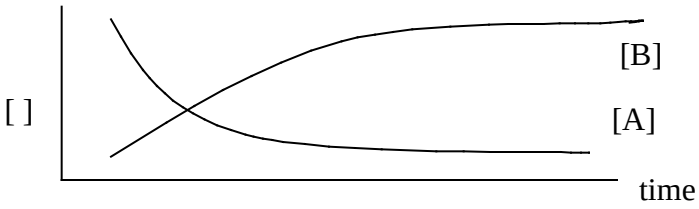
16 Kinetics

CH 302 Kinetics Study Guide (Memorize these two pages, they are all the background you need)

Reaction Rate: The most important issue in kinetics is a determination of the rate of a reaction and the data that comes from a plot of the rate data. In the concentration-time plot below for the reaction

$$aA \rightarrow bB$$



$$-\frac{\Delta[A]}{a\Delta t} = \frac{\Delta[B]}{b\Delta t} = \textbf{rate}$$

The rate is simply how fast A disappears (note the negative sign) and B appears as a function of time. The **instantaneous rate** is simply the tangent line at any time (the slope.) The lower case **a** and **b** are the reaction coefficients and are constants that make sure that rates at which things appear and disappear are the same (conservation of matter.)

Rate Laws (what affects the rate.) Of course you can ask the question, what factors affect the rate. There are four factors : **[A]**^{x} which is the concentration of A, the pre-exponential factor, **A**, which depends on the state of the reactants, **T**, the temperature, and $\mathbf{E_a}$, the activation barrier. With these factors we make a RATE LAW.

$$- \frac{\Delta[A]}{a\Delta t} = \frac{\Delta[B]}{b\Delta t} = \text{rate} = A \exp(-E_a/RT)[A]^x = k[A]^x$$

The first three terms **A** exp (-$\mathbf{E_a}$/R**T**) combine to make the **rate constant**, **k**.

Half the problems you do in kinetics use this **differential rate expression**. Among problems you can do:

- Calculate the instantaneous rate at any given time: measuring the slope of the tangent line
- Determining the order of a reaction (the exponent **x**) using a **method of initial rates**
- Calculate k, T, E_a, A, [ ] or x given known values.

HINT: This third type of problem is simple plug-and-chug except that you need to be able to manipulate the **exp** term effortlessly. Remember this is done using the inverse relationship **ln (exp x) = x**

Integrated Rate Law. You might think the **differential rate expression** above tells us just about all we need to know about reaction kinetics. Almost. The one thing it can't answer is the following simple but important question: Suppose a certain amount of compound reacts over time; how much is left at some later time? (for example, I have 100 molecules of A which reacts with a rate constant of $2x10^{-2}$ sec^{-1}. How much A is left after 1 s?) To work this problem we need to integrate the differential rate expression. Those of you who have had calculus can do this easily. The answers for the three most important reaction orders are shown below.

	order x = 0	order x = 1	order x = 2
differential rate law	$-\frac{\Delta[A]}{a\Delta t} = k$	$-\frac{\Delta[A]}{a\Delta t} = k\,[A]^1$	$-\frac{\Delta[A]}{a\Delta t} = k\,[A]^2$
integrated rate law	$[A] = [A_o] - akt$	$\ln [A] = \ln[A_o] - akt$	$1/[A] = 1/[A_o] + akt$

In each case, you can calculate how much is left from starting materials or formed as products given the starting amount, $[A_o]$, the rate constant, k, and the reaction time, t.

Reaction half life. As an aside, there is a special form of the integrated rate equation corresponding to when half of the starting material, [A] = 0.5 [A_o], has disappeared. The half-life was an important expression back when people didn't have calculators that could do **ln** functions, but now we do, so the half life expression is of little value. You can solve for this special case, or you can just use the regular integrated rate equation above.

More advanced kinetics topics:

Curve Fitting Integrated Rate Equations. It is possible to arrange the integrated rate expressions so they look like straight line functions, y = mx + b. For example,

$$\ln[A] = -akt + \ln [Ao]$$

$$y \quad m\,x \quad b$$

This means you can plot the ln of [A] at different times and get $\mathbf{[A_o]}$ from the y-intercept and the rate constant, **k**, from the slope.

Reaction mechanism. The rate law of a reaction does not have to correspond to the stoichiometry of a reaction. **If A + B → C + D it does not mean that rate = k $[A]^1[B]^1$**

Instead lots of complicated things might be going on in the form of a reaction mechanism. Maybe A → I_1, I_1 → I_2, I_2 + B → C +D where I_1 and I_2 are **reaction intermediates**. The reaction order is determined by everything that happens in this multi-step process BEFORE the **Rate Determining Step** (the slowest step in the reaction.) Thus, If A → I_1 is the slowest step, then whatever happens afterward doesn't affect the rate and the reaction rate law is just rate = k[A]

Kinetic Theories: Every chapter has it theories. This chapter has two.

Collision Theory: This theory suggests that sometimes reaction don't occur because even when molecules collide, maybe they don't collide in the right orientation. For example, maybe the δ^- part of a molecule needs to bump into the δ^+ part of another molecule, but instead bumps into the δ^-. Instead of a reaction, repulsion occurs instead of a reactive collision.

Transition State Theory. This theory suggests that even when molecules collide in the right orientation, they don't have enough energy to overcome an energy barrier to forming an intermediate **transition state**:

$$A + B—B \rightarrow \underset{\text{Transition state}}{A---B---B} \rightarrow A—B + B$$

There is an energy barrier to this transition state called the **activation energy, E_a,** that we saw in the rate law. This energy barrier is the reason I have to light a match to start a combustion reaction like $H_2 + O_2$. It is also the reason that a **catalyst** can be added to a reaction to lower a reaction barrier and make a reaction happen faster. An example of this was adding a metal oxide to hydrogen peroxide to make it react faster. Remember that the metal oxide wasn't part of the reaction, it was still there when the reaction ended. It simply made it easier to form the transition state.

Combining Arrenhius equations: How does one experimentally calculate the activation energy, Ea? One approach is to combine Arrenhius equations,

$K_1 = A \exp(-E_a/RT_1)$ $K_2 = A \exp(-E_a/RT_1)$ combine to yield

$$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$$

Experimentally, we can run a reaction at two different temperatures, measure two rate constants and then plot the data to obtain the activation energy, E_a, from the slope of the line.

