Chemical kinetics is the study of the speed or rate of a reaction under various conditions. Spontaneity is also important AND a spontaneous reaction does NOT imply a rapid reaction. The changing of diamond into graphite is spontaneous but so slow that it is not detectable even in a lifetime.
A mechanism is a sequence of events at the molecular level that controls the speed and outcome of the reaction.

FACTORS THAT AFFECT REACTION RATES

The following conditions affect the speed of a chemical process:

1. ***Nature of the reactants***--Some reactant molecules react in a hurry, others react very slowly.
   Pointers:
   o <u>Physical state</u>- gasoline $_{(l)}$ vs. gasoline $_{(g)}$; $K_2SO_{4(s)} + Ba(NO_3)_{2(s)} \rightarrow$ no rxn.; while both of these in the aqueous state react.

   o <u>Chemical identity</u> - What is reacting? Usually ions of opposite charge react very rapidly. Usually, the more bonds between reacting atoms in a molecule, the slower the reaction rate. Substances with strong bonds (larger bond energies) will react much more slowly. Examples: metallic sodium reacts much faster with water than metallic calcium. Oxidation of methane can be increased with an increase in temperature; photosynthesis is very slow and changes very little with an increase in temperature.

2. **Concentration of reactants**--more molecules, more collisions.

3. **Temperature**--heat >em up & speed >em up; the faster they move, the more likely they are to collide.
   o An increase in temperature produces more successful collisions that are able to overcome the needed activation energy, therefore, a general increase in reaction rate with increasing temperature.
   o In fact, a general rule of thumb is that a 10°C increase in temperature will double the reaction rate.
   o * This actually depends on the magnitude of the Ea* and the temperature range.

4. **Catalysts**--accelerate chemical reactions but are not themselves transformed.
   o Biological catalysts are proteins called enzymes.
   o A catalyst is a substance that changes the rate of reaction by altering the reaction pathway. Most catalysts work by lowering the activation energy needed for the reaction to proceed, therefore, more collisions are successful and the reaction rate is increased.
   o Remember! The catalyst is not part of the chemical reaction and is not used up during the reaction.* (May be homogeneous or heterogeneous catalysts.) Ex. H_2O_2 decomposes relatively slowly into H_2O and O_2; however; exposure to light accelerates this process AND with the help of MnO_2, it goes extremely FAST!! Note: A catalyst lowers the activation energy barrier. Therefore, the forward and reverse reactions are both accelerated to the same degree.
   o * (Some homogeneous catalysts actually appear in the rate law because their concentration affects the reaction. Ex. NO catalyzing O_3)

4. **Surface area of reactants**--exposed surfaces affect speed.
   o Except for substances in the gaseous state or solution, reactions occur at the boundary, or interface, between two phases.
   o The greater surface area exposed, the greater chance of collisions between particles, hence, the reaction should proceed at a much faster rate. Ex. coal dust is very explosive as opposed to a piece of charcoal. Solutions are ultimate exposure!
5. **Adding an inert gas has NO EFFECT** on the rate [or equilibrium] of the reaction.

THE COLLISION THEORY OF REACTION RATES

➢ Particles must collide.
➢ Only two particles may collide at one time.
➢ Proper orientation of colliding molecules so that atoms in the can come in contact with each other to become products.
➢ The collision must occur with enough energy to overcome the electron/electron repulsion of the valence shell electrons of the reacting species and must have enough energy to transform translational energy into vibrational energy in order to penetrate into each other so that the electrons can rearrange and form new bonds.
➢ This new collision product is at the peak of the activation energy hump and is called the *activated complex* or the transition state. At this point, the *activated complex* can still either fall to reactants or to products.
➢ With all of these criteria met, the reaction may proceed in the forward direction. Amazing that we have reactions occurring at all!
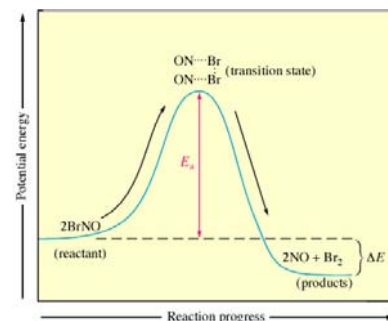
CHEMICAL REACTION RATES
The speed of a reaction is expressed in terms of its "rate", some measurable quantity is changing with time.

The rate of a chemical reaction is measured by the decrease in concentration of a reactant or an increase in concentration of a product in a unit of time.

$$\text{Rate} = \frac{\text{change in concentration of a species}}{\text{time interval}}$$

When writing rate expressions, they can be written in terms of reactant disappearance or product appearance.

* Rate is not constant, it changes with time. Graphing the data of an experiment will show an average rate of reaction. You can find the *instantaneous* rate by computing the slope of a straight line tangent to the curve at that time.

