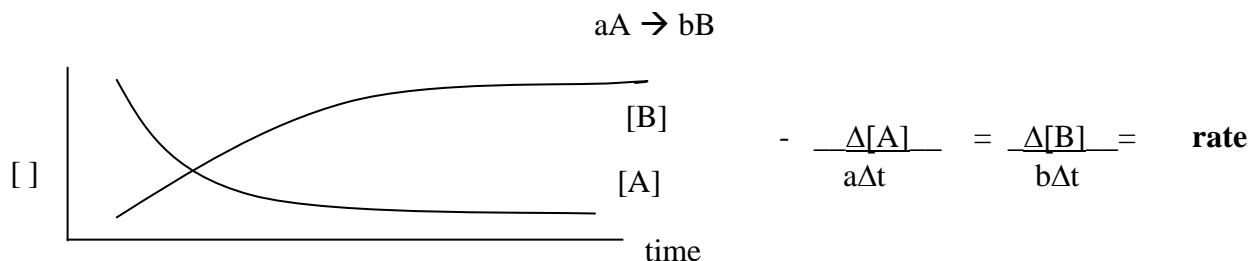


# Kinetics

First a CH 302 Kinetics Study Guide (Memorize these first three 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



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 **E<sub>a</sub>**, 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  $A \exp(-E_a/RT)$  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<sub>a</sub>, 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  $2 \times 10^{-2} \text{ sec}^{-1}$ . 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	$-\frac{\Delta[A]}{\Delta t} = k$	$-\frac{\Delta[A]}{\Delta t} = k [A]^1$	$-\frac{\Delta[A]}{\Delta t} = k [A]^2$
integrated rate law	$[A] = [A_0] - akt$	$\ln [A] = \ln[A_0] - akt$	$1/[A] = 1/[A_0] + akt$

In each case, you can calculate how much is left from starting materials or formed as products given the starting amount,  $[A_0]$ , 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,  $[A] = 0.5 [A_0]$ , 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,

$$\begin{array}{ccccc} \ln[A] & = & -akt & + & \ln [A_0] \\ y & & m x & & b \end{array}$$

This means you can plot the  $\ln$  of  $[A]$  at different times and get  $[A_0]$  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  $A + B \rightarrow C + D$  it does not mean that  $\text{rate} = k [A]^1[B]^1$**

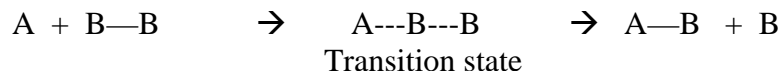
Instead lots of complicated things might be going on in the form of a reaction mechanism. Maybe  $A \rightarrow I_1$ ,  $I_1 \rightarrow I_2$ ,  $I_2 + B \rightarrow C + D$  where  $I_1$  and  $I_2$  are **reaction intermediates**. The reaction order is determined by everything that happens in this multi-step process BEFORE the **Rate**

**Determining Step** (the slowest step in the reaction.) Thus, If  $A \rightarrow I_1$  is the slowest step, then whatever happens afterward doesn't affect the rate and the reaction rate law is just  $\text{rate} = k[A]$

**Kinetic Theories:** Every chapter has its theories. This chapter has two.

**Collision Theory:** This theory suggests that sometimes reactions don't occur because even when molecules collide, maybe they don't collide in the right orientation. For example, maybe the  $\delta^-$  part of a molecule needs to bump into the  $\delta^+$  part of another molecule, but instead bumps into the  $\delta^-$ . 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**:



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 Arrhenius equations:** How does one experimentally calculate the activation energy,  $E_a$ ? One approach is to combine Arrhenius equations,

$$K_1 = A \exp(-E_a/RT_1) \quad K_2 = A \exp(-E_a/RT_2) \quad \text{combine to yield}$$

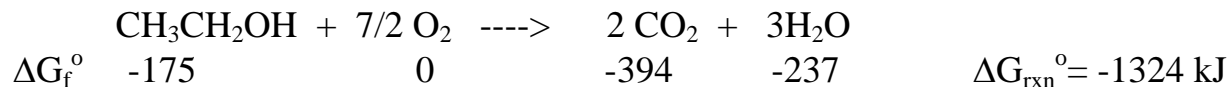
$$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$$

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.