Thermodynamics let's us down:

Okay, we've finished a four day primer on thermodynamics and you now know how to tell whether a reaction is spontaneous. Just do a ΔG^o Gibbs free energy calculation. Okay, let's take our knowledge and put it to good use:

Consider the combustion of ethanol:

$$CH_3CH_2OH + 7/2\ O_2 \text{ ----> } 2\ CO_2 + 3H_2O$$

ΔG_f^o	-175	0	-394	-237	ΔG_{rxn}^o= -1324 kJ

Clearly a strongly exothermic reaction. Except that you all know that ethanol doesn't react in the presence of O_2 or it wouldn't be such a popular beverage. What's going on? Has thermodynamics failed us?

Getting over the activation barrier:

Now consider what happens when I light a match over some liquid ethanol. Suddenly a reaction starts. After a while we would see that it has gone to completion. But it would take a while until all the ethanol had been combusted to form CO_2. Now consider a case where we have gaseous ethanol in a bottle. After we light a match the reaction is almost explosively fast. What is going on?

What Kinetics Tells Us:

Remember that thermodynamics can do nothing more than tell us whether things will react and the extent to which they react. It tells us that ethanol and O_2 will react and sure enough they do. But nothing we have learned before today explains the three experiments just shown:

1. Without a match, the reaction doesn't occur at all
2. As a liquid the reaction occurs at a slow rate over the course of minutes.
3. As a gas, the reaction occurs violently in a few seconds.

The explanations for these three observations come not from thermodynamics but rather from an understanding of chemical kinetics.

Chemical kinetics: the study of the **rate** and **mechanism** by which a reaction occurs.

Chemical rate: The amount of reactant consumed or product formed as a function of time

Chemical mechanism: the path by which a reaction occurs.

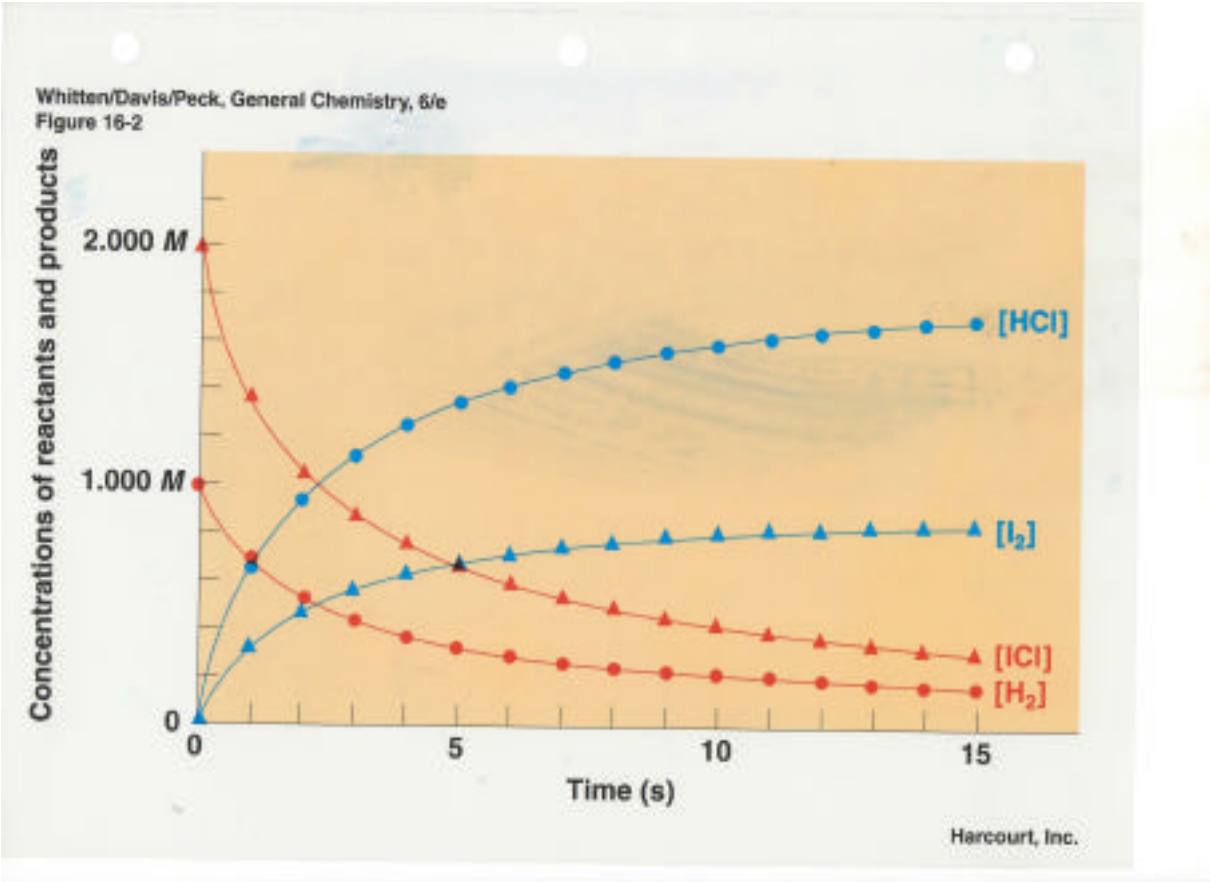
Remember how we stressed over and over about thermodynamics that we neither cared how fast or by what path a reaction occurred? Now you see why, we were just saving those topics for the kinetics chapter.

Rate of Reaction:

For a reaction

$$aA + bB \longrightarrow cC + dD$$

where the quantities A, B, C, D are concentrations of reactants and products and a,b,c,d are stoichiometric coefficients to balance the reaction, there will be a rate at which the reactants decrease in concentration and products increase in concentration for a particular time interval. This is shown in the concentration vs. time plot below.


Whitten/Davis/Peck, General Chemistry, 6/e
Figure 16-2
Concentrations of reactants and products
2.000 M
1.000 M
0
0
5
10
15
Time (s)
[HCl]
[I2]
[ICl]
[H2]
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The Rate Equation for the [ ] vs. t plots

Can we develop the math to describe this process? Shown below are the differential rate expressions for each of the products and reactants

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

As ΔT decreases, we better define the instantaneous concentration and for a specific time and write the equations replacing ΔT with a derivative, dT and Δ[A] with a derivative d[A].

