Things you should be able to do when we have finished kinetics:

1. Define rate

Rate law related

2. Given a chemical equation, write a *general rate law* for that reaction.
3. Given appropriate data, solve for the exponent and rate constant terms to obtain the *specific rate law*. This is really more of a math than chemistry activity. In lab you will need to obtain rate values from your data. Rate = ______________________________?????
4. Use a rate law to predict a rate (given concentrations) or to establish concentrations (given a desired rate).

Mechanism related

5. Recognize that a reaction may have a single step or multi-step mechanism. (Depends on the specifics of the system [specific rxn and conditions] under study.)
6. Recognize that the rate of a reaction with a multi-step mechanism is determined by the slowest (rate-limiting) step in the mechanism.
7. Understand how a reaction mechanism relates to the rate law for that reaction.

Collision Theory (based on Boltzmann) related

8. Understand (be able to make predictions) how and why temperature changes can alter reaction rates.
9. Understand (be able to make predictions) how and why the force of a collision influences whether or not a given collision can be productive.
10. Understand (be able to make predictions) how and why collision orientation influences whether or not a given collision can be productive.

Thermodynamic related

11. Be able to draw a reaction coordinate diagram that accurately relates k to activation energy.

Chemical Kinetics

1. numerical descriptions of how fast reactions (rxns.) occur
2. the intermediates that form during a rxn (re. mechanism)
3. applying thermodynamics & the kinetic molecular theory to go from the descriptive learning to *understanding*.

Our focus will be on gas and liquid phase (soln.) reactions.

Introduction

What is kinetics, and why should we care?

1. Kinetics examines how fast a rxn. proceeds.
2. When we really understand the details of kinetics we have more control over the rxn. *(Medicine & industry)*
3. Kinetic principles are the foundation of equilibrium
4. You will remain alive & healthy only as long as you can control the rates of chemical (and physical) processes in your body.

Two examples at the extremes of reaction rates:

1st: Formation of iron oxide from iron metal:

$$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$$

1. Formation of iron oxide is "rusting". (photo from Google images)
2. It took my Datsun B-210 ~ 9 years to rust.

2nd A more rapid way to oxidize a car:
http://www.youtube.com/watch?v=90Tta_vzsF0

Any thoughts about the chemical reaction in this video?

A. Reaction Rates. Do speed analogy to understand rates in general.

1. Defining rate: change per unit time   rate = $\frac{\text{concentration change}}{\text{time change}}$

2. Example:

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

How could you measure the rate?

a. Measure the concentration of H_2, Cl_2, or HCl at various times as the reaction proceeds.

b. Method: Pressure change, color change, *etc.*

3. Define rate as *increase* in product conc. per unit time or *decrease* in reactant conc./unit time. See animation Reaction_Rate.avi *(slope!)*

4. Let's try I_3^- using the data from the Kinetics lab

$$6\,H^+ + IO_3^- + 8\,I^- \rightarrow 3\,I_3^- + 3\,H_2O$$ (which has color?)

rate I_3^- formation = $\frac{\Delta [I_3^-]}{\Delta t}$

Trial #5

time (s)	Abs	$[I_3^-]$ (M)
30	0.013	4.56E-07
45	0.028	9.82E-07
60	0.039	1.37E-06
75	0.050	1.75E-06
90	0.062	2.17E-06
105	0.073	2.56E-06
120	0.088	3.09E-06
135	0.099	3.47E-06
150	0.112	3.93E-06

Shown above are trial #5 data from Sp 05.

a) While you can calculate an average rate between any two points on the graph ($\Delta y/\Delta x$), it is better for this experiment to use the slope for the line. The reason is that your rxn. should closely fit a straight line during the first three min. So

b) You will get a more reliable answer if you estimate $\Delta y/\Delta x$ for all of the points. You can do this by plotting the data {$[I_3^-]$ vs. t (y vs. x)} and using the trendline function.

Remember, slope = rate!!!

The slope of the line is **2.85×10^{-8} M/s** & the R^2 value = 0.9988. What does the R^2 value tell you?

