

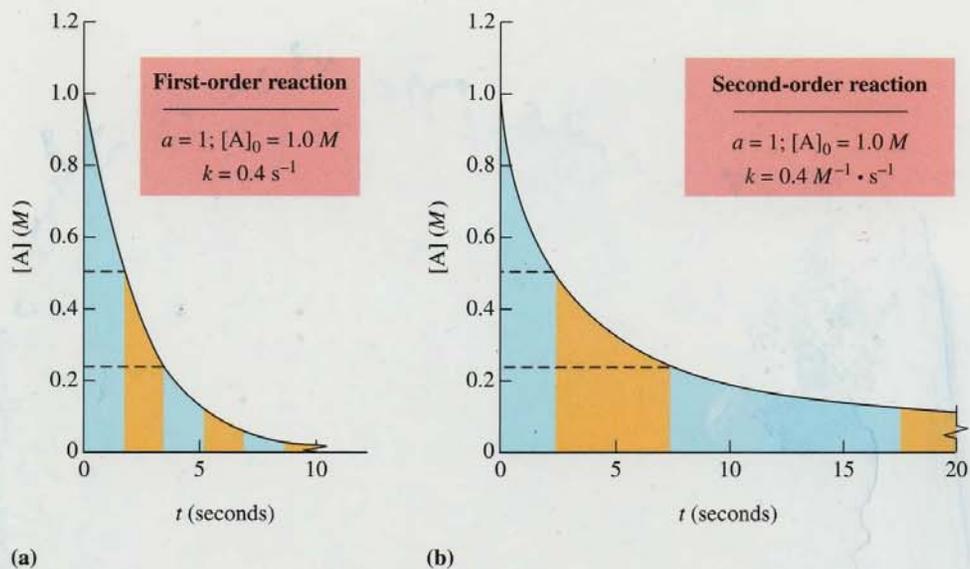
## Lecture 22: The Arrhenius Equation and reaction mechanisms.

As we wrap up kinetics we will:

- Briefly summarize the differential and integrated rate law equations for 0, 1 and 2 order reaction
- Learn how scientists turn model functions like the integrated rate laws into straight lines from which useful information can be found in the slope and y-intercept
- Learn about the three factors found in the rate constant: A,  $E_a$  and T are related in the Arrhenius equation
- Learn how the activation energy can be extracted from concentration time data using the combined Arrhenius equation
- Learn about two theories developed to explain kinetics: collision and transition state theory
- Learn about how the rate law for a reaction is created from the reaction mechanism
- Look at some famous catalysts

First, a summary of the differential and integrated rates laws from the first kinetics lectures:

In addition to the equations we have derived, note the 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.



**Table 16-2 Summary of Relationships for Various Orders of the Reaction**  
 $aA \rightarrow \text{Products}$

	Order		
	Zero	First	Second
Rate-law expression	$\text{rate} = k$	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$
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, $t_{1/2}$	$\frac{[A]_0}{2ak}$	$\frac{\ln 2}{ak} = \frac{0.693}{ak}$	$\frac{1}{ak[A]_0}$