$$\text{rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$$

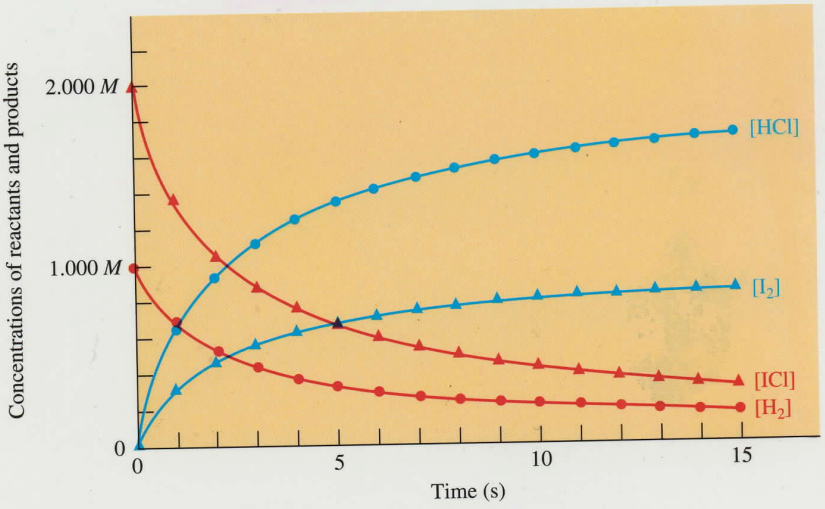
Note that the negative signs for A and B indicate the reactants are decreasing in concentration. Note also that by using the coefficients from the balanced reactions, we can equate the rates for each of the chemical species. Thus we have one rate of reaction and can obtain it from a measurement of any reactant or product.

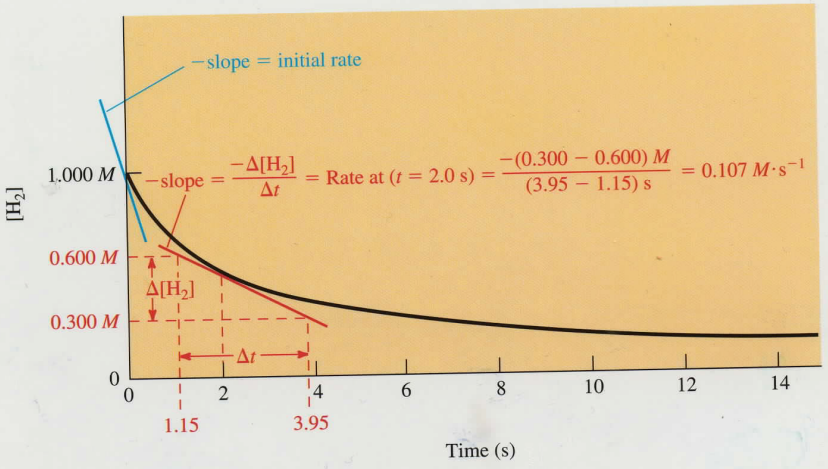
Concentration-Time Plots:

Ideally we would have some kind of detector that would allow us to follow the change in concentrations of a reaction as a function of time. We would be able to obtain plots that look like the one below from which at any point in time we would know exactly which species were present in the chemical system.

What we could also learn from these plots is the **instantaneous rate of reaction**. Consider just one of the reaction profiles above for a reactant decreasing in concentration over time. Note that initial the reactant is initially disappearing at a fast rate and that later in the reaction it slows down. If we want, we can get the instantaneous rate by measuring the slope at any point, for example by finding a tangent to the curve. Those of you who are turned on by math may recognize this as the way you were introduced to the concept of derivatives in calculus.

Transparency number 106 **Text Figures 16.2, 16.3, pages 597, 598**





Whitten/Davis/Peck, *General Chemistry and General Chemistry with Qualitative Analysis*, 5/e

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Mathematically, we could find the rate at any point if we knew the function for the curve and could take the derivative and solve for a particular time. Good news--we will learn how to make a function that fits this curve in a bit.

Factors Affecting Reaction Rate:

There are several factors that affect how fast a reaction happens; i.e., how steep the slope of the curve is:

1. nature of the reactant
2. concentration of reactants
3. temperature
4. presence of a catalyst.

We will examine each of these beginning today with the first two factors.

Nature of reactants. We have already seen a good example of how the physical state of a reagent affects reaction rate. Remember our ethanol reaction? When we combusted the liquid, the reaction took a while to reach completion. However when we made it into a gas in an enclosed volume, the rate skyrocketed. For the ethanol case, the reason the gas phase reaction went much faster is because the conditions made it possible for a greater number of ethanol molecules per unit time to encounter oxygen molecules.

Rule of thumb: In general, the greater the division of sample, either by increasing surface area or exposing the atoms or molecules in the gas phase, the faster the reaction.

Rate of reaction and reagent concentration:

A rate-law expression relates the rate of a reaction to concentration. For example, note in the example shown in class, the rate of reaction was observed to decrease as the concentration decreased.

Rate Law: For a reaction involving reactants A, B, ... , the rate is dependent on concentration as described by an equation with the following general form

$$\text{rate} = k[A]^x[B]^y.....$$

Here k is the rate constant and x and y are coefficients for the reaction, typically integer values, most commonly 0,1 and 2.

The coefficients **x** and **y** are NOT the coefficients associated with stoichiometry.

Order of a reaction: The order of a reaction is found by summing the coefficients.

reaction order = x + y + ...

Typical values for reaction orders are integers, most commonly 0, 1 and 2.

Review the handout on all the ways to do orders of reactions.

Example of reaction order:

$2N_2O_5 \text{ ----> } 4NO_2 + O_2$ rate = $k[N_2O_5]$

This reaction is first order in $[N_2O_5]$ and first order overall.

Example of reaction order:

$2NO + O_2 \text{ ----> } 2NO$ rate = $k[NO][O_2]$

This reaction is first order in NO and in O_2 and second order overall.

Things to remember about the rate constant, **k:**

1. It applies only to a specific reaction at a specific temp.
2. Its units depend on reaction order
3. Its value is independent of concentration
4. It does not change with time (although rate can)
5. You have to find k experimentally. You won't find it in a table in the appendix.

Experimental Determination of Rates: Method of Initial rates.

A simple method for determining rate constants is to run a particular reaction several times using different concentrations of starting materials and experimentally determining the initial rate of reaction. The difference in rates for a change in concentration can be related through the rate equation by adjusting the reaction order, x.

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

From this simple rate equation we see the effect of concentration on rate for a reaction orders 0, 1, and 2.

order	rate equation	effect of concentration on rate
0	rate = $k[A]^0 = k$	none
1	rate = $k[A]^1$	rate increases linearly with concentration
2	rate = $k[A]^2$	rate increases as the square of the concentration

Note also that having determined the order of a reaction, we can easily calculate the rate constant, k, by substituting a piece of rate data back into the rate equation.

Now a few examples:

Finding the Order and Rate Constant of a Reaction

Example 1. The following rate data were obtained at 25°C for the following reaction. What are the rate-law expression and the specific rate constant for this reaction?