Row Num	time (sec)	NO2 (mol/L)	NO (mol/L)	O2 (mol/L)
		Data Set 1: Data		
1	0	0.0100	0.0000	0.0000
2	50	0.0079	0.0021	0.0011
3	100	0.0065	0.0035	0.0018
4	150	0.0055	0.0045	0.0023
5	200	0.0048	0.0052	0.0026
6	250	0.0043	0.0057	0.0029
7	300	0.0038	0.0062	0.0031
8	350	0.0034	0.0066	0.0033
9	400	0.0031	0.0069	0.0035
10				
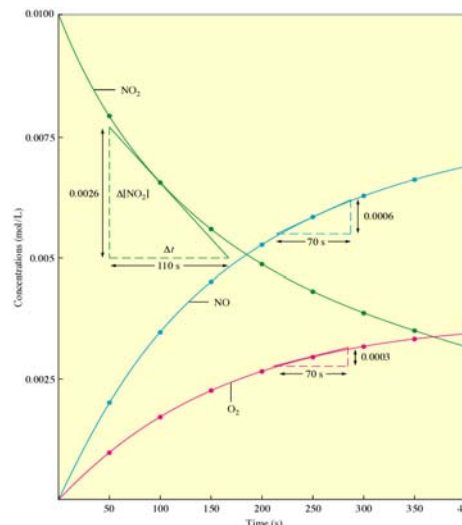
reaction rate--expressed as the Δ in concentration of a reagent per unit time or $\Delta[A]/\Delta t$

   focus either on the disappearance of reactants or the appearance of products
- rate of Δ of a reactant is always *negative*
- rate of Δ of a product is always *positive*
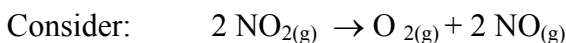
Consider: $2\ NO_{2(g)} \rightarrow O_{2(g)} + 2\ NO_{(g)}$
Oxygen can appear only half as rapidly as the nitrogen dioxide disappears while NO appears twice as fast as oxygen appears.

Examine the data table and calculate the AVERAGE rate at which $[NO_2]$ changes in the first 50.0 seconds: (Remember the square brackets are shorthand for molarity!)

$$RATE = \frac{-\Delta\ [NO_2]}{\Delta t} = \frac{-[.0079]-[0.0100]}{50.0\ s}$$
$$= -[-4.2 \times 10^{-5}\ mol/L \bullet sec]$$
$$= 4.2 \times 10^{-5}\ mol/L \bullet sec\ or\ M\ s^{-1}$$

Note that the rate is NOT constant but decreases with time. The rates given below are *average* rates.

$\dfrac{-\Delta\ [NO_2]}{\Delta t}$ $(\times 10^{-5})$	Time period (s)
4.2	$0 \rightarrow 50$
2.8	$50 \rightarrow 100$
2.0	$100 \rightarrow 150$
1.4	$150 \rightarrow 200$
1.0	$200 \rightarrow 250$

   To determine the value of the rate at a particular time, the **instantaneous rate**, compute the slope of a line tangent to the curve at that point. Why the negative on NO_2?

RELATIVE RATES: We can consider the appearance of products along with the disappearance of reactants. The reactant's concentration is declining, the products is increasing. Respect the algebraic sign AND respect the stoichiometry. [Divide the rate of change in concentration of each reactant by its stoichiometric coefficient in the balanced chem. eqn. and this is foolproof and a breeze!]

Thus.....

$$\text{Rate of reaction} = -\frac{1\Delta[NO_2]}{2\ \Delta\text{time}} = \frac{1\ \Delta[NO]}{2\ \Delta\text{time}} = \frac{\Delta[O_2]}{\Delta\text{time}}$$

Of course you can change these once the ratio is set. You might prefer -1 : +1 : +2

Relative Rates from the balanced equation:

Using the coefficients from the balanced equation, students should be able to give relative rates. For example: $4\ PH_{3\ (g)} \rightarrow P_{4(g)} + 6\ H_{2(g)}$

$$\text{Initial rate rxn.} = -\frac{1}{4}\left[\frac{\Delta[PH_3]}{\Delta time}\right] = +\left[\frac{[P_4]}{\Delta time}\right] = +\frac{1}{6}\left[\frac{\Delta[H_2]}{\Delta time}\right]$$

Exercise
What are the *relative* rates of change in concentration of the products and reactant in the decomposition of nitrosyl chloride, NOCl?

$2\ NOCl_{(g)} \rightarrow 2\ NO_{(g)} + Cl_{2(g)}$
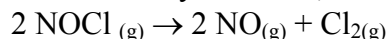
Differential RATE LAW: AN INTRODUCTION

Reactions are reversible. So far, we've only considered the forward reaction. The reverse is equally important. When the rate of the forward = the rate of the reverse we have EQUILIBRIUM! To avoid this complication we will discuss reactions soon after mixing--initial reactions rates, and not worry about the buildup of products and how that starts up the reverse reaction.

initial reaction rates--begin with pure reactants, mix thoroughly, then measure speed of rxn. over time

The presence of products can alter results dramatically and lead to confusing results. We'll be talking initial reaction rates throughout our discussions!

$$\text{Rate} = k[NO_2]^n = -\left[\frac{\Delta[NO_2]}{\Delta t}\right]$$

The rate expression or rate law expression is the relation between reaction rate and the concentrations of reactants given by a mathematical equation.