## Curve Fitting: Graphing the integrated rate equation.

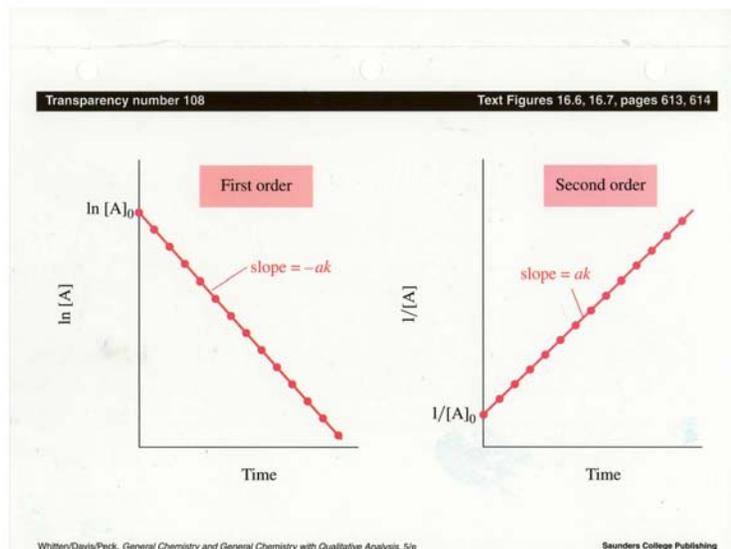
Something scientists do a lot is to try to find a best fit of a theoretical equation to experimental data. Let's see if there is any value in doing it for the integrated rate equations that were and are shown in the table above. Remember these are the equations that let us find out how much stuff we 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,  $[A_0]$ . 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.

$$\ln \frac{[A_0]}{[A]} = a \quad k \quad t$$

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

$$\ln \frac{a}{b} = \ln(a) - \ln(b) \qquad \ln [A_0] - \ln[A] = akt$$

Now let's rearrange:

$$\ln[A] = -akt + \ln[A_0]$$
$$y = mx + b$$

This ought to look an awful lot like a straight line function and in fact that is what we see in the graph above where a plot of  $\ln[A]$  versus time yields useful information.

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

$$\frac{1}{[A]} = akt + \frac{1}{[A_0]}$$

and for zero-order integrated rate equation:

$$[A] = -akt + [A_0]$$

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.

**Example.** To get you started on this with some real data, look at the plot of concentration time data on the next page—it is taken from the answer key of your worksheet. Note that for the data I recalculated the data by taking a natural log in one column and a reciprocal in another column.

I can now look at the results—only one of the columns will have data that has a straight line (the slope doesn't change). Which one is ?

Answer: The  $\ln [C]$  plot which corresponds to the first order integrated rate law equation. So it must be true that this is the data for a first order reaction and I can now go on and collect more kinetics data—like  $E_a$  with the combined Arrhenius equation.

The first step in Worksheet 14: Determining reaction order from integrated rate equation.

One method for determining order of reaction is indirect and unlikely to be asked on a test, but it really shows whether you know your kinetics. Note that the integrated rate law solutions for zero, first and second order expressions are different functions but all can be written in the form of a straight line. This means that if I plot the concentration, [A], as a function of time for each expression below, the correct order should yield a straight line function. For thrills lets do it for the data in a first order reaction, but apply the functions for all three equations. For each, create an association for x, y, b and m with [C],[C<sub>0</sub>], k and t.

Zero order	First order	Second order
$y = m x + b$	$y = m x + b$	$y = m x + b$
$[C] = -ck t + [C_0]$	$\ln [C] = -ck t + \ln [C_0]$	$1/[C] = ck t + 1/[C_0]$

Concentration- time data		2nd order	1st order	Zero order
time	[C]	1/[C]	ln [C]	[C]
0	?			
1	.12	8.33	-2.1	.12
2	.074	13.5	-2.6	.074
3	.044	22.7	-3.1	.044
4	.027	37.0	-3.6	.027
5	.016	62.5	-4.1	.016
6	.009	111	-4.6	.009
8	.0036	277	-5.6	.0036
10	.0013	769	-6.6	.0013

Isn't this exciting, notice that the only one that is a straight line is first order, hence the first order in [C]. Yet another way to find the order of a reaction!! This is the first step in working Worksheet 14.

## Reaction Mechanisms.

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



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  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

In a simple world the mechanism for the reaction would be

$$\text{rate} = k[\text{NO}_2][\text{CO}]$$

but what if I told you the actual rate law was

$$\text{rate} = k[\text{NO}_2]^2$$

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



$\text{NO}_3$  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?

