

Chemical kinetics is the study of the speed or rate of a reaction under various conditions. Thermodynamic favorability is also important AND a thermodynamically favorable reaction does NOT imply a rapid reaction. The changing of diamond into graphite is thermodynamically favorable, but so slow that it is not detectable even in a lifetime. Why? It has an enormous activation energy that must be overcome before the reaction may proceed. We must also consider the mechanism of the reaction which is a sequence of events at the molecular level that controls the speed and outcome of the reaction. Dust off all those algebraic “rate” skills you’ve been acquiring, they will come in mighty handy in this unit.

FACTORS THAT AFFECT REACTION RATES (loads of multiple choice points lurk within this section)

- 1. Nature of the reactants**—Some reactant molecules react in a hurry, others react very slowly. Why? The phase of matter comes into play; solids will react much more slowly than liquids or aqueous solutions.
 - Physical state matters a great deal. Consider gasoline(*l*) vs. gasoline(*g*).
 $\text{K}_2\text{SO}_4(s) + \text{Ba}(\text{NO}_3)_2(s) \rightarrow \text{no rxn.}$; while the reaction is rapid in aqueous solution.
 - Chemical identity - What exactly is reacting? Usually ions of opposite charge react very rapidly. Also, the more bonds between reacting atoms in a molecule, the slower the reaction rate. Why? More energy is required to separate the molecule into its “bits”. 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 simply because there are so many intermediate steps often requiring specific catalysts.
- 2. Concentration of reactants**—The more molecules present, the more collisions occur, the faster reaction proceeds, the greater its rate. Simple enough. It’s much like the crowded halls during the passing period!
- 3. Temperature**—“Heat ‘em up & speed ‘em up!”; the faster molecules move, the more likely they are to collide and the more energetic the collisions become. (We’re back to the passing period analogy.) In other words, the more likely “molecular damage” will occur. Bonds will be broken and new bonds will form.
 - 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.
 - In fact, a general rule of thumb is that a 10°C increase in temperature will double the reaction rate.
 - This actually depends on the magnitude of the activation energy, E_a^* and the temperature range.
- 4. Surface area of reactants**--exposed surfaces affect speed.
 - Except for substances in the gaseous state or solution, reactions occur at the boundary, or interface, between two phases. In other words, at the exposed surface of the substance.
 - Therefore, 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. Aqueous solutions are ultimate exposure!

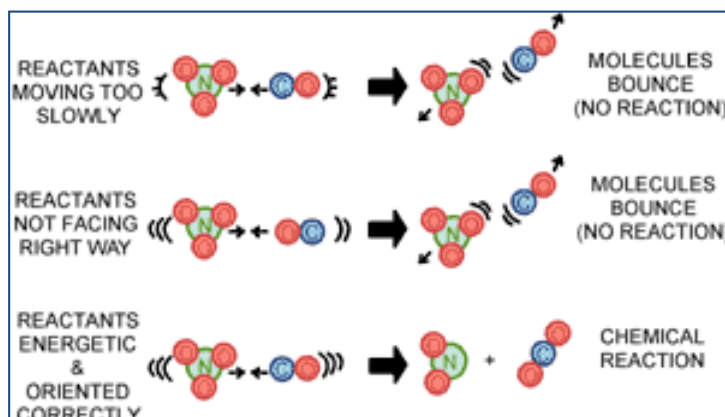
5. **Adding an inert gas has NO EFFECT** on the rate [or equilibrium] of the reaction since it is NOT in the reaction mechanism! This is a classic ruse with regard to test questions.
6. **Catalysis** is the increase in rate of a chemical reaction due to the participation of a substance called a *catalyst*. (Sounds like a circular argument, huh?) Unlike other reagents in the chemical reaction, a catalyst is not consumed, therefore it can be used again and again. A catalyst may participate in multiple chemical transformations. The effect of a catalyst may vary due to the presence of other substances known as inhibitors (which reduce the catalytic activity) or promoters (which increase the activity).
- Biological catalysts are proteins called enzymes. They are very “shape” specific to their substrate and have an active site that attracts the substrate using intermolecular forces. You may have studied the “lock and key” enzyme analogy in a prior biology class. Since their shape is mostly determined by IMFs (as opposed to actual chemical bonds), which are very temperature sensitive. Altering the pH or heating the enzyme easily disrupts the IMFs and causes the enzyme to denature (lose its three dimensional shape).
 - 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.
 - Remember! The catalyst is not part of the chemical reaction and is not used up during the reaction. Usually, the catalyst participates in the rate-determining or slowest step.
 - Catalysts may be homogeneous or heterogeneous catalysts. A homogeneous catalyst is in the *same phase* as the reactants. So, go ahead, guess what heterogeneous means in this context. Yep. A heterogeneous catalyst is in a different phase than the reactants. Heterogeneous catalysis offers the advantage that products are readily separated from the catalyst, and heterogeneous catalysts are often more stable and degrade much slower than homogeneous catalysts.

Example: 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: Since a catalyst lowers the activation energy barrier, the forward and reverse reactions are both accelerated to the same degree.

- Homogeneous catalysts actually appear in the rate law because their concentration affects the reaction.

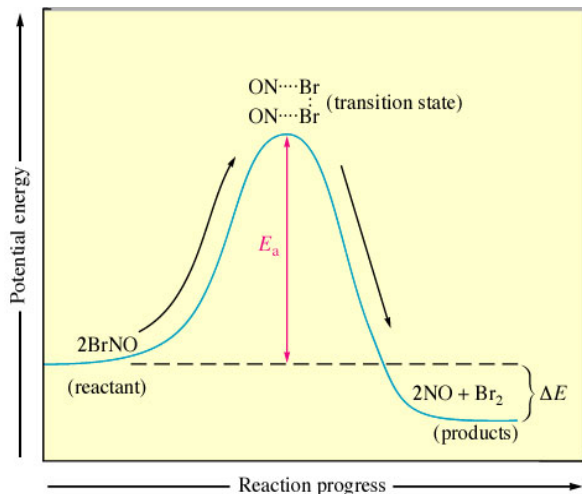
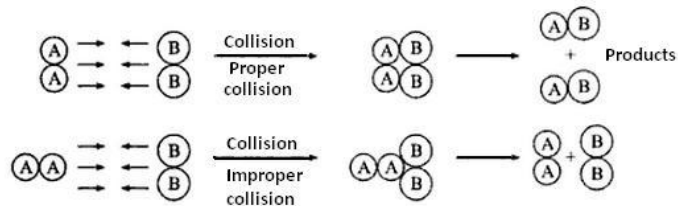
THE COLLISION THEORY OF REACTION RATES

The collision theory states that when suitable particles of the reactant hit with each other, only a certain percentage of the collisions cause any noticeable or significant chemical change; these successful changes are called successful collisions. The successful collisions have enough energy, also known as activation energy, at the moment of impact the coulombic attractions between each bonded atom and the shared electrons is overcome in the reactant molecules thereby breaking the preexisting bonds and form all new bonds. This results in the products of the reaction. Increasing the concentration of the reactant particles or raising the temperature, thus bringing about more collisions and therefore many more successful collisions, increases the rate of reaction.