CONCENTRATION AND REACTION RATE DATA

THE DIFFERENTIAL RATE LAW OR RATE EXPRESSION: Rates generally depend on reactant concentrations. *To find the exact relation between rate and concentration, we must <u>conduct experiments</u> and collect information.*

$$aA + bB \xrightarrow{\text{C}} xX$$
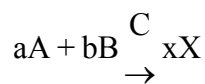
where C is a catalysts, the rate expression will *always* have the form:

Initial rxn rate = $k[A]^m[B]^n[C]^p$
k = rate constant
$[A]$ = concentration of reactant A
$[B]$ = concentration of reactant B
$[C]$ = concentration of the catalyst--won=t see this too often in AP
  m = order of reaction for reactant A
  n = order of reaction for reactant B
  p = order of reaction for the catalyst C

Exponents can be zero, whole numbers or fractions **AND MUST BE DETERMINED BY EXPERIMENTATION!!**

THE RATE CONSTANT, k

- temperature dependent & must be evaluated by experiment.
- Example: rate = $k[A]$
- and k is 0.090/hr, therefore when $[A]$ = 0.018 mol/L
- rate = (.0090/hr)(0.018 mol/L) = 0.00016 mol/(L• hr)

ORDER OF A REACTION
- order with respect to a certain reactant is the *exponent* on its concentration term in the rate expression
- order of the reaction is the sum of all the exponents on all the concentration terms in the expression
- DETERMINATION OF THE RATE EXPRESSION
    $aA + bB \rightarrow xX$

- initial rate = $k[A]_o^m[B]_o^n$
- the little subscript "o" means "original" or at "time zero"

1. **Zero order**: The change in concentration of reactant has no effect on the rate. These are not very common. General form of rate equation: **Rate = k**

2. **First order**: Rate is directly proportional to the reactants concentration; doubling [rxt], doubles rate. These are very common! Nuclear decay reactions usually fit into this category. General form of rate equation: **Rate = $k\,[A]^1 = k[A]$**

3. **Second order**: Rate is quadrupled when [rxt] is doubled and increases by a factor of 9 when [rxt] is tripled etc. These are common, particularly in gas-phase reactions. General form of rate equation: **Rate = k [A]^2 or Rate = k[A]^1[B]^1** which has an *overall* order of two (second order).

4. Fractional orders are rare, but do exist!

   Recall our general rate expression: Rate = k[A]^m[B]^n

   > If $m = 0$; reaction is zero order with respect to A
   > If $m = 1$; reaction is 1st order with respect to A
   > If $m = 2$; reaction is 2nd order with respect to A
   > If $n = 0$; reaction is zero order with respect to B
   > If $n = 1$; reaction is 1st order with respect to B
   > If $n = 2$; reaction is 2nd order with respect to B

Adding the orders of each reactant gives the *overall order* of the reaction.

EXAMPLE

Experiment Number	Initial Rate mol/(L• hr)	Initial concentration [A]$_o$	Initial concentration [B]$_o$
1	0.50×10^{-2}	0.50	0.20
2	0.50×10^{-2}	0.75	0.20
3	0.50×10^{-2}	1.00	0.20
4	1.00×10^{-2}	0.50	0.40
5	1.50×10^{-2}	0.50	0.60

APPLY "TABLE LOGIC"
   1. Look for two trials where the concentration of a reactant was held constant.
   2. Next, focus on the *other* reactant. Ask yourself how it's concentration changed for the same two trials. Was it doubled? Was it tripled? Was it halved?
   3. Once you have determined the factor by which the concentration of the *other* reactant was changed, determine how that affected the rate for those same two trials. Expect easy math! Did changing the concentration have zero effect on the rate? If so, then it is zero order. Did the rate double when the concentration of the *other* reactant was doubled? If so, it is first order. Did the rate quadruple as a result of the reactant's concentration doubling? If so, it is second order. Did the rate increase by a factor of eight? If so, it is third order.

      THINK of the concentration doubling as the number "two". So, *rate* = k[reactant] becomes, *rate* = $k[2]^m$ and you are trying to determine the value of m. If the *rate* doubled think (2 *rate*) = $k[2]^m$ and more simply 2 = $[2]^m$, so $m = 1$. If the rate quadrupled, then think simply, 4 = $[2]^m$ and m must equal 2 to make that a true statement, and so on…

   4. Finally, examine the data table again. This time look for trials where the concentration of the reactant you just determined the order for is held constant and repeat steps 1-3 above.

For our example data table, the rate stays the same regardless of the concentration of [A], therefore, it is zero order with respect to A. However, the rate doubles with a doubling of [B] and triples with a tripling of [B]. This indicates the rate is first order with respect to [B].

Summary: Initial reaction rate = $k[A]_o{}^0[B]_o{}^1 = k[B]_o{}^1 = k[B]$
          The overall reaction rate order = $1 + 0 = 1^{st}$ order overall.
Now. . .
Use a set of the data to calculate k:
0.0050 mol/(L•hr) = $k[0.20 \text{ mol/L}]^1$
   $k = 2.5 \times 10^{-2}$ /hr   or 2.5×10^{-2} hr^{-1}

You should get the same value with any line of data!