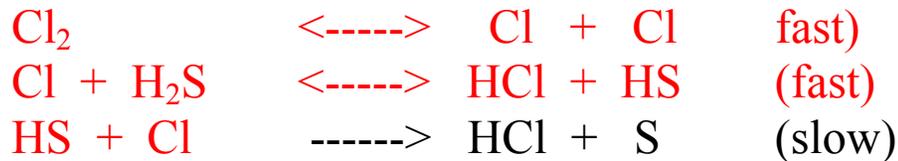
Before answering the question, it is necessary to consider the existence of a special reaction in the mechanism known as the rate-determining step.

**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?



Answer:  $\text{rate} = k [\text{H}_2\text{S}][\text{Cl}_2]/[\text{HCl}]$  is the result when only the data before the rds is used. Note the rate law is first order in HS and Cl, negative first order for [HCl] and first order overall.

## Collision theory.

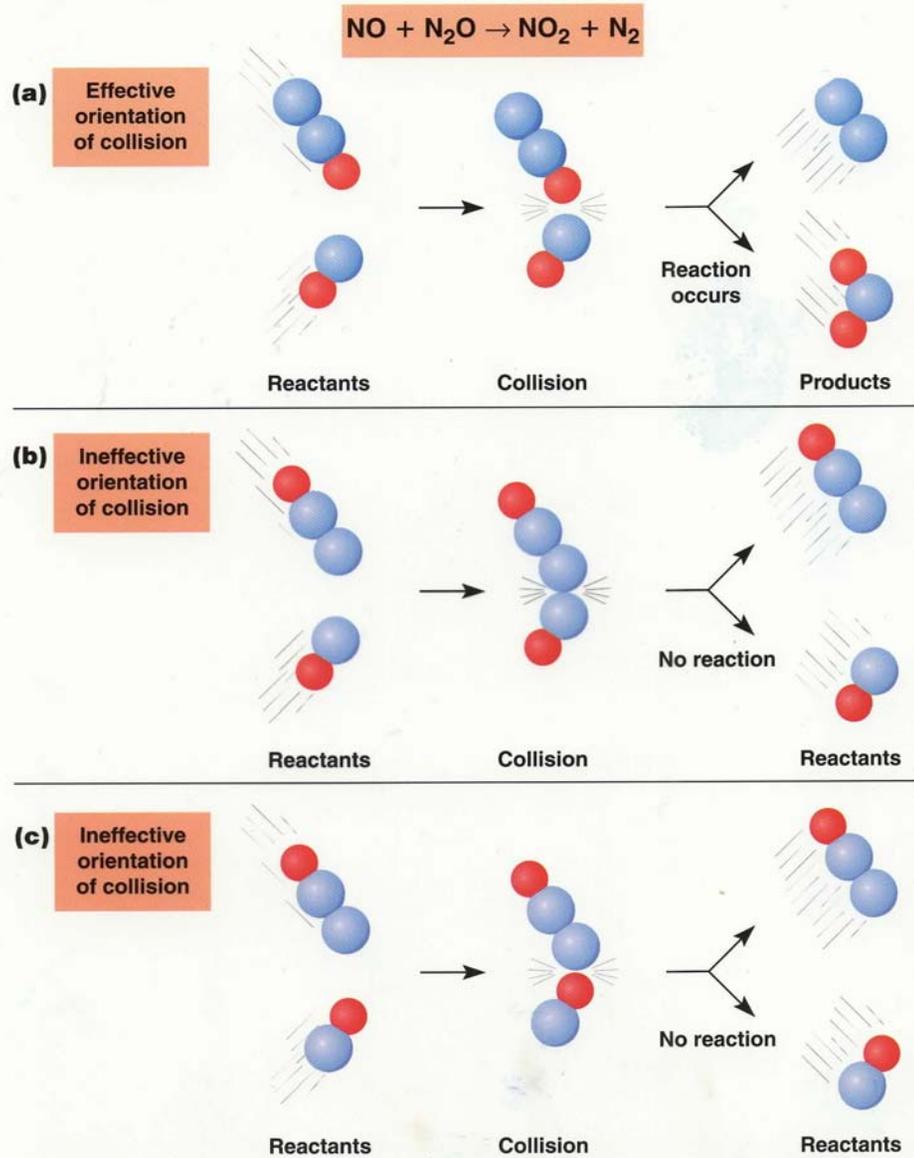
Something you can start to do that will make understanding science a lot easier is to get yourself down on the level of molecules and atoms and try to experience the world as they do. Kind of a “walking in another molecule’s shoes” perspective.

