreversible:**

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \xrightarrow{\mathrm{k}} \mathrm{C} + \mathrm{D}\quad \text{then}\ \frac{\mathrm{d[A]}}{\mathrm{dt}} = -k[\mathrm{A}][\mathrm{B}][\mathrm{M}] \tag{1.99}$$

**Opposing reactions (reversible),** ***e.g.***

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{C} + \mathrm{D}\ \textit{etc.} \quad \text{then } \frac{\mathrm{d[A]}}{\mathrm{dt}} = -k_1[\mathrm{A}][\mathrm{B}] + k_{-1}[\mathrm{C}][\mathrm{D}] \tag{1.100}$$

We have also come across:

**Parallel or simultaneous reactions:**

$$\begin{aligned} \mathrm{A} &\rightarrow \mathrm{Y} \\ &\rightarrow \mathrm{Z} \end{aligned} \tag{1.101}$$

**Consecutive reactions:**

$$\mathrm{A} \xrightarrow{k_1} \mathrm{X} \xrightarrow{k_2} \mathrm{Y} \xrightarrow{k_3} \mathrm{Z} \tag{1.102}$$

As seen from Eqs.(1.97) to (1.100), we can write down the rate equations for elementary reactions by simply balancing the loss and gain of each chemical.

In the multimedia, you can learn a lot concerning how some of these reactions occur by varying initial concentrations and rate constants. See Chemical Kinetics I0 multimedia and find: simultaneous, opposing and consecutive reactions.

Consider a two-step consecutive reaction:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{X} \xrightarrow{k_2} \mathrm{Z} \tag{1.103}$$

and from this we can write down the rates (Text Eq.(10.10) is missing a minus sign),

$$v_1 = \frac{d[\mathrm{A}]}{\mathrm{dt}} = -k_1[\mathrm{A}] \tag{1.104}$$

We can easily integrate this to give,

$$[\mathrm{A}] = [\mathrm{A}]_o \exp(-k_1 t) \tag{1.105}$$

How we can write down the gain and loss of the intermediate, X,

$$\frac{d[\mathrm{X}]}{\mathrm{dt}} = k_1[\mathrm{A}] - k_2[\mathrm{X}] \tag{1.106}$$

Substitute in Eq.(1.105) to give

$$\frac{d[\mathrm{X}]}{\mathrm{dt}} = k_1[\mathrm{A}]_o \exp(-k_1 t) - k_2[\mathrm{X}] \tag{1.107}$$

The integrated form is (for exams, you are not responsible for doing integrals, other than those in Table 9.1 for first three 0th , 1st and 2nd (type 1),

$$[\mathrm{X}]=[\mathrm{A}]_o \frac{k_1}{k_2-k_1}\left(\exp(-k_1 t)-\exp(-k_2 t)\right) \tag{1.108}$$

Finally the equation for the production of Z can be written down, but a simpler way is to use mass balance and deduce that all of Z comes from $[\mathrm{A}]_o$: and any time it must follow that,

$$[\mathrm{Z}]=[\mathrm{A}]_o-[\mathrm{A}]-[\mathrm{X}] \tag{1.109}$$

which we know from Eqs.(1.105) and (1.108), or substitution,

$$[\mathrm{Z}]=\frac{[\mathrm{A}]_o}{k_2-k_1}\left[k_2\left(1-\exp(-k_1 t)\right)-k_1\left(1-\exp(-k_2 t)\right)\right] \tag{1.110}$$

Using the multimedia, you should be able to reproduce the plots in Figure (10.1) and many others.

**Steady state approximation:** The above solution to the three coupled differential equations involves a difficult integration. In principle these integrations can always be obtained, although sometimes not in analytic form. In such cases, the integral can be solved numerically. In more complicated cases, the integrals are even more challenging, although, again, numerical methods work. In some cases it is possible to use the steady state approximations to simplify the calculations.