If the rate of I_3^- formation is 2.85×10^{-8} M/s, what is the rate of IO_3^- disappearance? __________

Rate Laws & Reaction Order (Demolition derby?)

Now that we know how to measure rates, what use are they?

A. We need to relate our numerical analysis of rxn. rate to a mental picture (model) of the atoms/molecules doing the rxn. Look at Boltzmann. How many collisions per 30 sec with: (428 K)

Comment re. statistics!

1. 5 NO_2 molecules (MW ~ 46 amu) & 2 CO (MW ~ 28 amu) _____
2. 50 NO_2 molecules and 2 CO ______

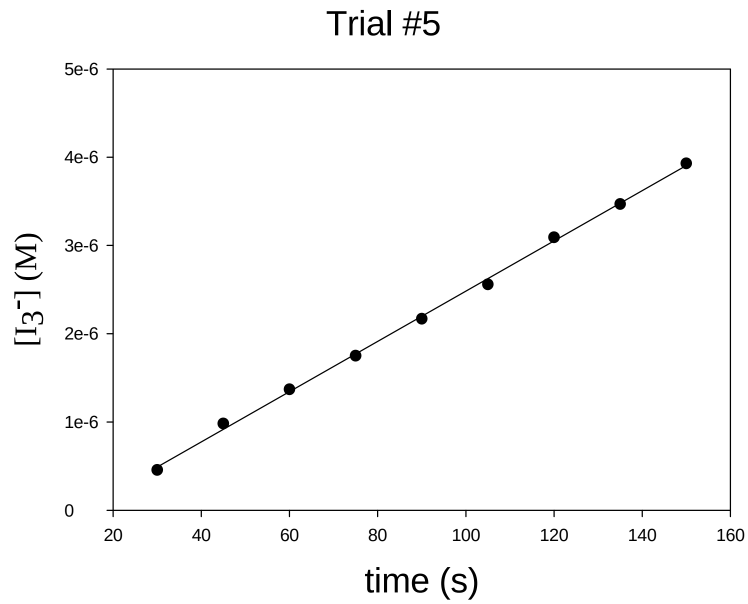
B. Consider the following general rxn.: $a\,A + b\,B \rightarrow$ Products

1. You can write a **general rate law** for this reaction in the form:

Rate = $k\,[A]^m\,[B]^n$ k is the **rate constant** specific for this rxn., temp., *etc.*

Note: a not necessarily = m and b not necessarily = n

Important: Changing [A] &



[B] changes the rxn rate. We'll discuss ways to alter *k* later.

2. Why does this equation work? (Collision-theory)
   a) Why does a *k* value have to be included?

   ____

   ____

   ____

   b) Why [A] *times* [B]? (See Boltzmann, above)

   c) Why is [A] raised to the *m* power? (Does *a* sometimes = *m?*)

   ____

   ____

3. What can you do with a rate law?
   a) Accurately predict what will occur. (Explosive rate?)
   b) Get an understanding of the rxn mechanism (more below)

C. Reaction order
   1. Overall reaction order = sum of all exponents in the rate law.
   2. Rxn order w/ respect to specific reactant = exponent for that reactant.

D. If you have a balanced chemical rxn., you still don't know the rate law.
   The rate law must be determined experimentally!!!
   How can we do that?

Experimental Determination of a Rate Law

One method is to measure initial rate at different [reactant]. Then see what exponent (remember *m* and *n*?) fits the data.

Rxn.: $6\,H^+ + IO_3^- + 8\,I^- \rightarrow 3\,I_3^- + 3\,H_2O$

Rate law (general form): rate = $k\,[IO_3^-]^m\,[I^-]^n$

You may be wondering what happened to the $[H^+]$ term. Two points with respect to that:

1. There are ways to set up the reaction conditions such that we make that term disappear (actually combine with *k*).
2. You are **categorically forbidden** from worrying about what happened to the $[H^+]$ term.