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 ( $\Delta G$  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.

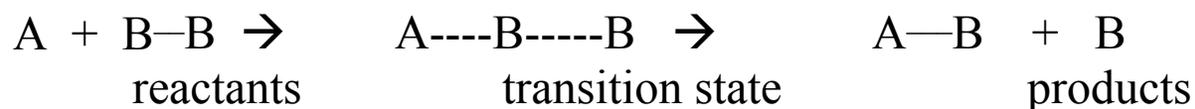


Look at the nice picture to understand why an orientation upon collision might not be appropriate. Note in this reaction that it would be nice for the side of a N<sub>2</sub>O molecule with an oxygen to encounter the side of an NO molecule with a nitrogen. Well this certainly doesn't have to happen--there 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.

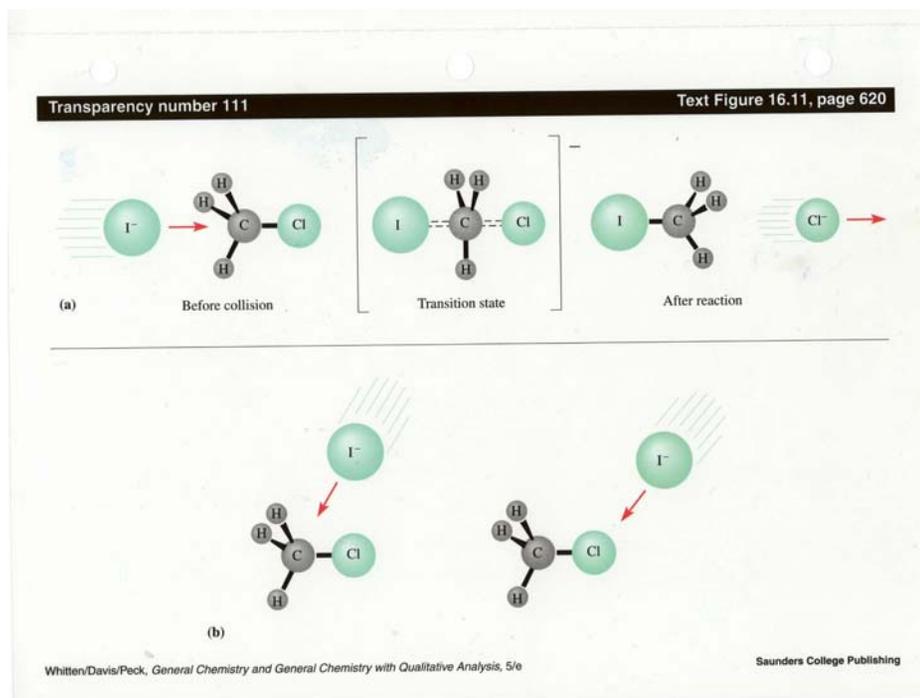
### Transition state theory.

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.

