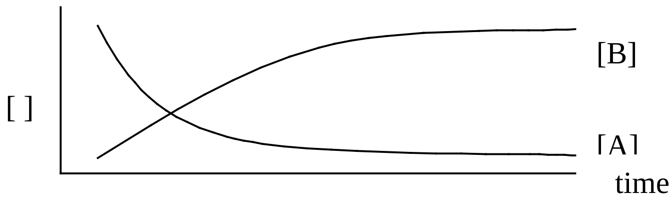
CH 302 Kinetics Study Guide

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. For the concentration-time plot below for the reaction aA → 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 **E_a**, the activation barrier. With these factors we make a RATE LAW.

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

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_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,

$$\underbrace{\ln[A]}_{y} = \underbrace{-ak}_{m}\underbrace{t}_{x} + \underbrace{\ln [Ao]}_{b}$$

This means you can plot the ln of [A] at different times and get **[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 → A---B---B → A—B + B

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

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

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

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.