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation C M/s or $M \cdot s^{-1}$
1	0.10M	0.10M	$2.0 \times 10^{-4}\ M \cdot s^{-1}$
2	0.20M	0.30M	$4.0 \times 10^{-4}\ M \cdot s^{-1}$
3	0.10M	0.20M	$2.0 \times 10^{-4}\ M \cdot s^{-1}$

First, use experiments 1 & 3: [A] constant, [B] doubles but rate unchanged order = 0 for [B]

Second, use expriments 1 & 2: [B] doesn't matter (order = 0.) [A] doubles and rate doubles order = 1 for [A]

$$\text{rate} = k[A]^1[B]^0 = k[A]$$

Third, find k: $k = \frac{\text{rate}}{[A]} = \frac{2 \times 10^{-4}\ (M)\ (5^1)}{0.1M} = 2 \times 10^{-3}\ s^{-1}$

so, all together,

$$\text{rate} = k[A]^1[B]^0 = 2 \times 10^{-3}\ s^{-1}\ [A]$$

Example 2.

Experiment	Initial [A]	Initial [B]	Initial [C]	Initial Rate of Formation of D
1	0.20M	0.10M	0.10M	2.0×10^{-4} *M*/min
2	0.20M	0.10M	0.20M	4.0×10^{-4} *M*/min
3	0.20M	0.10M	0.30M	2.0×10^{-4} *M*/min
4	0.40M	0.20M	0.40M	8.0×10^{-4} *M*/min

order = 0 for [C]

Second, hold [A] constant, ignore [C] in exp. 1 & 2: double [B], rate doubles order = 1

Third, hold [B] constant, ignore [C] in exp. 2 & 4, double [A], rate doubles order = 1.

$$\text{Rate } k[A]^1[B]^1$$

Integrated Rate Equation.

Recall that earlier I suggested it might be nice to know what the function was that described the relationship between concentration and time for a reaction curve. Here is our chance.

The good news is that the equations we will develop to describe the kinetic reactions fall into a few simple categories which are a function of the order of a reaction. In other words, all zero order reaction have the same shape to the curve; all first order reactions have the same shape to the curve; all second order reactions have the same shape to the curve.

The bad news is that we have to use calculus to find the equation.

Lets do it for just the first order integrated rate equation since it is really famous. This is the one that describes radioactive decay and a million other things.

Derivation of First Order Integrated Rate Equation:

For a reaction

$$aA \longrightarrow \text{products}$$

the rate is expressed by

$$\text{rate} = \frac{-1}{a}\frac{d[A]}{dt}$$

For a first order reaction, the rate is proportional to the first power of [A].

$$\frac{-1}{a}\frac{d[A]}{dt} = k[A]$$

Separating variables allows us to put concentration on one side and time on the other side.

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

Recognize that this derivative function only tells us about what is going on at a single point in time. We want to know what is happening over the entire reaction. To learn this, we integrate over the length of the reaction, from time = 0 to time, t, and the change in concentration, from the initial concentration of A, $[A_o]$.

$$\int \frac{-d[A]}{[A]} = \int akdt$$

Right about now I know you are thinking back to calculus and asking yourself what the integral for 1/A is--that's right it is a natural log function.

$$\frac{\ln [A_0]}{[A]} = akt$$

Now rearranging leaves us with the famous form of a first order integrated rate expression. Note that this equation gives us what we want: for any starting concentration and rate constant, you can stick in a time and it will tell you what the concentration is.

We can also obtain a value for the half-life of the reaction.

Reaction half-life: This is defined as the point where $[A] = 0.5[A_o]$ and with a little math is found to be

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{ak}$$

Note that the half life does not depend on how much material you start with for a first order reaction.

We could find solutions for the integrated rate equation for zero and second order reactions as well, using calculus as we did for the first order reaction. The resulting expressions and the half-life expressions are summarized in the table below.

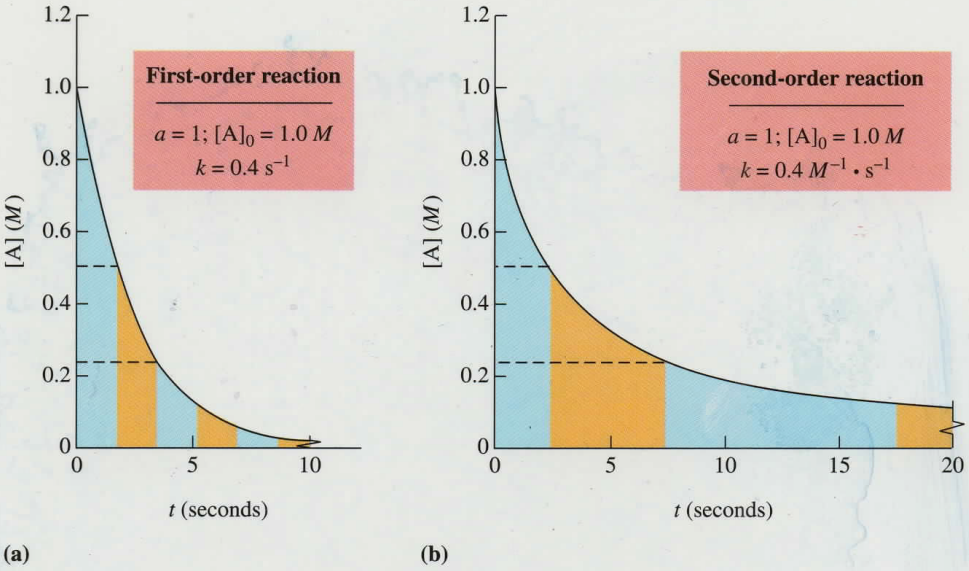


Table 16-2 ***Summary of Relationships for Various Orders of the Reaction aA → Products***

	Order		
	Zero	***First***	***Second***
Rate-law expression	rate $= k$	rate $= k[A]$	rate $= k[A]^2$
Integrated rate equation	$[A] = [A]_0 - akt$	$\ln \frac{[A]_0}{[A]} = akt$ or $\log \frac{[A]_0}{[A]} = \frac{akt}{2.303}$	$\frac{1}{[A]} - \frac{1}{[A]_0} = akt$
Half-life, $t_{1/2}$	$\frac{[A]_0}{2ak}$	$\frac{\ln 2}{ak} = \frac{0.693}{ak}$	$\frac{1}{ak[A]_0}$

Comparison curves for first and second order integrated equations are also provided. In plot (a) note that in the first $t_{1/2}$ of 1.73 s, the concentration of A falls from 1.0M to 0.5M. It falls again by half from 0.5M to 0.25M in the next 1.73 s. And on and on. Contrast this with a second order reaction in (b) where during the first 2.5 s $t_{1/2}$, the concentration falls from 1.0M to 0.5M. However the second $t_{1/2}$ takes 5 s for the concentration to be cut in half; the third $t_{1/2}$ takes 10 s. Note the concentration dependence of $t_{1/2}$ for all reactions that are not order one.