Ugly algebraic method is sometimes necessary:

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{k[\text{reactant}]^m [\text{reactant}]^n}{k[\text{reactant}]^m [\text{reactant}]^n}$$

Select a trial where one reactant concentration is held constant SO THAT IT CANCELS; the k's will also cancel
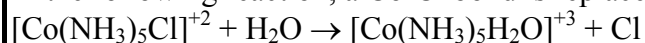
   Using trails 1 & 4:
   $\dfrac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \dfrac{\cancel{k}\,\cancel{[0.50]^m}\,[0.20]^n}{\cancel{k}\,\cancel{[0.50]^m}\,[0.40]^n}$ so…. ½ = [½]^n and ∴ n must be ONE to make that true! It

It's just the long-hand version of table logic.

If you have a case where one reactant is never held constant, then you can either add an "expect" column to the table since you usually can determine the order of at least one reactant and can predict the "expected" change in the rate. Then proceed as usual and compare your "expected rate" to the actual rate for doubling the concentration of the *other* reactant. OR just plug into ugly algebra, just use the method that makes you both quick and accurate!

Exercise
In the following reaction, a Co-Cl bond is replaced by a Co-OH$_2$ bond.
$[Co(NH_3)_5Cl]^{+2} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{+3} + Cl$
          Initial rate = $k\{[Co(NH_3)_5Cl]^{+2}\}^m$
Using the data below, find the value of m in the rate expression and calculate the value of k.

Exp.	Initial Concentration of $[Co(NH_3)_5Cl]^{+2}$ (mol/L)	Initial rate mol/(L• min)
1	1.0×10^{-3}	1.3×10^{-7}
2	2.0×10^{-3}	2.6×10^{-7}
3	3.0×10^{-3}	3.9×10^{-7}
4	1.0×10^{-3}	1.3×10^{-7}

Exercise

The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation

$$BrO_3^- (aq) + 5 Br^- (aq) + 6 H^+ (aq) \rightarrow 3 Br_2 (l) + 3 H_2O (l)$$

The table below gives the results of four *experiments*. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant. What is the value of k? What are the units of k?

Experiment	Initial $[BrO_3^-]$	Initial $[Br^-]$	Initial $[H^+]$	Measured initial rate (mol/L•s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

TWO TYPES OF RATE LAW

➢ **Differential rate law**—data table contains concentration and rate data. Use table logic or ugly algebra to determine the orders of reactants and the value of the rate constant, k.

➢ **Integrated rate law**—data table contains concentration and time data. Use graphical methods to determine the order of a given reactant. The value of the rate constant k is equal to the absolute value of the slope of the *best* fit line which was decided by performing 3 linear regressions and analyzing the regression correlation coefficient r. Not nearly as hard as it sounds!

INTEGRATED RATE LAW: CONCENTRATION/TIME RELATIONSHIPS
When we wish to know how long a reaction must proceed to reach a predetermined concentration of some reagent, we can construct curves or derive an equation that relates concentration and time.

Set up your axes so that *time* is always on the *x*-axis. Plot the concentration of the reactant on the *y*-axis of the first graph. Plot the natural log of the concentration (ln [A], NOT log[A]) on the *y*-axis of the second graph and the reciprocal of the concentration on the *y*-axis of the third graph. You are in search of linear data! Here comes the elegant part... If you do the set of graphs in this order with the *y*-axes being "**c**oncentration", "**n**atural log of concentration" and "**r**eciprocal concentration", the alphabetical order of the *y*-axis variables leads to 0, 1, 2 orders respectively for that reactant.

Zero order	First order	Second order
k = negative slope	k = negative slope	k = the slope
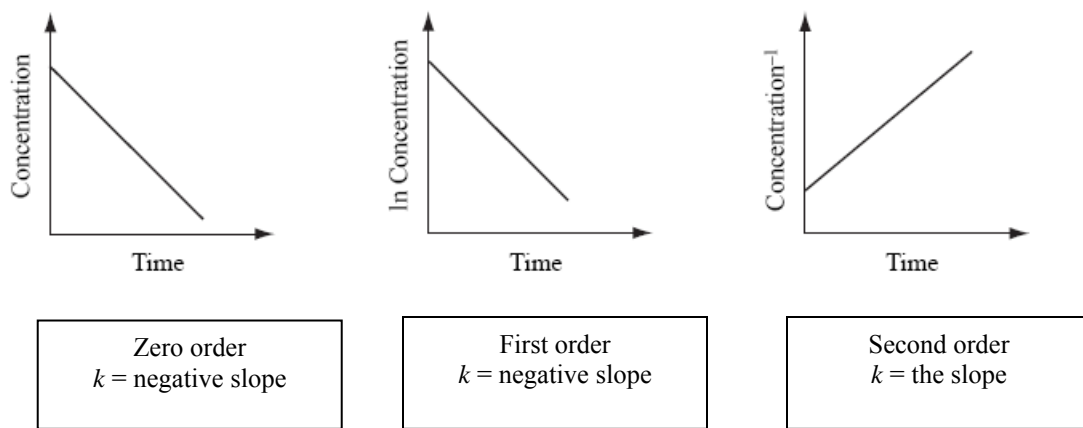
You can now easily solve for either time or concentration once you know the order of the reactant. Just remember $y = mx + b$. Choose the set of variables that gave you the best straight line (*r* value closest to ±1) and insert them in place of *x* and *y* in the generalized equation for a straight line. "A" is reactant A and A_o is the initial concentration of reactant A at time zero [the *y*-intercept].