Essential Components of the Collision Theory

- Particles must collide.
- Most often, only two particles may collide at one time.
- Proper orientation of colliding molecules is essential so that molecules come into contact with each other to form products.



- The collisions 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. We speak of such collisions as “**effective collisions**”.
- 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 fall back to the products.

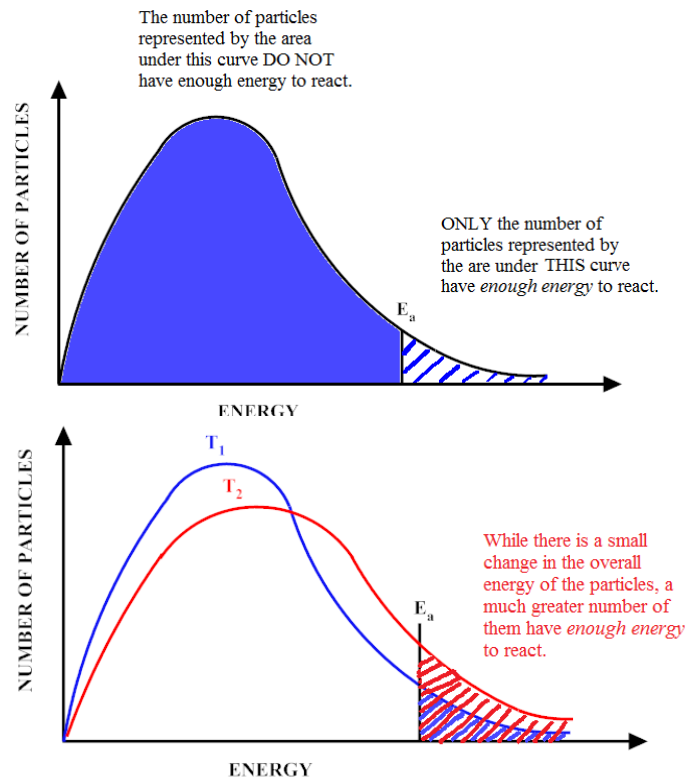
With all of these criteria met, the reaction may proceed in the forward direction. It's amazing that we have reactions occurring at all!

You can mark the position of activation energy E_a on a Maxwell-Boltzmann distribution to get a diagram like the one shown right. If the temperature is increased, the molecules speed up and collide more frequently with more energetic collisions.

Only those particles represented by the area to the right of the activation energy mark will react when they collide. The great majority don't have enough energy, and will simply bounce apart.

If we increase the temperature from T_1 to T_2 , more molecules are energetic enough to achieve the E_a , thus more molecules react and the overall reaction rate increases. Notice how many more molecules are to the right of the activation energy and thus will react when they collide.

A general rule of thumb is that reaction rate doubles for each 10 °C rise in temperature!



TYPES OF CHEMICAL REACTION RATES

The speed of a reaction is expressed in terms of its “rate” which is equal to some measurable quantity that is changing with time.

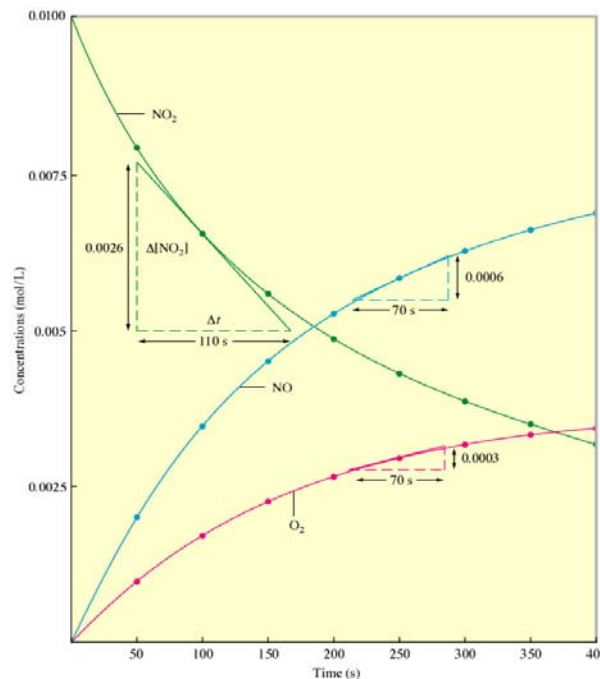
The rate of a chemical reaction is measured by the decrease in concentration of a reactant or an increase in concentration of a product in a unit of time.

$$\text{Generally speaking, Rate} = \frac{\text{change in concentration of a species}}{\text{time interval}} = \frac{\Delta[\text{reactants}]}{t}$$

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.

Time (s)	[NO ₂]	[NO]	[O ₂]
0	0.1000	0.0000	0.0000
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035



1. **Instantaneous Reaction Rate** which is simply the “rate at a given instant of time”, hence its name! You probably know how to do this from math class... especially if you are currently enrolled in Pre-Calculus or Calculus. Go ahead; it’s OK to show off! Examine the graph on the previous page. Note the shapes of the curves in relation to the concentration data presented for each substance. Note the slope of each of the lines drawn tangent to a given curve.