## Kinetic Lecture 1: Thermodynamics let's us down:

Okay, we've finished a three month primer on thermodynamics and you now know how to tell whether a reaction is spontaneous. Just do a  $\Delta G^\circ$  Gibbs free energy calculation. Okay, let's take our knowledge and put it to good use:

Consider the combustion of ethanol:



Clearly a spontaneous reaction. Except that you all know that ethanol doesn't react in the presence of  $\text{O}_2$  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  $\text{CO}_2$ . 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  $\text{O}_2$  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.

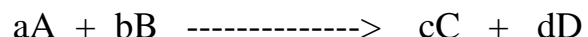
**Chemical rate:** The amount of reactant consumed or product formed as a function of time

**Chemical mechanism:** the path by which a reaction occurs.

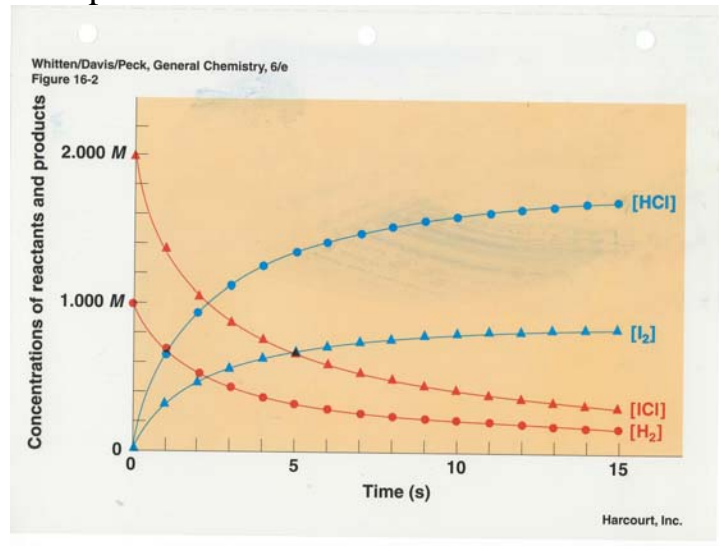
Remember how we stressed over and over about thermodynamics that we neither cared how fast or by what path a reaction occurred? Now you see why, we were just saving those topics for the kinetics chapter.

### Rate of Reaction:

For a reaction



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.



## 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  $\Delta t$  decreases, we better define the instantaneous concentration and for a specific time and write the equations replacing  $\Delta t$  with a derivative,  $dT$  and  $\Delta[A]$  with a derivative  $d[A]$ .

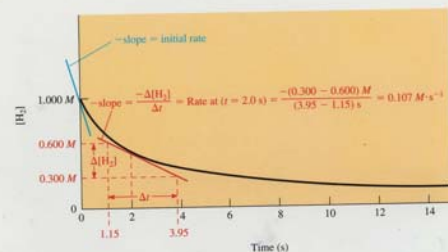
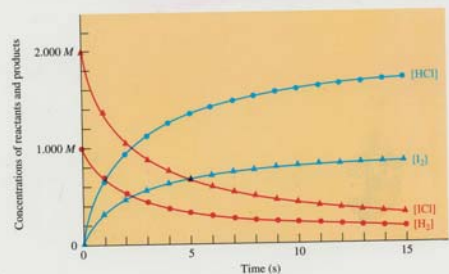
$$\text{rate} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{1}{c} \frac{d[C]}{dt}$$

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 initially 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.



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

Saunders College Publishing

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

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

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.

$$\text{reaction order} = x + y + \dots$$

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

I will be providing a handout and worksheet on all the ways to determine orders of reactions.