In the multimedia under consecutive reactions, look at the suggestions and choose the rate constants to see how the [X] intermediate is almost a constant over a long time interval. If

$$k_2 >> k_1 \tag{1.111}$$

then physically you can visualize that the formation of [X] is slow, but as soon as it is formed, it quickly produces the product. Hence the concentration of X must be small and almost constant over the time of the experiment. The first step is the rate determining or slow step. Under these conditions, we have,

$$\frac{d[\mathrm{X}]}{\mathrm{dt}}=0 \tag{1.112}$$

Verify Figure (10.1) using the multimedia in the text book. Using Eq.(1.112) in Eq.(1.107), means that,

$$\frac{d[\mathrm{X}]}{\mathrm{dt}}=0=k_1[\mathrm{A}]_o\exp(-k_1 t)-k_2[\mathrm{X}] \tag{1.113}$$

so that,

$$[\mathrm{X}] = \frac{k_1}{k_2}[\mathrm{A}]_o \exp(-k_1 t) \cong \frac{k_1}{k_2}[\mathrm{A}]_o \tag{1.114}$$

In this we have used the fact that because of Eq.(1.112) we have, on the time scale of the experiment, $\exp(-k_1 t) \cong 1$ and $\exp(-k_2 t) \cong 0$ and Eq.(1.110) becomes equal to [X],

$$[\mathrm{Z}] = \frac{[\mathrm{A}]_o k_1}{k_2} = [\mathrm{X}] \tag{1.115}$$

This makes sense because as soon as $\mathrm{X}$ is formed by the slow first step, it quickly changes to $\mathrm{Y}$. Hence in the steady-state approximation, the concentration of $\mathrm{X}$ is small throughout the reaction as we assumed.

Follow through the equations in the text, (10.21) to (10.36) for the steady-state approximation to,

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{\mathrm{k}_1}{\rightleftarrows}} \mathrm{X} \xrightarrow{\mathrm{k}_2} \mathrm{Z} \tag{1.116}$$

We will come back to this when we treat enzyme kinetics, but the steady-state solution is,

$$[\mathrm{Z}] = \frac{k_1 k_2}{(k_{-1} + k_2)}[\mathrm{A}][\mathrm{B}] \tag{1.117}$$

In example 10.2, the idea of a pre-equilibrium is discussed. Before a reaction can take place, in that example, it was necessary to form a complex ion. This formation constitutes the establishment of a condition required for the reaction to take place.

Pre-equilibrium can play a role in the rate-controlling or rate-determining step of a reaction. This step is not necessarily the one with the largest rate constant. Rather it is the step that has the most influence on the overall rate of the reaction. We have seen in Eq.(1.103) that if $k_2 >> k_1$, the first step is the rate controlling step, but for Eq.(1.116), there may be an equilibrium between $\mathrm{A}$ and $\mathrm{B}$ and $\mathrm{X}$. If $k_2 >> k_{-1}$ then Eq.(1.117) becomes

$$[\mathrm{Z}] = \frac{k_1 k_2}{k_2}[\mathrm{A}][\mathrm{B}] = k_1[\mathrm{A}][\mathrm{B}] \tag{1.118}$$

which makes sense because the reverse reactions, via $k_{-1}$, is swamped by the forward reaction to the product by $k_2$. However, even though $k_2 >> k_{-1}$, the formation of the product depends upon $k_1$ and not $k_2$. It also depends upon the concentration of the reactants. In this case, the first forward step, governed by the value of $k_1$, is the rate-determining step.

In the opposite limit, $k_2 << k_{-1}$ Eq.(1.117) gives

$$[\mathrm{Z}] = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}][\mathrm{B}] = k_2 K[\mathrm{A}][\mathrm{B}] \tag{1.119}$$

where now the equilibrium constant comes into the picture, $K = \frac{k_1}{k_{-1}}$. This is the equilibrium constant for establishing the pre-equilibrium. The rate determining step depends upon $k_2$ and well as $K$. It is often considered that the second step, with a small rate constant, is the rate-determining step because after the equilibrium has been established, it is $k_2$ that determines how fast the products are formed, even though this rate constant is relatively small.