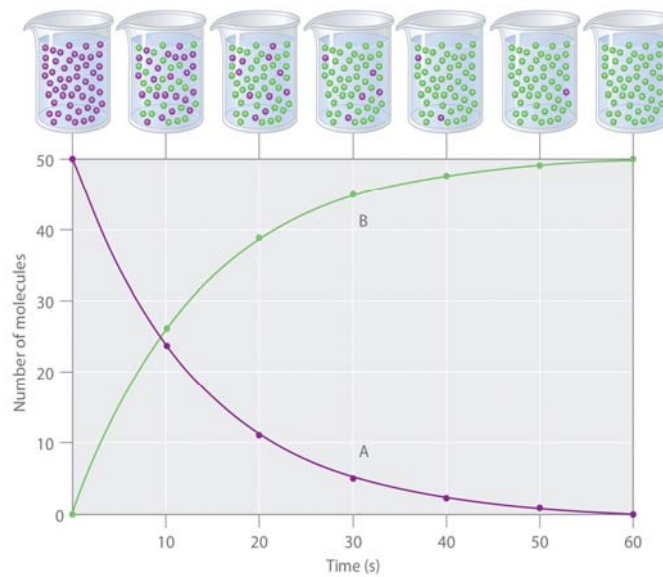
To determine the value of the rate at a particular instant of time, known as the **instantaneous rate**, simply compute the slope of a line tangent to the curve at that point in time. Be particular with regard to your vocabulary when describing how to do this process. Writing, “take the tangent...” earns no points. Why not?

Shall we practice?

Use this technique to determine the instantaneous rate for the reactant at 10 s and at 20 s.

Use this technique to determine the instantaneous rate for the product at 10 s and at 20 s.

What has happened to this system at 60 seconds? Practice determining the instantaneous rate for both substances at 20 minutes and 30 minutes.



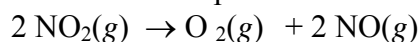
2. **Relative Reaction Rate** is expressed as the change in concentration of a reactant per unit time or $\frac{\Delta[A]}{\Delta \text{time}}$

You should 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*

Also, the word relative here doesn't refer to family members, it refers to terms that relate to each other in the context of a given chemical system.

Consider the reaction for the decomposition of nitrogen dioxide once again:



A cursory analysis of the stoichiometry of the equations reveals that oxygen gas can appear only half as rapidly as the nitrogen dioxide gas disappears while NO gas appears twice as fast as oxygen appears.

The simplest way to obtain relative rate expressions is to place a one over each coefficient in the balanced equation (if a coefficient is "missing", it is understood that its coefficient is "1").

Next, apply the appropriate algebraic sign (-) for reactants since they are disappearing as time goes by, (+) for products since they are appearing as time goes by. Always respect the algebraic sign AND respect the stoichiometry.

Thus,

$$\text{Initial Rate of Reaction} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = +\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t}$$

Of course you can change these once the ratio is set if you have an aversion to fractions. Simply multiply ALL the terms by the same factor to eliminate the fractions. In this case, multiply each term by 2. So, you might prefer -1 : +2 : +1

Shall we try another? Consider this reaction and write all the relative rate terms for the reactants and products.



$$\text{Rate} = -\frac{1}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = +\frac{\Delta[\text{P}_4]}{\Delta t} = +\frac{1}{6} \frac{\Delta[\text{H}_2]}{\Delta t}$$

It's OK to shorten "initial rate of reaction" to simply "rate". It's OK to leave the + off a coefficient. We are doing it here for emphasis! Again, you may prefer to multiply through to eliminate the fractions, but you should work on your prejudices against them! (I still campaign that using the fractions is easier.)

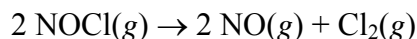
$$\text{Rate} = -\frac{3}{12} \frac{\Delta[\text{PH}_3]}{\Delta t} = +\frac{12}{12} \frac{\Delta[\text{P}_4]}{\Delta t} = +\frac{2}{12} \frac{\Delta[\text{H}_2]}{\Delta t}$$

which becomes

$$\text{Rate} = -3 \frac{\Delta[\text{PH}_3]}{\Delta t} = +12 \frac{\Delta[\text{P}_4]}{\Delta t} = +2 \frac{\Delta[\text{H}_2]}{\Delta t}$$

Exercise 1

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



$$\text{Initial rate rxn.} = -\frac{1}{2} \frac{\Delta[\text{NOCl}]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = +\frac{\Delta[\text{Cl}_2]}{\Delta t}$$

3. DIFFERENTIAL Rate Law or Rate Expression (often referred to without the “differential”)

Reactions are reversible. So far, we’ve only considered the forward reaction. The reverse is equally important. When the *rate* of the forward is equal to the *rate* of the reverse we have EQUILIBRIUM! To avoid this complication we will discuss reactions soon after mixing, before things get too messy. So, we will deal with initial reactions rates, thus we need not worry too much about the buildup of products and how that starts up the reverse reaction.

The Method of Initial Reaction Rates--begin with pure reactants, mix thoroughly, then measure speed of rxn. over time. How? Count number of bubbles, measure mass of precipitate, use spectroscopy to measure color change, etc.

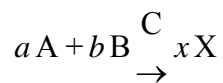
The presence of products can alter results dramatically and lead to confusing results. We’ll be talking *initial reaction rates* throughout our discussions!

$$\text{Rate} = k[\text{NO}_2]^n = -\left[\frac{\Delta[\text{NO}_2]}{\Delta t}\right]$$

The rate expression or rate law expression is the relation between reaction rate and the concentrations of reactants given by a mathematical equation. Be on the lookout for either symbolism for rate and never, ever forget rate is equal to a change in some measurable quantity per unit time.

Analyzing CONCENTRATION--RATE data allows us to determine the differential rate law expression. It’s time to master the lingo!

Rates generally depend on reactant concentrations. *To find the exact relation between rate and concentration, we must conduct experiments, collect data and subsequently interpret the data.* You’ll get your crack at the data in just a bit. First, examine the generic reaction below:



“C” is a catalysts, the rate expression will *always* have the form:

$$\text{Initial rxn rate} = k[\text{A}]^m[\text{B}]^n[\text{C}]^p$$

*note the catalyst is included only if it is homogenous (in the same phase of matter as the reactants)

k = rate constant

$[\text{A}]$ = molar concentration of reactant A & $[\text{B}]$ = molar concentration of reactant B

$[\text{C}]$ = molar 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

We call the exponents “orders” and they can be zero, whole numbers or fractions which **MUST BE DETERMINED BY EXPERIMENTATION!!**

THE RATE CONSTANT, k

- k is most definitely temperature dependent & must be evaluated by experiment
- Example: $\text{rate} = k[\text{A}]$
- Example: Suppose k is determined to be 0.090/hr, \therefore when $[\text{A}] = 0.018 \text{ mol/L}$
- Then, $\text{rate} = k(0.090/\text{hr})[0.018 \text{ mol/L}] = 0.00016 \text{ mol}/(\text{L}\cdot\text{hr}) = 1.6 \times 10^{-4} \text{ mol}/(\text{L}\cdot\text{hr})$
- Yeah, I know...those units look frightful! Have faith, we have a way to simplify determining them.