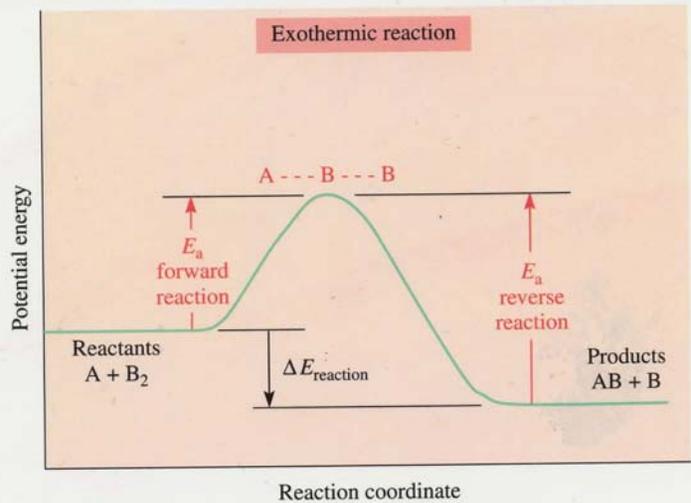


The most famous example of this, which they will ram down your throat for most of organic chemistry, is the infamous S<sub>N</sub>2 reaction. The "transition state" intermediate is shown in the picture below for substitution of F<sup>-</sup> onto an organic molecule that eliminates Cl<sup>-</sup>. Note the intermediate "transition state" occurs for an instant when both the Cl<sup>-</sup> and F<sup>-</sup> are attached.

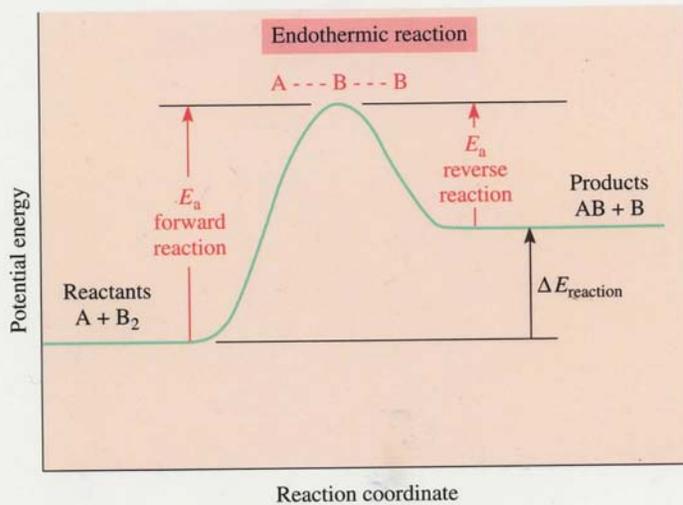


**Activation energy and the transition state.** The amount of energy that must be provided to achieve a transition state is known as the activation energy,  $E_a$ . Examples of this activation energy barrier for an exothermic and an endothermic reaction are shown below.

Note that even when a reaction is exothermic, it is necessary to introduce energy to the system to create the transition state—this additional energy hill is what keeps  $H_2$  and  $O_2$  from exploding when they are together despite being thermodynamically favorable. Note also that for an endothermic reaction,  $E_a$ , even more energy than predicted thermodynamically must be provided for the reaction to occur.



(a)

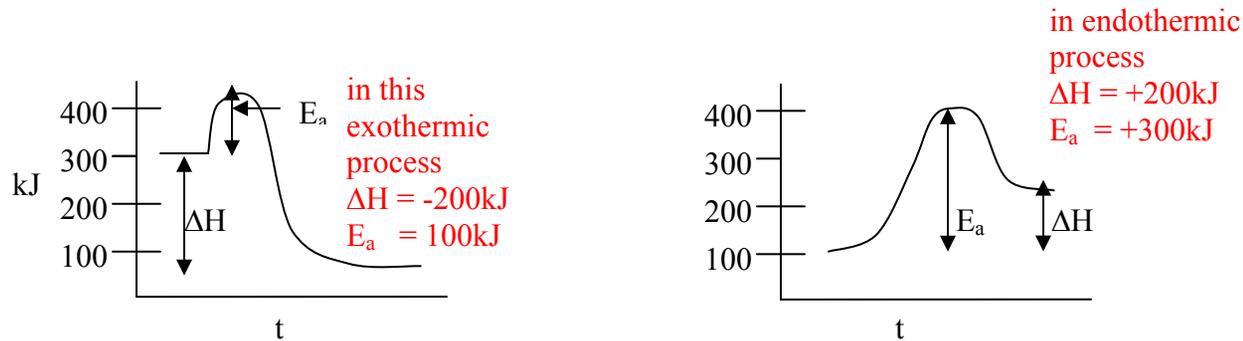


(b)

**Extracting numbers from an energy diagram.** You should be able to describe this energy profile that relates kinetics to thermodynamics in a bit more quantitative fashion.