Summary:

- The slowest step is not always the rate controlling step.
- The rate determining step depends upon the relative values of the rate constants.
- The rate determining step is generally dependent upon the concentrations of the reactants, see Eqs.(1.115), (1.118) and (1.119)

**Dynamic equilibrium and detailed balance**: Following from our discussion of the relationship between the forward and reverse rate constant and equilibrium for opposing reactions, we can extend the treatment to many steps. These steps must set up equilibria

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{X} + \mathrm{Z} \tag{1.120}$$

and might go through a series of steps,

$$\begin{aligned} \mathrm{A} + \mathrm{B} &\rightleftarrows \mathrm{M}_1 + \mathrm{M}_2 \\ \mathrm{M}_1 + \mathrm{M}_2 &\rightleftarrows \mathrm{M}_3 + \mathrm{M}_4 \\ \mathrm{M}_3 + \mathrm{M}_4 &\rightleftarrows \mathrm{M}_5 + \mathrm{M}_6 \\ \mathrm{M}_5 + \mathrm{M}_6 &\rightleftarrows \mathrm{X} + \mathrm{Z} \end{aligned} \tag{1.121}$$

Each step has a forward, $k_i$ and a reverse, $k_{-i}$ rate constant. At equilibrium, each step is of the form,

$$k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} = k_{-1}[\mathrm{M}_1]_{\mathrm{eq}}[\mathrm{M}_2]_{\mathrm{eq}} \tag{1.122}$$

so for each step with have,

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\mathrm{M}_1]_{\mathrm{eq}}[\mathrm{M}_2]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} \tag{1.123}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[\mathrm{M}_3]_{\mathrm{eq}}[\mathrm{M}_4]_{\mathrm{eq}}}{[\mathrm{M}_1]_{\mathrm{eq}}[\mathrm{M}_2]_{\mathrm{eq}}} \tag{1.124}$$

*etc*. Combining these gives,

$$\begin{aligned} \mathrm{A} + \mathrm{B} &\rightleftarrows \cancel{\mathrm{M}_1} + \cancel{\mathrm{M}_2} \\ \cancel{\mathrm{M}_1} + \cancel{\mathrm{M}_2} &\rightleftarrows \cancel{\mathrm{M}_3} + \cancel{\mathrm{M}_4} \\ \cancel{\mathrm{M}_3} + \cancel{\mathrm{M}_4} &\rightleftarrows \cancel{\mathrm{M}_5} + \cancel{\mathrm{M}_6} \\ \cancel{\mathrm{M}_5} + \cancel{\mathrm{M}_6} &\rightleftarrows \mathrm{X} + \mathrm{Z} \end{aligned} \tag{1.125}$$

and

$$\begin{aligned} K &= \frac{k_1k_2k_3k_4}{k_{-1}k_{-2}k_{-3}k_{-4}} = \frac{\cancel{[\mathrm{M}_1]_{\mathrm{eq}}[\mathrm{M}_2]_{\mathrm{eq}}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} \times \frac{\cancel{[\mathrm{M}_3]_{\mathrm{eq}}[\mathrm{M}_4]_{\mathrm{eq}}}}{\cancel{[\mathrm{M}_1]_{\mathrm{eq}}[\mathrm{M}_2]_{\mathrm{eq}}}} \times \frac{\cancel{[\mathrm{M}_5]_{\mathrm{eq}}[\mathrm{M}_6]_{\mathrm{eq}}}}{\cancel{[\mathrm{M}_3]_{\mathrm{eq}}[\mathrm{M}_4]_{\mathrm{eq}}}} \times \frac{[\mathrm{X}]_{\mathrm{eq}}[\mathrm{Z}]_{\mathrm{eq}}}{\cancel{[\mathrm{M}_5]_{\mathrm{eq}}[\mathrm{M}_6]_{\mathrm{eq}}}} \\ K &= \frac{[\mathrm{X}]_{\mathrm{eq}}[\mathrm{Z}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} \end{aligned}$$

(1.126)

Depending on the relative sizes of the rate constants, the equilibrium lies either more to the products or the reactants. Once equilibrium is established, in spite of the forward and reverse rates, the system remains at equilibrium. The **principle of microscopic reversibility** states that reactants are still being converted to products, and products are forming reactants. However, no macroscopic change is observed. In other words, the forward and reverse rates are equal. This does not mean that $K$=1, but rather that the forward and reverse processes are taking place but they do not change the equilibrium.

The **principle of detailed balance** is almost the same, just stated differently. Microscopic reversibility refers to the forward and reverse rates. Detailed balance refers to collisions, stating that each collision, which moves the reaction forward, has a counterpart in another collision that leads to reactants becoming products. At equilibrium the two types of collisions maintain equilibrium.

The distinction is not critical.

### Michaelis-Menten Enzyme Kinetics

This is explained well in the book and is not reproduced here. See Section 10.9, and the section on Enzyme Kinetics.