THE SCOOP ON “ORDERS”

- The “*order*” with respect to a certain reactant is simply the *exponent* on its concentration term in the rate expression. We must *analyze concentration & rate data* to make this determination. (Patience, it’s coming...)
- The “*overall order*” of the reaction is simply the sum of all the exponents on all the concentration terms in the expression.

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 = $k[\text{A}]^1 = k[\text{A}]$**
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 = $k[\text{A}]^2$ or Rate = $k[\text{A}]^1[\text{B}]^1$** which has an *overall* order of two (second order).
4. Fractional orders are rare, but do exist!

Recall our general rate expression: $\text{Rate} = k[\text{A}]^m[\text{B}]^n$

If $m = 0$; Say, “The reaction is zero order with respect to A.”

If $m = 1$; Say, “The reaction is 1st order with respect to A.”

If $m = 2$; Say, “The reaction is 2nd order with respect to A.”

If $n = 0$; Say, “The reaction is zero order with respect to B.”

If $n = 1$; Say, “The reaction is 1st order with respect to B.”

If $n = 2$; Say, “The reaction is 2nd order with respect to B.”

Again, summing all of the orders for each reactant gives the *overall order* of the reaction.

NOW, you know enough to work some examples! Try to contain your excitement...

Example: Ponder the following experimental data for the reaction $A + B \rightarrow \text{Product}$

Experiment Number	Initial Rate mol/(L•hr)	Initial concentration [A] ₀	Initial concentration [B] ₀
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

Method 1: “TABLE LOGIC”

1. Examine the data with an analytical eye. Look for two trials where the concentration of a reactant was held constant. Why? It's good experimental design! Meanwhile, you want a comparison where the other reactant's value changed by a factor of 2, 3, 4, $\frac{1}{2}$, etc. For example, Experiments # 1 & 4 make a good choice. [A] was held constant and [B] was doubled. This allows you to focus *solely* on the effect manipulating the concentration of [B] has on the overall rate.
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? Doubling is my personal favorite since even on my worst day; I can multiply by 2, divide by 2, square 2 and even cube 2 in my head, sans calculator.

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!

In our example using trials 1 & 4 [A] is held constant at 0.5 M while [B] is doubled from trial 1 [0.2] → trial 4 [0.4]. Ask yourself, “What effect did that have on the rate?”

Well, the respective rates increased from $0.50 \times 10^{-2} M h^{-1}$ to $1.00 \times 10^{-2} M h^{-1}$ (since the “ $\times 10^{-2} M h^{-1}$ ” part is the same for both, it's just plain simpler to think $0.50 \rightarrow 1.0$) which is a doubling, so the rate increased by $(2)^?$. Well the only way to double the rate is to multiply it by $(2)^1$, so the exponent we seek is “1”, thus we say it is “first order with respect to reactant B”.

Which so far, makes our rate law expression $\text{rate} = k[A]^? [B]^2$

3. What if changing the concentration of a given reactant had zero effect on the rate? In other words the rate was unaffected, if so, then the reaction is *zero order* for that reactant. Why? (any number)⁰ = 1 which, as a multiplier is code for “unaffected”.

SUMMARY

Upon selecting two trials where the concentration of one (or more) reactant's concentration was held constant, ask yourself...

- ❖ Did the rate double (2^1) when the concentration of the *other* reactant was doubled? If so, it is *first order* for that reactant.
- ❖ Did the rate quadruple (2^2) when the concentration of the *other* reactant was doubled? If so, it is *second order* for that reactant.
- ❖ Did the rate increase by a factor of eight (2^3) when the concentration of the *other* reactant was doubled? If so, it is *third order* for that reactant.
- ❖ Did the rate remain constant (2^0) when the concentration of the *other* reactant was doubled? If so, it is *zero order* for that reactant.

Still don't get it? THINK of the concentration doubling as the number "two".

So, $rate = k[\text{reactant}]$ becomes, $rate = k[2]^m$ and you are trying to determine the value of m .

If the *rate* doubled think $(2 \times rate) = k[2]^m$ and more simply, since the k is *constant* you can ignore it for now, and think " $2 = [2]^m$ " $\therefore m = 1$ or else we just broke the 11th commandment!

If the rate quadrupled, then think simply, " $4 = [2]^m$ " $\therefore m$ must equal 2 to make that a true statement.

By the way, if you've never listened to a screencast of your AP Chemistry notes, now may be the time!

Go to www.apchemistrynmsi.wikispaces.com, find a quiet place and your favorite beverage.

4. Finally, examine the data table again. Same song, second verse! This time, with feeling. Look for trials where the *concentration of the reactant you just determined the order for is held constant* and repeat the steps above with the reactant whose concentration is being varied.

Experiment Number	Initial Rate mol/(L•hr)	Initial concentration [A] ₀	Initial concentration [B] ₀
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

Examine trials 1-3. The concentration of [B] is held constant AND the rate remains the same *regardless* of the concentration of [A]. What gives?

The reaction it is *zero order* with respect to A.

Double check all results by examining trials 3-5. 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 $rate = k[A]_0^0[B]_0^1 = k[B]_0^1 = k[B]$

(the superscript outside and above the “molarity” brackets indicates the order of that reactant, the subscript outside and below the molarity bracket means at “time zero” or “original” concentration if you prefer)

The overall reaction rate order = $1 + 0 = 1^{\text{st}}$ order overall.

Calculating the Value of the Rate Constant, k

Select a set of the data to calculate k , gasp! I’m choosing Experiment 1 (for lack of imagination). Get started by writing your newly determined rate law expression:

$$Rate = k[B]^1$$

$$\therefore k = \frac{Rate}{[B]^1} = \frac{0.0050 \frac{\cancel{\text{mol}}}{\cancel{\text{L}} \cdot \text{hr}}}{0.20 \frac{\cancel{\text{mol}}}{\cancel{\text{L}}}} = 0.025 \text{ hr}^{-1} = \frac{2.5 \times 10^{-2}}{\text{h}} \text{ or } 2.5 \times 10^{-2} \text{ h}^{-1}$$

You should get the same value with any line of data! Test it, I’m sure you’re still skeptical...