Example: What are  $E_a$  and  $\Delta H$  for the exothermic and endothermic reactions below?

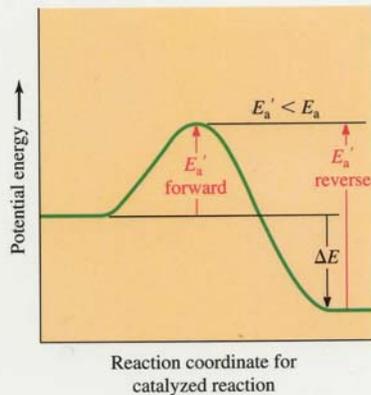
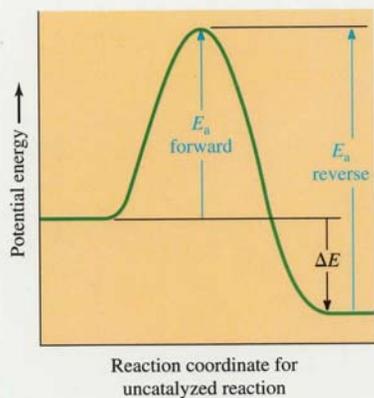
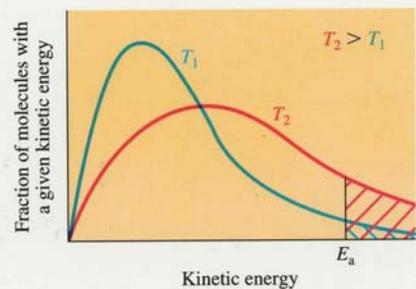
Answer: Note the height of  $E_a$  determines rate of reaction because the bigger  $E_a$ , the smaller  $k$ .



**How do you overcome an activation barrier?**

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.



We'll look at each approach.

**Temperature and the Arrhenius equation.** A while back a guy named Arrhenius 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 Arrhenius did, and got an equation named after him:

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

where  $k$  is the rate constant found in our rate law in lecture 1,  $E_a$  is the activation energy necessary to create the transition state,  $R$  is the gas law constant,  $T$  is temperature, and  $A$  is the pre-exponential constant related to the state of the reaction.

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  $T$ ,  $(-E_a/RT)$  is a smaller number, therefore,  $A \exp(-E_a/RT)$  is a larger number. This means the rate constant will be larger and the rate faster.

**for activation energy:** If you decrease  $E_a$ ,  $(-E_a/RT)$  is a smaller number, therefore  $A \exp(-E_a/RT)$  is a larger number. This means the rate constant will be larger and the rate 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 Arrhenius equations.** Assume that for the same reaction, we have two reaction rates, each occurring at a separate temperature.

$$k_1 = A \exp(-E_a/RT_1) \quad k_2 = A \exp(-E_a/RT_2)$$

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

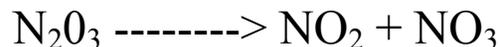
$$\ln \frac{k_2}{k_1} = (E_a/R)(1/T_1 - 1/T_2)$$

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  $[A_0]$ . Note we can do it as well by fitting the Arrhenius equation to a straight line.

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

Wow!! By obtaining rate constants as a function of temperature, we have a way to extract  $E_a$  from the slope of the line. You can do this in the concentration time worksheet I provided you.

**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  $9.16 \times 10^{-3} \text{ s}^{-1}$  at  $0^\circ\text{C}$ .  $E_a$  is 88 kJ/mol. If the temperature is raised  $2^\circ\text{C}$ , what is the new rate constant?