Curve Fitting: Graphing the integrated rate equation.

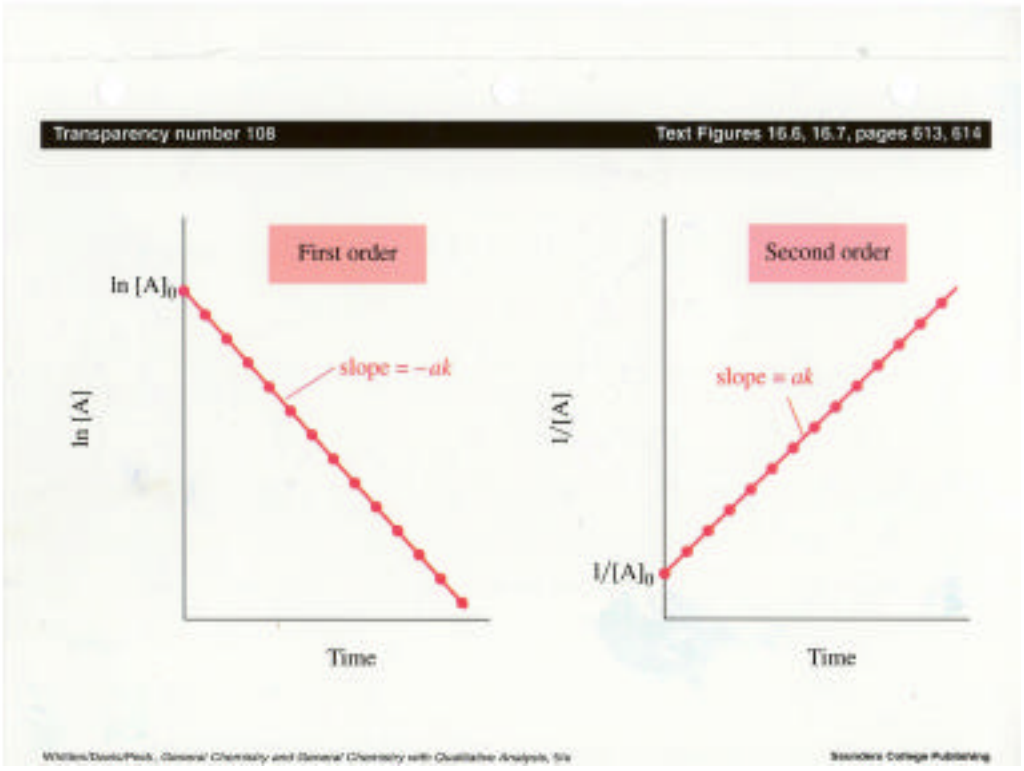
Something scientists do a lot is to try to find a best fit of a theoretical equation to experimental data. Let's see if there is any value in doing it for the integrated rate equations that were and are shown in the table above. Remember these are the equations that let us find out how much stuff we have after a reaction has been going on awhile.

In trying to fit experimental data, it is important to know what kind of function will fit the data. Scientists hope to find simple relationships like straight lines or parabolas because they aren't crazy about doing hard math either. Well the good news for the integrated rate equations is that each of them can be arranged to fit a straight line.

Remember that a straight line has the form:

$$y = mx + b$$

with two constants, a slope, m, and a y-intercept, b. The dependent y-variable is plotted as a function of the independent x-variable.



One of the reasons scientists try to fit their data is that parameters like the slope or y-intercept actually correspond to important scientific information. For example, in doing kinetics, a couple important pieces of information are the rate constant, k, and the amount of starting material in a reaction, $[A_o]$. Wouldn't it be great if we could extract that kind of information from a kinetics plot?

Let's try to fit the first order integrated rate equation we derived to a straight line plot.

$$\ln \frac{[A_o]}{[A]} = akt$$

Using a bit of knowledge about the properties of log functions, we can rewrite the natural log term as a subtraction.

$$\ln \frac{a}{b} = \ln(a) - \ln(b) \qquad \ln [A_o] - \ln[A] = akt$$

Now let's rearrange: $\ln[A] = -akt + \ln[A_o]$

This ought to look an awful lot like a straight line function and in fact that is what we see in the graph above.

We can do the same for the second order integrated rate equation:

$$\frac{1}{[A]} = akt + \frac{1}{[A_o]}$$

and for zero-order integrated rate equation:

$$[A] = -akt + [A_o]$$

This idea of fitting data to a known function for the purpose of extracting useful scientific information is incredibly important in science. It is presented as yet another example of an effort to make math real to budding scientists like you. More than understanding its application here to kinetics, I'd rather you recognize the general concept of fitting functions to experimental data because you will do it a lot during your science courses at UT. For example, you will probably have to do it again before the end of the kinetics chapter for an entirely different application.

Reaction Mechanisms.

If life was really simple, then a reaction mechanism for a reaction like:

$$A + B \text{ -----> } AB$$

would simply involve a bimolecular reaction between A and B. The rate expression for the reaction would be

$$\text{rate} = k[A][B]$$

and the reaction would be first order in [A] and [B]. Sadly, it is rarely this simple. Instead reactions often go through a series of simple steps which taken together make up the reaction pathway.

reaction mechanism: The step-by-step process by which a reaction occurs. It usually involves a series of smaller unimolecular or bimolecular reaction steps.

Example. Reaction of $NO_2 + CO \text{ -----> } NO + CO_2$

In a simple world the mechanism for the reaction would be

$$\text{rate} = k[NO_2][CO]$$

but what if I told you the actual rate law was

$$\text{rate} = k[NO_2]^2$$

This result should tell you right off that experimental kinetics is hard. The result above is indeed the experimentally verified mechanism for the reaction, found by the same methods we used in method of initial rates. So what is happening in this reaction? No one really knows for sure, but several mechanisms have been postulated including

$NO_2 + NO_2 \text{ -----> } NO_3 + NO$
$NO_3 + CO \text{ ----> } NO_2 + CO_2$

$NO_2 + CO \text{ -----> } NO + CO_2$

NO_3 is referred to here as a reaction intermediate. It is neither a reactant nor a product of the reaction, but is postulated to exist for a brief time in the reaction process.