Method 2: “UGLY ALGEBRAIC METHOD”

Sometimes, the “Ugly Algebraic Method” is necessary. Some folks actually like this better, we here at NMSI don’t judge! Make getting started with this method easy on yourself. Select a trial where one reactant concentration is held constant SO THAT IT CANCELS, and lucky for you, the k ’s will also cancel greatly simplifying the math.

Use the general set-up below and substitute data from the data table. I’m choosing trials 1 & 4 since $[A]$ is held constant at 0.50 M:

$$\frac{rate_1}{rate_2} = \frac{k_1 [\text{reactant}]^m [\text{reactant}]^n}{k_2 [\text{reactant}]^m [\text{reactant}]^n} \text{ becomes } \frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{k_1 [0.50]^m [0.20]^n}{k_2 [0.50]^m [0.40]^n}$$

Commence canceling like terms!

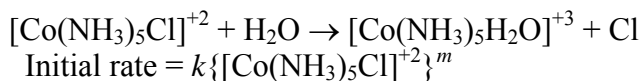
$$\frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{\cancel{k_1} [0.50]^m [0.20]^n}{\cancel{k_2} [0.50]^m [0.40]^n} \text{ becomes } \frac{0.50}{1.00} = \frac{[0.20]^n}{[0.40]^n} \text{ which simplifies to } \frac{1}{2} = \left[\frac{1}{2} \right]^n \therefore n = 1$$

It’s just the long-hand version of table logic. Either way works, employ the method you like best.

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. (Screencast time again!) OR just plug into ugly algebra. Again, employ the method that makes *you* both quick and accurate!

Exercise 2

In the following reaction, a Co–Cl bond is replaced by a Co–OH₂ bond.



Using the data below, find the value of m in the rate expression and calculate the value of k .

Experiment	Initial Concentration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ (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}

$$m = 1; k = 1.3 \times 10^{-4} \text{ min}^{-1}$$

Exercise 3

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



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}

$$\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2; \text{ overall order} = 4; k = 8.0 \text{ L}^3/\text{mol}^3\cdot\text{s}$$

What we've explored thus far is termed differential rate law or simply rate law, it's the method we use when the data presented is concentration & time data. IF the data presented is concentration and rate data, we need a new method!

So, there are TWO TYPES OF RATE LAW which implies to different approaches are needed. Hey, you're half-way there!

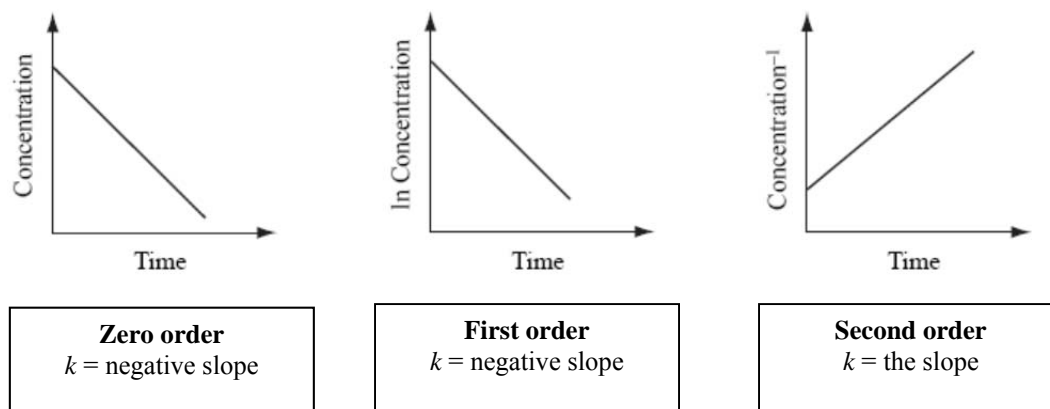
- **Differential rate law**—data table contains **concentration and rate data**. Use table logic or ugly algebra to determine the orders of reactants and the value of the rate constant, k .
- **Integrated rate law**—data table contains **concentration and time data**. Use graphical methods to determine 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 is decided by performing 3 linear regressions and analyzing the regression correlation coefficient r . Not nearly as hard as it sounds! Fire up your graphing calculator.

INTEGRATED RATE LAW: CONCENTRATION-TIME DATA

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 “concentration”, “natural log of concentration” and “reciprocal concentration”, the alphabetical order of the y-axis variable leads to 0, 1, 2 orders respectively for *that* reactant.



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_0 is the initial concentration of reactant A at time zero [the y-intercept].

	$y = mx + b$
zero order	$[A] = -kt + [A_0]$
first order	$\ln[A] = -kt + \ln[A_0]$
second order	$1/[A] = kt + 1/[A_0]$

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

Graphing Calculator Tutorial 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).

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

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

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.

Turn on your calculator and let's start draining those batteries!

If you need a calculator tutorial on entering data into lists, batch transforming list, graphing data, running a linear regression, graphing the regression equation and subsequently using the equation to solve integrated rate problems in a flash, go here: <https://vimeo.com/14866721> If that is blocked, try the links from www.apchemistrynmsi.wikispaces.com

Exercise 4

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



The following results were collected:

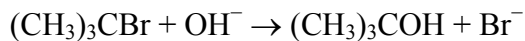
$[\text{N}_2\text{O}_5]$	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

- (a) Determine the rate law and calculate the value of k .
- (b) Determine the concentration of $\text{N}_2\text{O}_5(g)$ at 250 s. Does your calculated answer make sense? Justify your answer.
- (c) Determine the concentration of $\text{N}_2\text{O}_5(g)$ at 600 s. Does your calculated answer make sense? Justify your answer.
- (d) At what time is the concentration of $\text{N}_2\text{O}_5(g)$ equal to 0.00150 M ? Explain how you know your answer is correct.

Ans: rate = $k[\text{N}_2\text{O}_5]$; $k = -\text{slope of graph of } \ln [\text{N}_2\text{O}_5] \text{ vs. } time = 6.93 \times 10^{-3} \text{ s}^{-1}$; 0.0177 M ; 0.00156 M ; 606 s

Exercise 5

For the reaction of $(\text{CH}_3)_3\text{CBr}$ with OH^- ,



The following data were obtained in the laboratory.