A. To get *m*, you will compare exp. trials #1-3 with #4-6. Here are some data from Sp 05 (for most students, the <u>$[I^-]$ was the same in all of those trials</u>, and the $[IO_3^-]$ was twice as high in trials #4-6 as #1-3):

rate for #1-3 = 1.35×10^{-8} M/s rate for #4-6 = 2.70×10^{-8} M/s

$$\frac{\text{rate}_{4\text{-}6}}{\text{rate}_{1\text{-}3}} = \frac{k\,[IO_3^-]_{4\text{-}6}^m\,[I^-]^n}{k\,[IO_3^-]_{1\text{-}3}^m\,[I^-]^n}$$

$$\frac{2.70 \times 10^{-8}\text{ M/s}}{1.35 \times 10^{-8}\text{ M/s}} = \frac{k\,[2]^m\,[I^-]^n}{k\,[1]^m\,[I^-]^n}$$

Can you see that the *k* & $[I^-]^n$ terms will cancel?

$$\frac{2.70 \times 10^{-8}\text{ M/s}}{1.35 \times 10^{-8}\text{ M/s}} = \frac{[2]^m}{[1]^m}$$

$$\frac{2}{1} = \frac{2^m}{1^m}$$

If you can't see what *m* =, just try some integer values.

Some zen possibilities:

If $m = 1$, the rate should have doubled, if $m = 2$, the rate should have quadrupled, if $m = 3$, rate should have gone up by a factor of 8, *etc.*

Logic $2^1 = 2$, $2^2 = 4$, $2^3 = 8$, *etc.*

This is because $2^m/1^m = (2/1)^m$. That is, you can factor out the *m*. Try a few examples on your calculator if you don't believe it.

Looking at the data, we can see that the rate doubled:

2.70/1.35 = 2, **therefore, *m* = 1.**

B. Following this logic, you can determine *n*. What reactions should we compare to accomplish this? Trials. #______ and # _______.
Note: In this case we want $[IO_3^-]$ to be constant.

C. Now that we know *m* = 1and *n* = ____, do we have enough information to determine *k*?

Solve for *k* in the space at right:

Reaction Mechanisms *What is really happening during the rxn?*

Is there more to the numerical analysis that we have been doing than meets the eye? A *reaction mechanism* describes the actual changes that occur during a chemical rxn.

A. Terms

1. A one mechanism step is called an *elementary reaction* or *step.*
2. The *molecularity* of a reaction refers to the number of separate molecules or atoms on the reactant side of an elementary rxn.
   a) *unimolecular* = one
   b) *bimolecular* = two
   c) *termolecular* = three (These are uncommon.)

B. Let's look at a mechanism for

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$$

1. Experiments have suggested a two step process:

1st step: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$

2nd step: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

The molecularity of the 1st step is ______________.
The molecularity of the 2nd step is ______________.

2.While some of the reaction components are unstable, one component of elementary rxns. is *very* unstable. That is NO_3. A component like NO_3 that exists transiently (for a really short time) in the mechanism is a *reaction intermediate.*

3. Notice that the sum of the individual elementary steps must add up to the overall, balanced molecular equation:

1st step: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$

2nd step: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

$$NO_2(g) + \mathbf{NO_2(g)} + \mathbf{NO_3(g)} + CO(g) \rightarrow NO(g) + \mathbf{NO_3(g)} + \mathbf{NO_2(g)} + CO_2(g)$$

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Terms occurring on both reactant & products sides of the sum are shown in bold. When these terms are dropped, the equation ***must*** match the original, balanced overall rxn. Look at 2Energy_Activation.exe

Key point: Multiple reaction pathways always exist. Which pathway is the most important?????

____

How does a mechanism relate to a rate law?

The balanced molecular equation for a rxn. describes the reactant & product ratios (stoichiometry), not necessarily the mechanism. ***However, the rate law for the rate limiting step in a mechanism does define the rate law for the overall rxn.***

A. The rate limiting step in any process is the slowest step. (Think about waiting in line.) Have you ever worked on/seen an assembly line?