Constructing reaction rate-laws from postulated mechanisms.

Suppose you come up with a proposed mechanism for a reaction. Is there a procedure for creating the rate law?

Before answering the question, it is necessary to consider the existence of a special reaction in the mechanism known as the rate-determining step.

rate determining step (RDS): The slowest step in the reaction.

For example, in the two-step reaction above, each of the equations has its own reaction rate. The one that is slowest is the RDS. In determining the rate expression from a mechanism, we never consider steps that come after the RDS.

Example:

What is the rate law for the following reaction mechanism?

Cl_2 <-----> Cl + Cl fast)
Cl + H_2S <-----> HCl + HS (fast)
HS + Cl ------> HCl + S (slow)

Cl_2 + H_2S ------> S + 2HCl (net rxn)

rate = k [HS][Cl]

Collision theory.

Something you can start to do that will make understanding science a lot easier is to get yourself down on the level of molecules and atoms and try to experience the world as they do. Kind of a "walking in another molecule's shoes" perspective.

For example, we've talked about thermodynamics and you know how to determine whether a reaction is spontaneous. But as we've seen, just because a reaction is spontaneous doesn't mean that it is going to happen. You've got to get small to understand why. Imagine you are a molecule with an intense desire to react with another molecule. Whether in solution or the gas phase, the first thing you have to do is get close to the species with which you will react--basically you need to collide with another molecule. This concept lays the foundation for **the collision theory** of reaction rates.

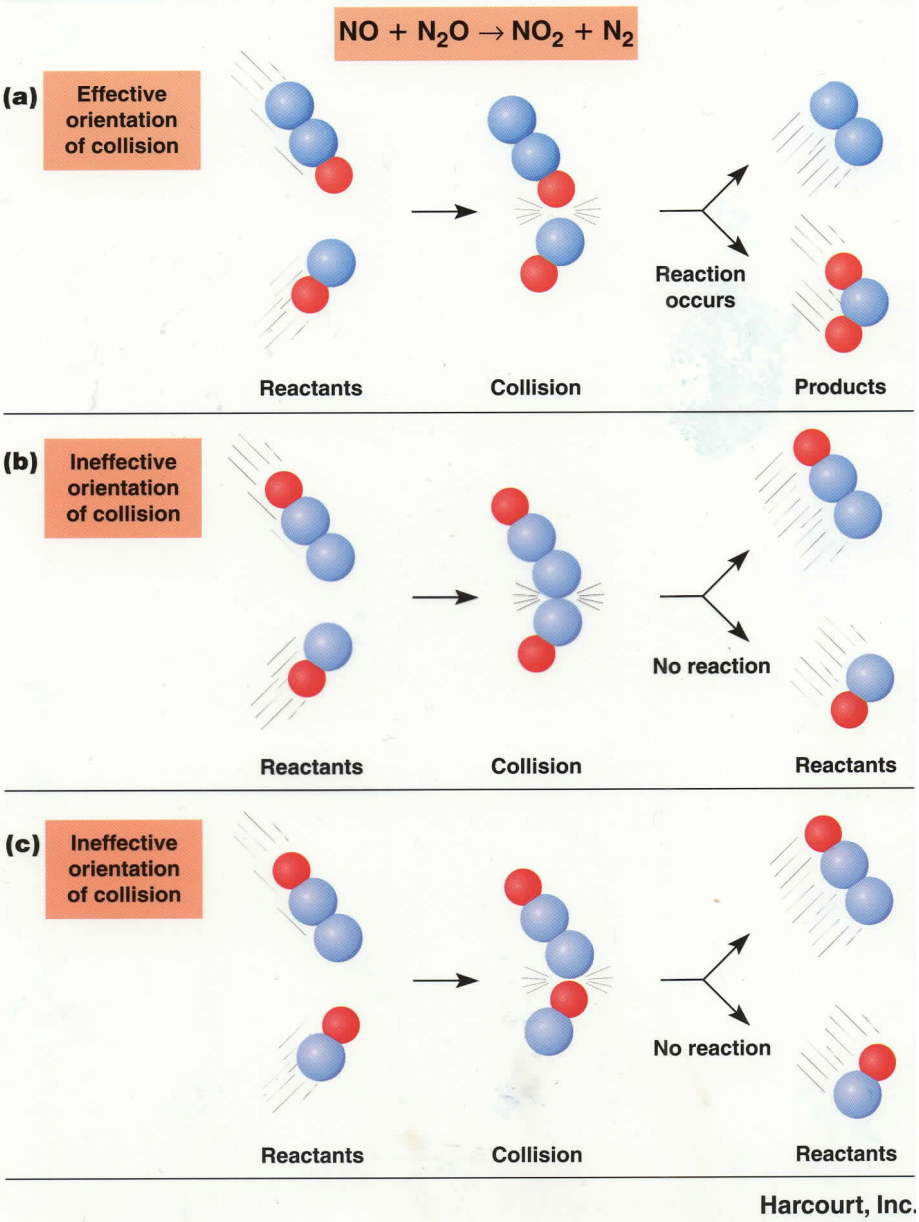
The problem is that just because a collision occurs doesn't mean a reaction will occur. Why?

Reasons that reactions don't have to occur when a thermodynamically-favorable (ΔG is -) collision occurs:

1. Collision theory: the orientation or angle of the molecules is not conducive to reaction.

2. Transition state theory: there is insufficient energy to create an transition complex.

Whitten/Davis/Peck, General Chemistry, 6/e
Figure 16.9



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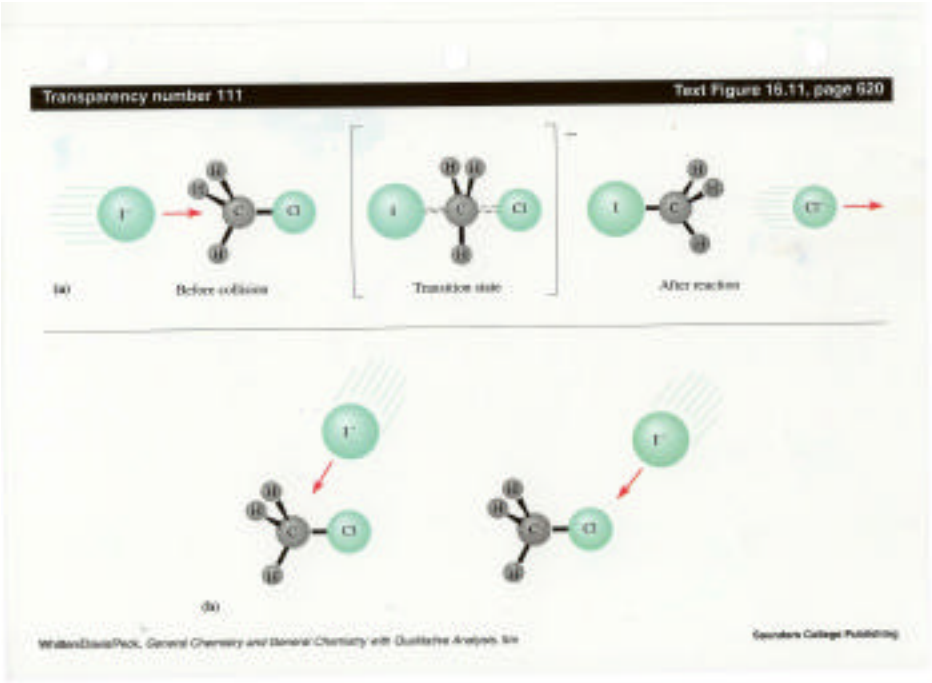
Look at the nice picture to understand why an orientation upon collision might not be appropriate. Note in this reaction that it would be nice for the side of a N_2O molecule with an oxygen to encounter the side of an NO molecule with a nitrogen. Well this certainly doesn't have to happen--there are far more orientations that are unlikely to be reactive than will be reactive. It is beyond the scope of the chapter to discuss examples in detail, but for those of you heading to organic chemistry, you will spend an enormous amount of time looking at mechanisms that are strongly dependent on the orientation of the collision.

Transition state theory.

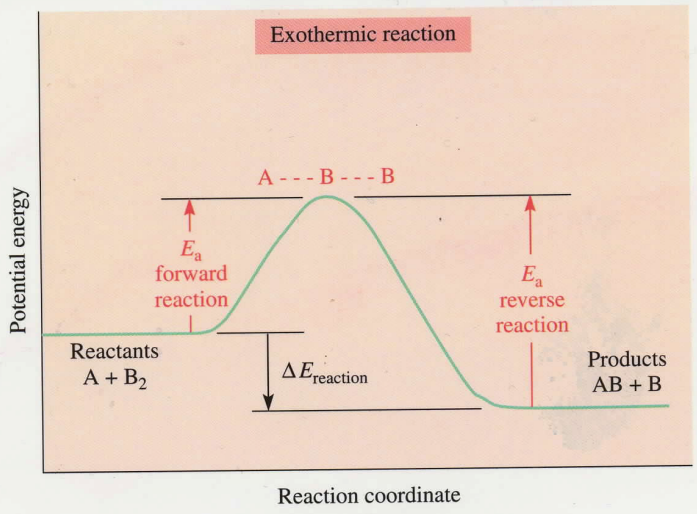
Recall that for me to initiate the spontaneous ethanol combustion reaction, I had to raise the temperature of the system by lighting a match. The reason for this follows from transition state theory that recognizes that a certain amount of energy must be made available when a collision between reactants occurs so that an activation barrier can be overcome.

The reason for this is that at the point that a reaction occurs, some bonds in the stable reactant molecules must be broken and formed so that a transition state complex can be formed between the two reactants.

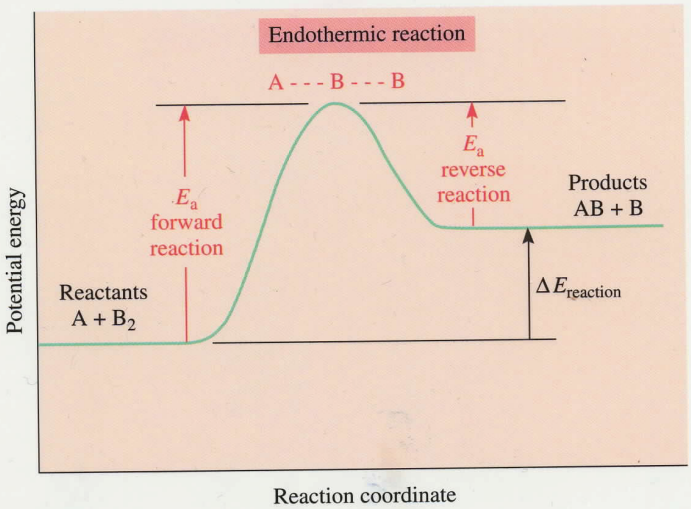

Transparency number 111
Text Figure 16.11, page 620
(a)
Before collision
Transition state
After reaction
(b)

A + B—B ----->	A----B-----B ------>	A—B + B
reactants	transition state	products

The amount of energy that must be provided is known as the activation energy, E_a. Examples of this activation energy barrier for an exothermic and an endothermic reaction are shown below.



(a)



(b)

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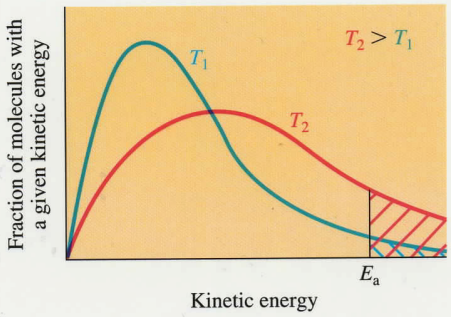
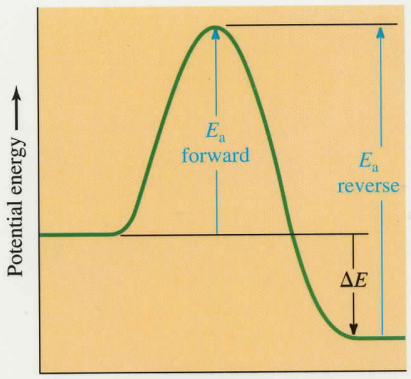
Note that even when a reaction is exothermic, it is necessary to introduce energy to the system to create the transition state. Note also that for an endothermic reaction, E_a, more energy than ΔE_{rxn} must be provided for the reaction to occur.

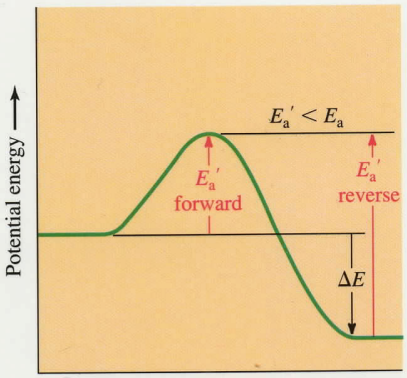
A question you might now ask is, what can be done to overcome this activation barrier which keeps otherwise thermodynamically favorable reactions from happening. We can do two things:

1. Provide the necessary energy to form the transition state, i.e. raise the energy of the reactants by raising the temperature of the system (lighting a match)

2. Make the activation barrier smaller. This is done by adding a catalyst to the system which has the effect on activation energy shown below.