TIME (s)	$[(\text{CH}_3)_3\text{CBr}]$
0	0.100
30.0	0.074
60.0	0.055
90.0	0.041

- (a) Determine the order of this reaction. Sketch your graph.
- (b) Determine the value of the rate constant and include proper units.
- (c) At what time is the concentration of $(\text{CH}_3)_3\text{CBr}$ equal to $[0.086]$? Justify your answer.
- (d) At what time is the concentration of $(\text{CH}_3)_3\text{CBr}$ equal to $[0.025]$? Justify your answer.
- (e) What is the concentration of $(\text{CH}_3)_3\text{CBr}$ after 2 minutes? Justify your answer.

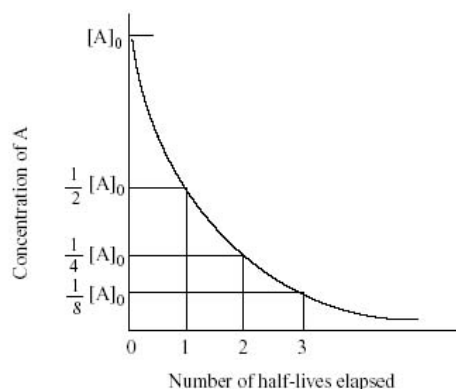
(a) A straight line with a negative slope; 1st order since plot of $\ln[(\text{CH}_3)_3\text{CBr}]$ vs. *time* is linear;
(b) $k = 9.9 \times 10^{-3} \text{ s}^{-1}$; (c) 15.0 s; (d) 140 s; (e) 0.0304 M

DETERMINING HALF-LIFE ($t_{1/2}$)

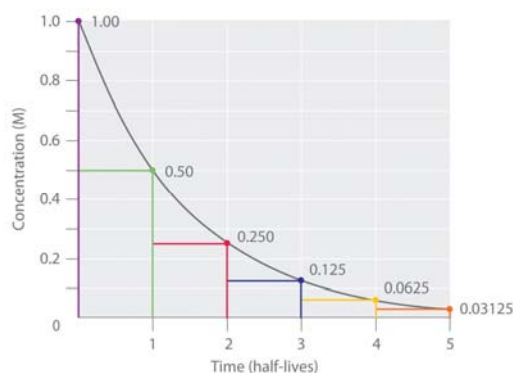
Half-life is defined as the time required for one half of one of the reactants to disappear. Well, that seems logical enough. Finally, a concept with a simple name! You probably remember dealing with half-life in the context of ^{14}C and using it to approximate the age fossils and such. Or, you may have heard it in a medical sense such as injecting ^{131}I which is an important radioisotope of iodine into a patient. It has a radioactive decay half-life of about eight days and is associated with nuclear energy, medical diagnostic and treatment procedures, especially those involving the thyroid gland.

We will focus on the half-life for first order reactions only. Be thankful! Since you are all smart students, you will need to be able to analyze this verbally, graphically and algebraically. Which sounds worse than it is. Again, you already know most of this!

Concept

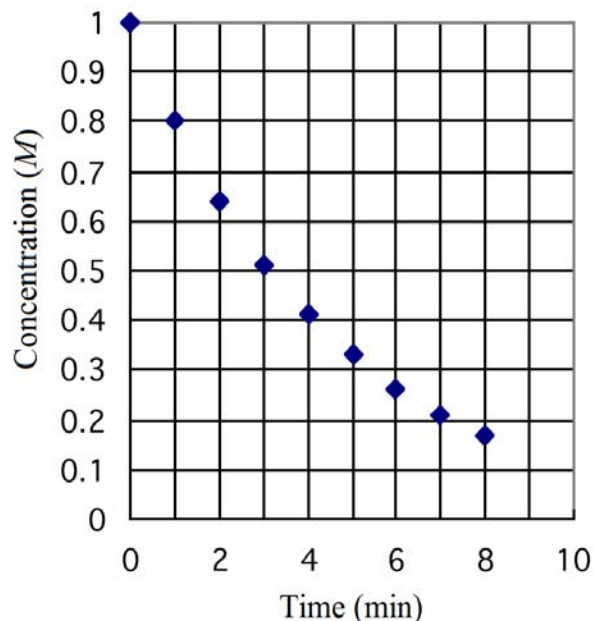


Numerical Interpretation of Concept



The data points plotted on the graph pictured right represent concentration-time data collected for the radioactive decay of Element Q. Your task is to **supply the graph with an appropriate title** and answer the following questions:

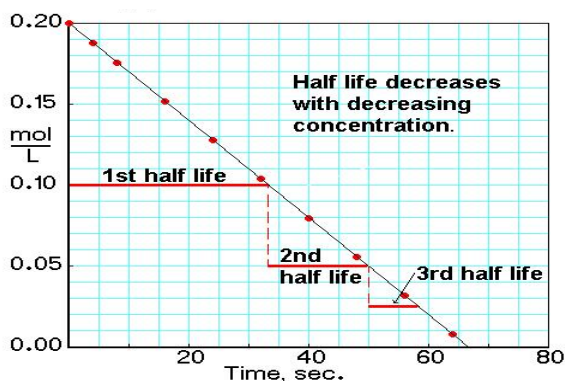
1. While you may at a glance be unable to determine the order of this reaction, you can definitely determine which order it is NOT! So, which order is *not* the order for this reaction?
2. What is the half-life of Element Q?
3. What is the molar concentration of Element Q after a second half-life has elapsed?
4. At what time has 75% of the original sample decayed?



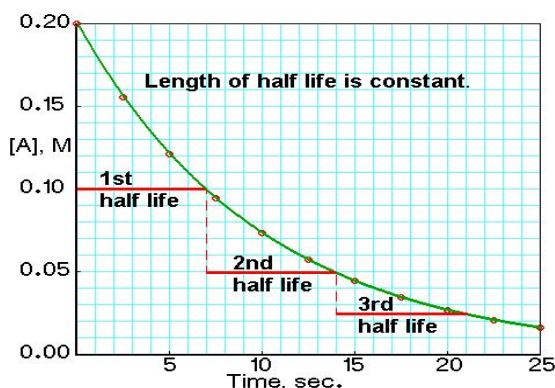
Why do we “care” about half-lives of only 1st order reactions? Because they are the only reactions for which *the length of the half-life is constant* and this course is equivalent to a “first-year” university chemistry course so Calculus is not required, thus we focus on the chemical situation where the math is “simple”.