B. When the overall rxn. occurs in a single step, then the rate law is determined by the molecular equation.

Example: $CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$

$$\text{Rate} = -\Delta [CH_3Br] / \Delta t = k [CH_3Br] [OH^-]$$

C. When a rxn. occurs with more than one elementary step, usually one of the elementary steps is much slower than the others. This is the rate limiting step.

1. Let's go back and look at the rxn. of NO_2 with CO:

Balanced rxn.: $NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$

Proposed mechanism:

1st step: $NO_2(g) + NO_2(g) \xrightarrow{k_1} NO(g) + NO_3(g)$

2nd step: $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$

The 1st step is the "slow" step in this sequence. By slow, I mean slow relative to the 2nd step. That is, $k_1 << k_2$.

This means that the rate of the overall process can be no faster than the rate of step 1. Can we write a rate law for the 1st elementary rxn.?

$$\text{Rate} = -\Delta\ [NO_2]\ /\ \Delta t = k_1\ [NO_2]^2$$

The experimentally determined rate law rxn. does turn out to be:

$$\text{Rate} = -\Delta\ [NO_2]\ /\ \Delta t = k\ [NO_2]^2$$

Therefore, our mechanism predicted the correct rate law.

There is a mutually reinforcing relationship between the mechanism and the rate law: *The rate law <u>helps</u> to confirm the mechanism and the mechanism gives us insight into the rate law.*

What is the order of the NO_2-CO rxn.: Overall? ____________

With respect to NO_2? _____

With respect to CO? ______

Does this seem logical?

Reaction Rates and the Effect of Temperature on k

This equation will help us relate the rate constant, *k*, to other chemical ideas (collision theory, steric hindrance, *etc*.). It helps to unify our thought about kinetics.

A. Reaction rates tend to increase with increasing temperature. Why is this so?

1. Consider the rxn.: $O(g) + HCl(g) \rightarrow OH(g) + Cl(g)$
   In this rxn. the H−Cl bond must be broken. Think about overlap of electron clouds.

$$\vec{O} \quad \overset{\leftarrow}{H}{-}Cl \rightarrow O\cdots H\cdots Cl \rightarrow O{-}H + Cl$$

2. Do electrons normally repel each other? (Y or N?)

3. The intermediates in a rxn. are usually very unstable & high in potential energy. Terms:
   a) activation energy (E_a) *See 1Energy_Activation.rm*
   b) transition state (synonym: activated complex)
   Try to relate the process of going from reactants to the transition state to some human activity. (Mountain climbing?)

B. Some of the thoughts behind this part of kinetics started with analysis of collision rates in the gas phase.
   1. At 20° C and 1 atm, each gas molecule has about **10^9 collisions/sec**. Imagine a reaction occurring with each collision. **BOOM!!!** This does seem consistent with the rates of explosive chemical rxns., it clearly is not consistent with the rates of most chemical rxns.

So, for most rxns., only a small % of the collisions result in a rxn. These productive collisions have appropriate ***energy*** *&* ***orientation.***

2. The fraction of collisions with enough energy to reach E_a is related to the Boltzmann Distribution. Assume for a given reaction we need a velocity greater than 1000 m/s to reach E_a.
   a) Look at Boltzmann at 302 K for O_2 (MW = 32). What % of the O_2 molecules have a velocity greater than 1000 m/s?
   b) Now increase the temperature to around 600 K. Does the fraction with a velocity greater than 1000 m/s increase?

This is why increasing T increases the rxn. rate, <u>by increasing k.</u>

C. Go back to our previous example of a gas phase rxn.:

$$O(g) + HCl(g) \rightarrow OH(g) + Cl(g)$$

1. What if O collides with the Cl side of the HCl molecule, instead of the H side?

$$H-\overrightarrow{Cl} \qquad \overleftarrow{O} \quad \rightarrow \quad \text{No H to O bonding occurs.}$$

2. Chemists describe a *steric factor*, *p*, that describes the fraction of collisions that have the appropriate *orientation* for the rxn. to occur. This can get messy, but if two atoms of a diatomic reactant are about the same size, $p \approx 0.5$. (Electrostatics?) *Diatomic*? See 1Orientation.avi

D. We can view *k* as being determined by collision energy related factors and collision orientation factors.

E. Why would anyone care about this stuff?
Knowledge is power!
1. If you understand a rxn., you can modify it to change the rate, improve efficiency, and so on.
2. Enzyme inhibitors based on transition-state analogs.
3. Catalytic antibodies = made-to-order catalysts.