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

$$E_a = 88.000 \text{ J/mol} \qquad R = 8.314 \text{ J/mol} \cdot \text{K}$$

$$k_1 = 9.16 \times 10^{-3} \text{ s}^{-1} \quad \text{at} \quad T_1 = 0.0^\circ\text{C} + 273 \text{ K}$$

$$k_2 = ? \quad \text{at} \quad T_2 = 2.0^\circ\text{C} + 275 \text{ K}$$

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

$$k_2 = 1.32 (9.16 \times 10^{-3} \text{ s}^{-1}) = 1.21 \times 10^{-2} \text{ s}^{-1}$$

We see that a very small temperature difference, only  $2^\circ\text{C}$  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 reaction  $\text{C}_2\text{H}_5\text{I} \text{ ---} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$

At 600K,  $k = 1.6 \times 10^{-5} \text{ s}^{-1}$ . At 700K,  $k = 6.36 \times 10^{-3} \text{ s}^{-1}$  What is  $E_a$ ?

Substituting into the combined Arrhenius:

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

## 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° 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 a later lecture on famous catalysts,

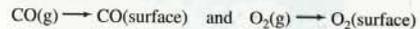
catalyst	Substance that increases reaction rate by reducing $E_a$ . This is done by making alternative pathways available for reaction. Catalysts are not consumed in a reaction.
enzyme	A biological catalyst. All those biological sounding words that end in <b>-ase</b> are enzymes. For example, anhydrase 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.

An example of heterogeneous catalysis in which carbon monoxide is converted efficiently into carbon dioxide.

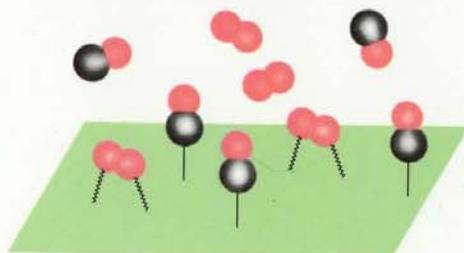
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(a) *Adsorption*: CO and O<sub>2</sub> reactant molecules become bound to the surface:



The CO molecules are linked through their C atoms to one or more metal atoms on the surface. The O<sub>2</sub> molecules are more weakly bound.

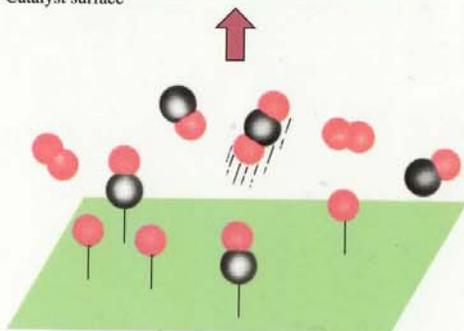
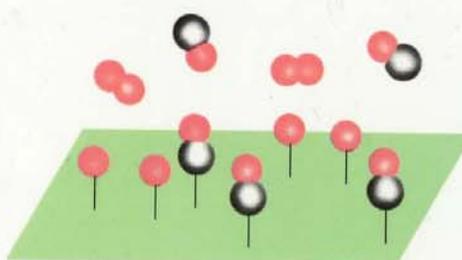


Catalyst surface

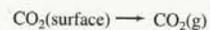
(b) *Activation*: The O<sub>2</sub> molecules dissociate into O atoms, which are held in place more tightly:



The CO molecules stick to the surface, but they migrate easily across the surface.

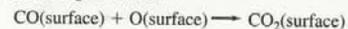


(d) *Desorption*: The CO<sub>2</sub> product molecules leave the surface:



Fresh reactant molecules can then replace them to start the cycle again [back to step (a)].

(c) *Reaction*: O atoms react with bound CO molecules, to form CO<sub>2</sub> molecules:



The resulting CO<sub>2</sub> molecules bind to the surface *very poorly*.