I still can't resist the comparison, though! Examine the Concentration vs. Time Graphs below:

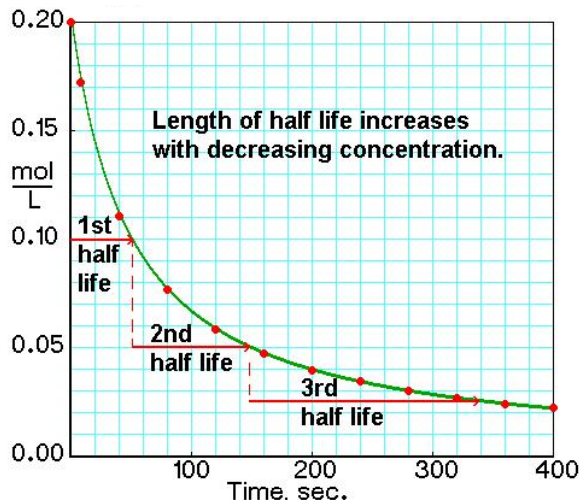
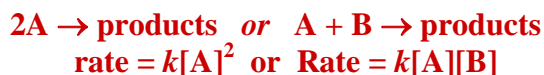
Zero Order Reaction



First Order Reaction



Second Order Reaction



What is alike about each graph?

What is different about each graph?

What is the significance of the lengths of the horizontal red lines associated with each half-life?

Indulge me in a derivation. (That means you can skip this unless you're in Calculus—you might actually find it interesting!)

The half-life, $t_{\frac{1}{2}}$ is a timescale by which the initial population (reactants in our case) is decreased by half of its original value. We can represent the relationship by the following equation:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt \quad \text{where } A_0 \text{ means "concentration at time = zero"}$$

By definition, when $t = t_{\frac{1}{2}}$, $[A] = \frac{[A]_0}{2}$

Substitute, and we arrive at $\ln\left(\frac{[A]_0}{\frac{[A]_0}{2}}\right) = kt_{\frac{1}{2}}$; clean it up a bit

$$\ln\left(\frac{\cancel{[A]_0}}{\cancel{[A]_0}/2}\right) = kt_{\frac{1}{2}} \text{ becomes } \ln\left(\frac{1}{1/2}\right) = kt_{\frac{1}{2}} \text{ which then becomes } \ln(2) = kt_{\frac{1}{2}}$$

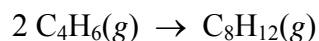
Rearrange once again to solve for $t_{\frac{1}{2}}$ and arrive at what's on the formula sheet for the AP Chemistry Exam:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k} \text{ which is almost downright friendly!}$$

Notice that, for first-order reactions, the half-life is *independent of the initial concentration of reactant*, which is a unique aspect to first-order reactions.

Exercise 6

Butadiene reacts to form its dimer according to the equation



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

[C ₄ H ₆]	Time (± 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) Determine the order of this reaction? Write the rate law expression. Justify your answer. Sketch a graph as part of your explanation.
- (b) Determine the value of the rate constant for this reaction?
- (c) Determine the half-life for the reaction under the conditions of this experiment?

2nd since plot of 1/[C₄H₆] vs. time yields a straight line with a |slope| = $k = 6.14 \times 10^{-2} \text{ M/s}$; 1630 s

Exercise 7

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?

$3.47 \times 10^{-2} \text{ min}^{-1}$; 40 minutes

Exercise 8

The rate constant for the first order transformation of cyclopropane to propene is $5.40 \times 10^{-2} \text{ hr}^{-1}$. Calculate the half-life of this reaction. What fraction of the cyclopropane remains after 51.2 hours? What fraction remains after 18.0 hours?

12.8 hr; 0.063; 0.38

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, $1.0 \times 10^{-3} \text{ M}$, 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!

SUMMARY:

Note $k = |\text{slope}|$ for ANY linearized graph.

	ORDER		
	Zero	First	Second
Rate law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Units of rate constant:	$M \text{ time}^{-1}$ or M/time	time^{-1} or $1/\text{time}$	$M^{-1} \text{ time}^{-1}$ or $\frac{1}{M \cdot \text{time}}$
Integrated rate law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Relationship of rate constant to slope of straight line:	Slope = $-k$	Slope = $-k$	Slope = k
Plot needed to give a straight line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Half-life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

REACTION MECHANISMS

A mechanism represents the sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products.

1. Must be determined by experiment!
2. Must agree with overall stoichiometry!
3. Must agree with the experimentally determined rate law!

The vocabulary of mechanisms involves **elementary steps** & **molecularity** which describes the number of molecules that participate in an atomic rearrangement. Add these terms into your explanations.

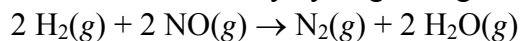
- *unimolecular*: involves one reactant molecule that collides with a solvent or background molecule thereby becoming collisionally activated. In this state the reactant molecule is thermodynamically favorable for converting into product
- *bimolecular*: involves a collision between *two* reactant molecules
- *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 predicted from the stoichiometry of the elementary step as per the table below:*

ELEMENTARY STEP	MOLECULARITY	RATE EXPRESSION
$A \rightarrow \text{products}$	unimolecular	rate = $k[A]$
$A + B \rightarrow \text{products}$	bimolecular	rate = $k[A][B]$
$A + A \rightarrow \text{products}$	bimolecular	rate = $k[A]^2$
$2 A + B \rightarrow \text{products}^*$	termolecular*	rate = $k[A]^2[B]$

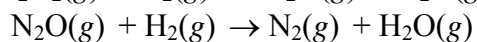
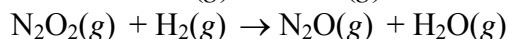
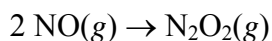
- THE PHYSICAL SIGNIFICANCE OF RATE EXPRESSIONS FOR ELEMENTARY STEPS
 - the more molecules the more collisions, the faster the rate
 - the faster the molecules are moving, the more likely they will collide, the faster the rate
- MOLECULARITY AND ORDER
 - an **elementary step** is a reaction whose rate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

Exercise 9

Nitrogen oxide is reduced by hydrogen to give water and nitrogen,



and one possible mechanism to account for this reaction is



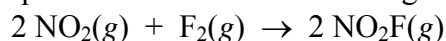
What is the molecularity of each of the three steps? Show that the sum of these elementary steps yields the net reaction.

bimolecular; unimolecular; unimolecular

- REACTION MECHANISMS AND RATE EXPRESSIONS
 - ✓ are determined by experiment and **MUST** agree with the experimentally determined rate law
 - ✓ the slowest step is the **rate determining step**
 - ✓ 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**
 - ✓ **reaction intermediate**--produced in one step but consumed in another
 - ✓ **catalyst**--goes in as a reactant, comes out as an unharmed product and **DOES NOT** show up in the final overall rxn.