Catalysis *How we make life go.*

A. Catalysts work by decreasing activation energy.

B. They do this by creating a different *reaction pathway.*

Analogy: Take a 600 pound cow from the 1st floor of the Smith Building to the 4th floor. Think of two different pathways.

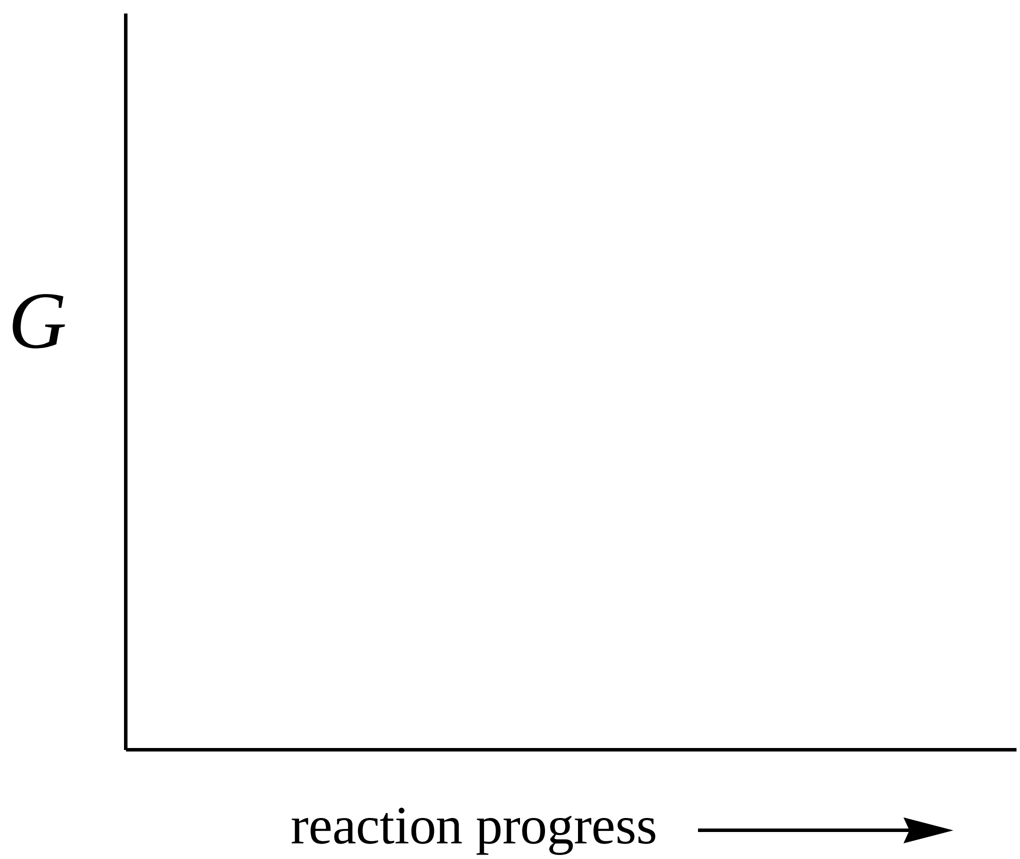
1. ____

2. ____

3. Another way? See: http://www.youtube.com/watch?v=WzWQhA5_kU4

Disclaimer: I am not advocating abuse of cattle!

C. Do catalysts speed up the rate of the reverse rxn. too? A reaction coordinate diagram will help answer that question:



What components of the diagram relate to kinetics? ______________________________

____

How might these components be useful in a medical context? ______________________

____

____