$$y = mx + b$$

zero order $\quad\quad\quad\quad$ $[A] = -kt + [A_o]$
first order $\quad\quad\quad\quad$ $\ln[A] = -kt + \ln[A_o]$
second order $\quad\quad\quad$ $1/[A] = kt + 1/[A_o]$

Also recognize that $|$ slope $| = k$, since the rate constant is NEVER negative. If you are asked to write the rate expression [or rate law] it is simply Rate = $k[A]^{\text{order you determined from analyzing the graphs}}$

<u>Using the graphing calculator:</u> Set up your calculator so that *time* is always in L1.
Use L2, L3 and L4 to display the *y*-variables. Remember the list for what is placed on the *y*-axis is alphabetical (concentration, natural log of concentration and reciprocal concentration).

$\quad\quad$ L1 = time (*x*-variable throughout!)
$\quad\quad$ L2 = concentration $\quad\quad\quad\quad\quad\quad$ [A] $\quad\quad$ straight line = zero order
$\quad\quad$ L3 = ln concentration $\quad\quad\quad\quad\quad$ ln [A] $\quad\quad$ straight line = first order
$\quad\quad$ L4 = reciprocal concentration $\quad\quad$ 1/[A] $\quad\quad$ straight line = second order

Use this system to set up the data given in the following exercise.

Exercise

The decomposition of N_2O_5 in the gas phase was studied at constant temperature.

$$2 \, N_2O_5(g) \longrightarrow 4 \, NO_2(g) \; + \; O_2(g)$$

The following results were collected:

$[N_2O_5]$	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Determine the rate law and calculate the value of k.

What is the concentration of $N_2O_5(g)$ at 600 s?

At what time is the concentration of $N_2O_5(g)$ equal to 0.00150 M ?

We are going to perform 3 linear regressions to determine the order of the reactant. They will be L1,L2; L1,L3; L1,L4. Next, we will determine which regression has the best r-value [linear regression correlation coefficient in big people language!] We will also paste the best regression equation Y= so that we can easily do other calculations commonly required on AP Chemistry Exam problems.

1. To begin let's do some housekeeping. Press CLEAR repeatedly until your home screen is cleared.
2. Press 2nd + 4 to paste the ClrAllLists command on your screen. Press ENTER to execute the command.
3. Press 2nd 0 to access the catalogue. Press ▼ repeatedly to scroll down the alphabetical list of commands until you reach DiagnosticsOn. Press ENTER ENTER to paste the command on your screen and execute the command. If you skip this step, you will never see the r-value!
4. Press STAT ENTER to enter data into your lists. Put times in L1 and concentrations (or absorbances) in L2.

5. Batch transform the concentrations into ln[concentration] and place them into L3. How? Press ▶ and ▲ to get to the "tippy top" of L3. Next, press [LN][2nd][2] to calculate the natural logs of the concentrations stored in L2 and plop them into L3.

6. Batch transform the concentrations into reciprocal concentrations by pressing ▶ and ▲ to get to the "tippy top" of L4. Press [2nd][2][x^{-1}] to calculate the reciprocals of the concentrations stored in L2 and plop them into L4.

7. Press [STAT][▶] to get to CALC and then press [4] to choose LinReg. The command will be pasted on your screen. Press [2nd][1][,][2nd][2][,][VARS][▶][ENTER][ENTER][ENTER] to add L1, L2, Y1 to your screen. That translates to "Oh, wise calculator, please run a linear regression picking up the *x*-values from L1, the *y*-values from L2 and paste the regression equation ($y = mx + b$ format) into Y1 so that it will graph and I may use it to quickly solve additional problems." Your screen now displays the statistics for the regression. You are in search of an *r* that is closest to ±1. Jot down your *r* for L1,L2.

8. Press [2nd][ENTER] to get the LinReg L1, L2, Y1 on the screen again. Use your ◀ arrow to position your cursor over L2. Press [2nd][3] to replace L2 with L3 and press [ENTER] to calculate the new regression statistics. Jot down your *r* for L1, L3.

9. Press [2nd][ENTER] to get the LinReg L1, L3, Y1 on the screen again. Use your ◀ arrow to position your cursor over L3. Press [2nd][4] to replace L3 with L4 and press [ENTER] to calculate the new regression statistics. Jot down your *r* for L1, L4.

10. Determine the *best r*-value.
   - IF it was L1, L2 then zero order for that reactant.
   - IF it was L1, L3 then first order for that reactant.
   - IF it was L1, L4 then second order for that reactant.

11. Press [2nd][ENTER] as many times as it takes you to get back to the LinReg command that generated the *best r*-value. Calculate the regression again. Why?
   Because |slope| = *k* & Rate = $k[\text{rxt}]^{\text{order}}$

To answer the rest of the questions in our example:

12. Press [2nd][Y=] to turn ON and set up your stat plot to *match* the pair of lists that led to the best regression statistics.