Exercise 10

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



The *experimentally* determined rate law is

$$\text{Rate} = k [\text{NO}_2][\text{F}_2]$$

A suggested mechanism for the reaction is

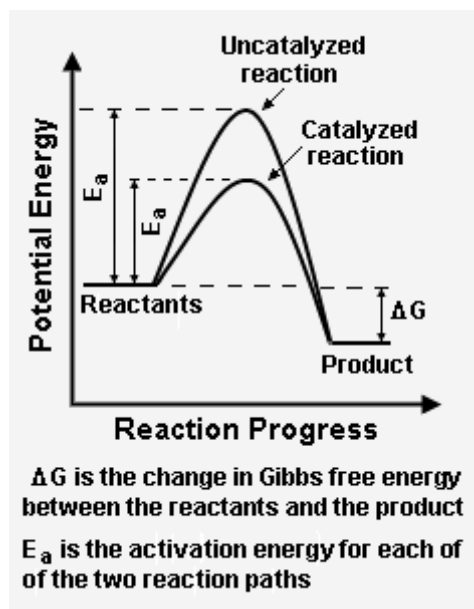
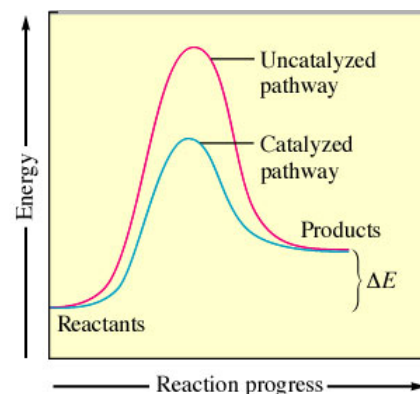


Is this an acceptable mechanism? That is, does it satisfy the two requirements? Justify your answer.

Yes. It is bimolecular in the first step which is the slow step, which yields a rate law expression that agrees with the experimentally determined rate law that was given.

CATALYSIS

Catalysis is the increase in rate of a chemical reaction due to the participation of a substance called a *catalyst*. Unlike other reagents in the chemical reaction, *a catalyst is not consumed*. Catalysts function by lowering the activation energy of an elementary step in a reaction mechanism, and by providing a new and faster reaction mechanism. The effect of a catalyst may vary due to the presence of other substances known as inhibitors (which reduce the catalytic activity) or promoters (which increase the activity). Important classes in catalysis include acid-base catalysis, surface catalysis, and enzyme catalysis.



How do they do their job? They *alter the mechanism* so the activation energy barrier can be lowered, thus *speeding up* the reaction by offering a different pathway for the reaction.

Collisions must be *effective* which is code for having enough “Umph!” or sufficient energy AND for having the correct orientation.

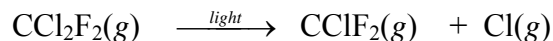
The overall ΔE is NOT changed for the process, BUT the activation energy IS lowered.

Biological catalysts are called *enzymes* which are *proteins with specific shapes*. ATP synthetase is the most important enzyme in the human body! Death occurs when an organism runs out of ATP.

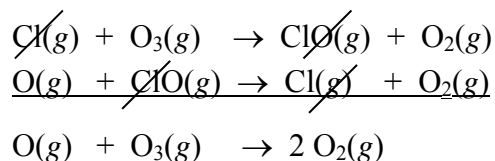
You need to interpret graphs such as the one above left in terms of kinetics and thermodynamics!
You also need to be able to label the REVERSE rxns.

HOMOGENEOUS CATALYSTS—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:



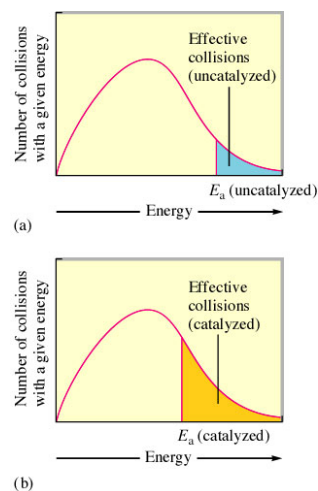
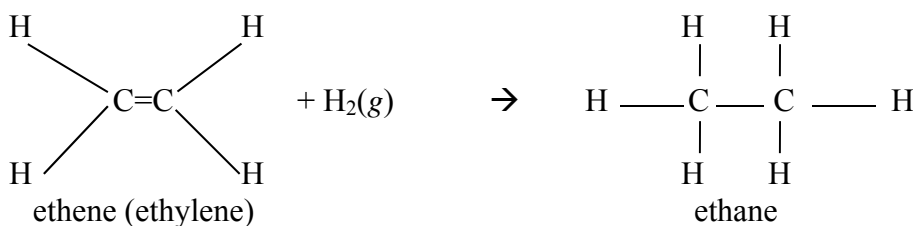
These chlorine atoms can catalyze the decomposition of ozone by forming a new reaction intermediate, thus thinning the atmospheric ozone layer that protects Earth from harmful UV rays :



HETEROGENEOUS CATALYST—exists in a 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] $\text{C}=\text{C}$ bonds are converted into $\text{C}-\text{C}$ bonds by adding a pair of hydrogens “across the double bond”.

A simple example of *hydrogenation* involves ethylene:



Acid-Base Catalysis is an acceleration of a chemical reaction by the addition of an acid or a base, the acid or base itself not being consumed in the reaction. The catalytic reaction may be acid-specific (acid catalysis), as in the case of decomposition of the sugar sucrose into glucose and fructose in sulfuric acid. This is also an example of a *dehydration* reaction.



Mixing sucrose with dilute sulfuric acid in a beaker (a, right) produces a simple solution. Mixing the same amount of sucrose with concentrated sulfuric acid (a, left) results in a dramatic reaction (b) that eventually produces a column of black porous graphite (c) and an intense smell of burning sugar.

Taken from: http://2012books.lardbucket.org/books/general-chemistry-principles-patterns-and-applications-v1.0/section_18_01.html

Wanna see? (You have no idea how bad this smells!) <http://www.youtube.com/watch?v=GzQDdrcJEbE>

The reaction pictured right 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 stabilizing the transition state.

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 contain platinum and 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!