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We'll look at each approach.

Temperature and the Arrenhius equation. A while back a guy named Arrenhius thought he would develop an empirical (experimentally-derived) expression that defined what k, the rate constant, was. You will remember that about all we've done with k to this point is give it a number. We haven't asked, how is k defined? Well Arrenhius did, and got an equation named after him:

$$k = A\exp(-Ea/RT)$$

where k is the rate constant found in our rate expressions on p. 34, E_a is the activation energy necessary to create the transition state, R is the gas law constant, T is temperature, and A is a constant you don't need to know about yet.

For our purposes we will assume that the constants A and R, are not to be messed with. So we will concentrate on T and E_a. The question of interest is, how do T and E_a affect the rate constant. If we wanted to make a reaction faster by speeding up the rate constant, what would we want to do?

(I want you to play with the equations using a calculator) but I'll give the kind of reasoning you should use:

for temperature: If you increase T, (-Ea/RT) is a amaller number, therefore, Aexp(-Ea/RT) is a larger number. This means the rate constant will be larger and the rate faster.

for activation energy: If you decrease Ea, (-Ea/RT) is a smaller number, therefore Aexp(-Ea/RT) is a larger number. This means the rate will be faster.

Temperature and rates: A really good question you might ask about a reaction rate, is, just how much can I speed up the reaction by raising the temperature. We all have the intuitive idea that cranking up the heat gets a reaction done faster; after all, it is how we get food to the dinner table faster. But can we come up with a quantitative description?

Combining Arrenhius equations. Assume that for the same reaction, we have two reaction rates, each occurring at a separate temperature.

$$k_1 = A\exp(-Ea/RT_1) \qquad k_2 = A\exp(-Ea/RT_2)$$

I'm not going to do the math, but when all is done, the following equation is formed.

$$\ln\frac{k_2}{k_1} = (Ea/R)(1/T_1 - 1/T_2)$$

Example. How to find how fast does a reaction rate changes when we increase the temperature. The rate constant for a first order reaction is 9.16 x 10^{-3} s^{-1} at 0ºC. E_a is 88 kJ/mol. If the temperature is raised 2ºC, what is the new rate constant?

$$N_2O_3 \text{ --------> } NO_2 + NO_3$$

First we tabulate the values, remembering to convert temperature to Kelvin scale.

E_a = 88.000 J/mol		R = 8.314 J/mol · K
k_1 = 9.16 X 10^{-3} s^{-1}	at	T_1 = 0.0°C + 273 K
k_2 = ?	at	T_2 = 2.0°C + 275 K

We use these values in the "two temperature" from of the Arrhenius equation. Taking inverse (natural) logarithms of both sides.

$$k\ 2 = 1.32\ (9.16\ X\ 10^{-3}\ s^{-1}\ ) = 1.21\ 10^{-2}\ s^{-1}$$

We see that a very small temperature difference, only 2°C causes an increase to the rate constant (and hence in the reaction rate for the same concentrations) of about 32%.

Example. How to experimentally determine an activation energy, E_a.

For the rxn C_2H_5I ---> $C_2H_4 + HI$

At 600K, K= 1.6 X 10^{-5} s^{-1}. At 700K, k = 6.36 X10^{-3} s^{-1} What is E_a? Substituting into the combined Arrhenius:

$$E_a = 2.09 \text{ X}10^{-5} \text{ J/mol or } 209 \text{ kJ/mol.}$$

TIME OUT. Time out to see curve-fitting in action again!! Remember how a few short pages ago, we saw the utility in fitting a straight line to some experimental data to get values for k and $[A_o]$. Note we can do it as well by fitting the Arrhenius equation to a straight line.

$$\ln k_2 = \left(\frac{-E_a}{R} \cdot \frac{1}{T_1} - \frac{1}{T_2}\right) + \ln k_1$$

Wow!! By obtaining rate constants as a function of temperature, we have a way to extract E_a from the slope of the line.

Catalysts.

Recall that rather than raising the temperature of a system, we can speed up a reaction by lowering the activation energy. This can be a real advantage, say in the human body where cranking the temperature up 20^{o} to speed up a metabolic process probably isn't a good idea. This is why the human body is teeming with catalysts called enzymes. Again a detailed discussion of catalysts is well outside a general chemistry course. So just a few vocabulary words are provided to make you sound intelligent when talking to friends. You'll get this stuff in detail in biochemistry and physical chemistry courses.

catalyst	Substance that increases reaction rate by reducing E_a. This is done by making alternative pathways available for reaction. Catalysts are not consumed in a reaction.
enzyme	A biological catalyst. All those biological sounding words that end in **-ase** are enzymes. For example, anhydrase or oxidase or pepcidase
homogeneous catalyst	A catalyst which exists in the same phase as the reactants.
heterogeneous catalyst	A catalyst that is in a different phase from the reactants. Typically they are solids. The most famous is the dreaded catalytic converter in you car exhaust system that keeps the environment clean by breaking down incomplete combustion products. However this comes at the expense of having the family automobile be able to cruise at 120 MPH.

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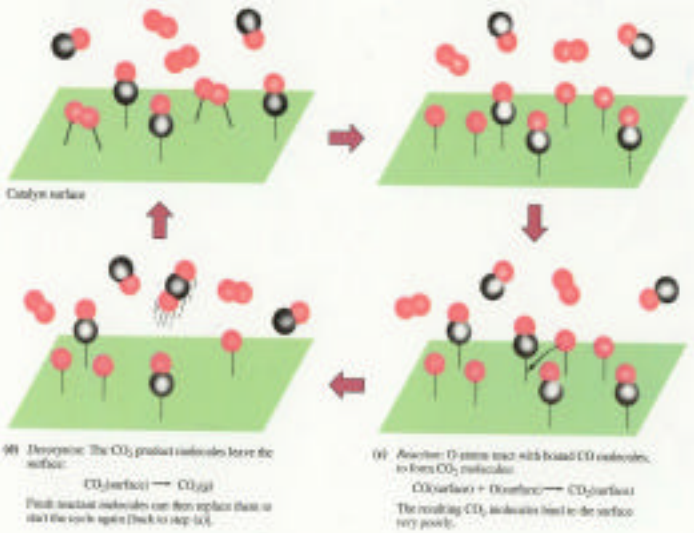
Text Figure 16.18, page 633



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