13. Press [ZOOM][9] to fit your data to the graph window and display your regression line. The regression equation is in your Y= if you care to look at it.

Once you have the CORRECT equation for the reaction's rate law in your calculator so that it can draw the CORRECT linear regression line…

14. Press [WINDOW] to check the max and min *x* and *y*-values that the Zoom 9 command assigned to the graph window. You can now solve for any concentration EXACTLY between those max and min values. What if your window doesn't have the proper time or ln[conc.] or 1/[conc.] range? CHANGE IT!

15. To solve for *time*, display your graph by pressing [GRAPH].

16. Press ⎡2nd⎤⎡TRACE⎤ to get to calculate then choose ⎡1⎤ which is "value". Now your screen has the graph displayed AND in the lower left corner an X= with a flashing cursor. Enter the time you want the concentration for and voila! Trouble is that the *x*-value may be either ln[conc.] or 1/[conc.], so you are not finished yet. Jot down the *x*-value. To get the anti natural log, press ⎡2nd⎤⎡LN⎤ and the *x*-value you wrote down. If you need the reciprocal, type in the value and press ⎡x⁻¹⎤ to calculate the concentration. NOTE: If the time is outside your window range, you'll get an error message which is a reminder to reset your window.

17. To solve for a concentration is only a tad more complicated. Press ⎡Y=⎤ and ⎡▼⎤ to get to Y2. Type in the concentration value with the proper function (such as ln or reciprocal) applied to it that corresponds to the time that you seek. Press ⎡GRAPH⎤. If you see an intersection, peachy. If you do not, then adjust your window.

18. With the graph displaying an intersection, press ⎡2nd⎤⎡TRACE⎤ to get to calculate but press ⎡5⎤ to choose "intersection". Press ⎡ENTER⎤⎡ENTER⎤⎡ENTER⎤ to display the time value that you seek.

HALF-LIFE AND REACTION RATE FOR FIRST ORDER REACTIONS, $t_{1/2}$

- the time required for one half of one of the reactants to disappear.
- $[A] = 2[A]_o$ or $\dfrac{[A]}{[A]_o} = 2$ so... $\ln \dfrac{[A]}{[A]_o/2} = k\,t_2$ and... $\ln 2 = t_2$
- Rearrange , evaluate ln 2 and solve for t_2 and you get

$$t_2 = \frac{0.693}{k}$$

Exercise
A certain first-order reaction has a half-life of 20.0 minutes.
a. Calculate the rate constant for this reaction.

b. How much time is required for this reaction to be 75% complete?

Exercise

The rate constant for the first order transformation of cyclopropane to propene is 5.40×10^{-2}/hr. What is the half-life of this reaction? What fraction of the cyclopropane remains after 51.2 hours? What fraction remains after 18.0 hours?

Exercise

For the reaction of $(CH_3)_3CBr$ with OH^-,

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$
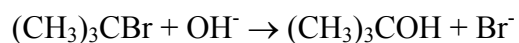
The following data were obtained in the laboratory.

TIME (s)	$[(CH_3)_3CBr]$
0	0.100
30	0.074
60	0.055
90	0.041

Plot these data as $\ln [(CH_3)_3CBr]$ versus time. Sketch your graph.

Is the reaction first order or second order? What is the value of the rate constant?

Exercise 12.5

Butadiene reacts to form its dimer according to the equation

$$2\ C_4H_6\ (g)\ \rightarrow\ C_8H_{12}\ (g)$$

The following data were collected for this reaction at a given temperature:

$[C_4H_6]$	Time ($\pm$ 1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

a. What is the order of this reaction? Explain. Sketch your graph as part of your explanation. Write the rate law expression:

b. What is the value of the rate constant for this reaction?

c. What if the half-life for the reaction under the conditions of this experiment?

HALF-LIFE AND REACTION RATE FOR ZERO ORDER REACTIONS, $t_{1/2}$
- the time required for one half of one of the reactants to disappear, BUT
  - Rate $= k[A]^0 = k$ (a big fat 1) $= k$
  - Integrated rate law is $[A] = -kt + [A]_o$

- $[A] = 2[A]_o$ or $\dfrac{[A]}{[A]_o} = 2$ so...

$$\frac{[A]_o}{2} = -k\,t_{1/2} + [A]_o$$

$k\,t_{1/2} = \dfrac{[A]_o}{2k}$ solve for $t_{1/2}$, $t_{1/2} = \dfrac{[A]_o}{2k}$ for a ZERO order rxn.

Zero-order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur. The enzyme or catalyst may be come saturated and therefore an increase in the [reactant/substrate] has no effect on the rate.

INTEGRATED RATE LAWS FOR REACTIONS WITH MORE THAN ONE REACTANT

- Must [still] be determined by experiment! But we use a technique called "swamping".
- Flood the reaction vessel with high concentrations of all but one reactant and perform the experiment. The reactants at high concentrations like say, 1.0 M compared to the reactant with a low concentration say, 1.0×10^{-3} M, stay the same.
  - "In English"—the rate is now dependent on the concentration of the little guy since the big guy's aren't changing, therefore the rate $= k'$ [little guy]
  - We now re-write the rate as a **pseudo-rate-law** and k' is a **pseudo-rate-constant**

This is what is happening in the Crystal Violet lab!

A SUMMARY:

Table 12.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	*First*	*Second*
Rate law:	Rate $= k$	Rate $= k[A]$	Rate $= k[A]^2$
Integrated rate law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$
Plot needed to give a straight line:	$[A]$ versus t	$\ln[A]$ versus t	$\dfrac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line:	Slope $= -k$	Slope $= -k$	Slope $= k$
Half-life:	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$

REACTION MECHANISMS
The sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants
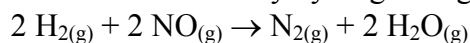to products.
   - Must be determined by experiment! Must agree with overall stoichiometry AND the
     experimentally determined rate law!
   - ELEMENTARY STEPS
       - **molecularity**--number of molecules that participate in an atomic rearrangement
       - unimolecular: involves one reactant molecule

       - bimolecular: involves a collision between two reactant molecules

       - termolecular: simultaneous collision between three reactant molecules **[very rare!]***

   - RATE EXPRESSIONS FOR ELEMENTARY STEPS--*the rate expression cannot be predicted
     from overall stoichiometry. The rate expression of an elementary step is given by the product
     of the rate constant and the concentrations of the reactants in the step.*

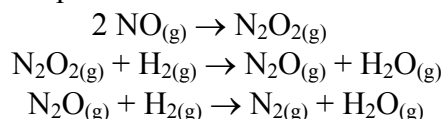| ELEMENTARY STEP	MOLECULARITY	RATE EXPRESSION
A→ products	unimolecular	rate = $k[A]$
A + B → products	bimolecular	rate = $k[A][B]$
A + A → products	bimolecular	rate = $k[A]^2$
2 A + B → products*	termolecular*	rate = $k[A]^2[B]$

   - THE PHYSICAL SIGNIFICANCE OF RATE EXPRESSIONS FOR ELEMENTARY STEPS
       - the more molecules the more collisions, the faster the rate
       - the faster the molecules are moving, the more likely they will collide, the faster the rate
   - MOLECULARITY AND ORDER
       - an **elementary step** is a reaction whose rate law can be written from its molecularity
       - NOT true of the overall reaction order!

Exercise
Nitrogen oxide is reduced by hydrogen to give water and nitrogen,
      $2 H_{2(g)} + 2 NO_{(g)} \rightarrow N_{2(g)} + 2 H_2O_{(g)}$
and one possible mechanism to account for this reaction is
         $2 NO_{(g)} \rightarrow N_2O_{2(g)}$
      $N_2O_{2(g)} + H_{2(g)} \rightarrow N_2O_{(g)} + H_2O_{(g)}$
 $N_2O_{(g)} + H_{2(g)} \rightarrow N_{2(g)} + H_2O_{(g)}$

What is the molecularity of each of the three steps? Show that the sum of these elementary steps is the
net reaction.

- REACTION MECHANISMS AND RATE EXPRESSIONS
  - determined by experiment
  - the rate of the overall reaction is limited by, and is exactly equal to, the combined rates of all elementary steps ***up to and including the slowest step in the mechanism***
  - the slowest step is the **rate determining step**
  - **reaction intermediate**--produced in one step but consumed in another.
  - **catalyst**--goes in, comes out unharmed and DOES NOT show up in the final rxn.

Exercise

The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

$$2 \, NO_2 \, (g) \; + \; F_2 \, (g) \; \rightarrow \; 2 \, NO_2F \, (g)$$
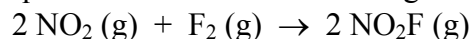
The *experimentally* determined rate law is

$$Rate = k \, [NO_2][F_2]$$

A suggested mechanism for the reaction is

$$NO_2 \; + \; F_2 \; \rightarrow \; NO_2F \; + \; F \qquad \text{Slow}$$

$$F \; + \; NO_2 \; \rightarrow \; NO_2F \qquad \text{Fast}$$

Is this an acceptable mechanism? That is, does it satisfy the two requirements? Justify.

Go Directly to the "Arrhenius Made Easy" Handouts. Do not pass "GO". Do not collect $200.

12.8 CATALYSIS
Alter the mechanism so the activation energy barrier can be lowered.
- Catalysts are not altered during the reaction--they serve to lower the activation energy and speed up the reaction by offering a different pathway for the reaction
- ΔE is NOT changed for the process
- Biological catalysts are enzymes--proteins w/ specific shapes ATP synthetase is the most important enzyme in the human body!
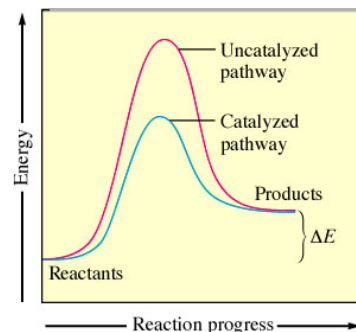
HETEROGENEOUS CATALYST--different phase than reactants, usually involves gaseous reactants adsorbed on the surface of a solid catalyst
- **adsorption**—refers to the collection of one substance on the surface of another
- **absorption**—refers to the penetration of one substance into another; water is absorbed by a sponge
- hydrogenation of unsaturated hydrocarbons—especially important in converting unsaturated fats [oils] into saturated fats [solids like Crisco]
- C=C bonds are converted into C-C bonds by adding a pair of hydrogens "across the double bond"
- A simple example of hydrogenation involves ethylene:

H   H
 \   /
  C=C   + H$_2$ (g)   →   H —— C —— C —— H
 /   \ | |
H   H   H   H
  ethene (ethylene)   ethane
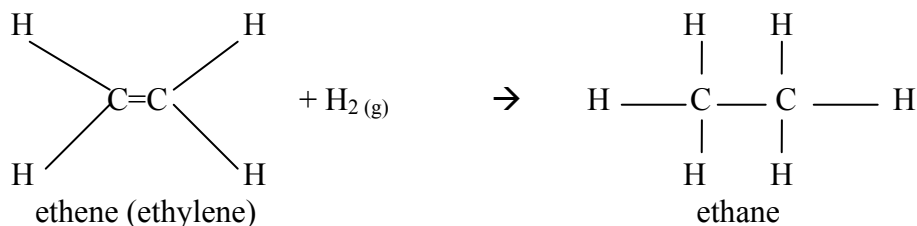
This reaction uses a solid catalyst in the form of Pt, Pd, or Ni. The hydrogen and ethylene adsorb on the catalyst surface where the reaction occurs. The catalyst allows for metal-hydrogen interactions that weaken the strong H-H bonds and facilitate the reaction. Typically involves 4 steps:
1. Adsorption and activation of the reactants
2. Migration of the adsorbed reactants on the surface
3. Reaction of the adsorbed substances
4. Escape, or desorption, of the products

Catalytic converters are also heterogeneous catalysts. They have been placed in automobiles since 1974. [I know! You weren't born yet! Don't rub it in.] Gasoline containing lead RUINS the catalytic converter in your car!
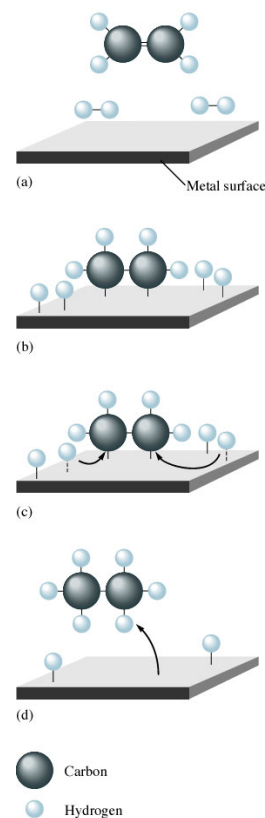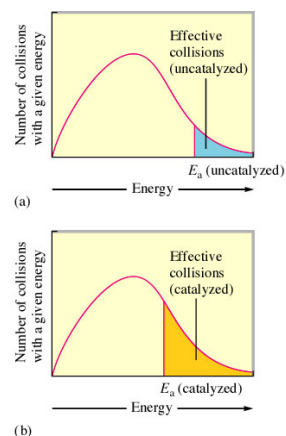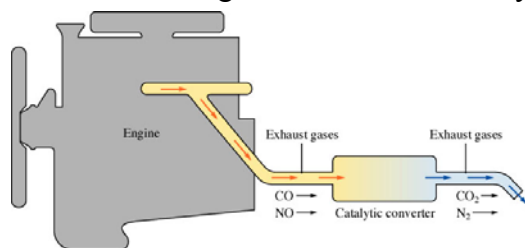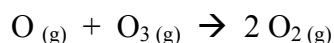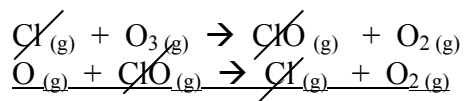
HOMOGENEOUS CATALYST—exists in the same phase as the reacting molecules.
Freons or chlorofluorocarbons [CFC**'s**] were used until recently as refrigerants and as propellants in aerosol cans. Freon-12 (CCl_2F_2) is relatively inert and thus remains in the environment for a long time. Eventually they migrate upward into the upper atmosphere and are decomposed by high-energy light. Among the decomposition products are chlorine atoms:

$$CCl_2F_{2\,(g)} \xrightarrow{\;light\;} CClF_{2\,(g)} + Cl_{(g)}$$
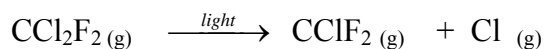
These chlorine atoms can catalyze the decomposition of ozone:

$$\cancel{Cl}_{(g)} + O_{3\,(g)} \rightarrow \cancel{ClO}_{(g)} + O_{2\,(g)}$$
$$\underline{O_{(g)} + \cancel{ClO}_{(g)} \rightarrow \cancel{Cl}_{(g)} + O_{2\,(g)}}$$

$$O_{(g)} + O_{3\,(g)} \rightarrow 2\,O_{2\,(g)}$$

READ THE LAST COUPLE OF PAGES OF THIS CHAPTER FOR SOME GREAT DESCRIPTIVE STUFF! (That translates into multiple choice points!)