Public Health Announcement Reminder

How to avoid getting sick...

- Use only your own water bottle
- Don’t let anyone use your water bottle
- Don’t kiss anyone anywhere, anytime
- Wash your hands often

Where have we been and where are we going?

A-Stoichiometry
D-Gases
B-Reactions & Electrochemistry
F-Equilibrium
C-Thermochem /Thermodynamics
E-Kinetics
G-Acid Base Equilibrium
H-Quantum
I-Bonding & Geometry
J-IPFs (InterParticle Forces)

Kinetics: Reaction Rates & Mechanisms

Unit E

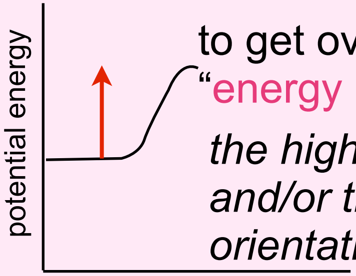
for Exciting!!

So where have we been, where are we now? Where are we going?

- Chemical Reactions
  - ✓ What is reacting, what is produced?
- Stoichiometry
  - ✓ How much of each reactant do we need?
  - ✓ How much of each product is produced?
- Equilibrium
  - ✓ To what extent does a reaction proceed before “stopping?”
- Thermodynamics
  - ✓ Under the conditions does a reaction move forward or reverse? Is a reaction spontaneous?
  - ✓ How do energy and entropy affect the spontaneity?
- Kinetics
  - ✓ How fast does a reaction happen?
  - ✓ What factors affect that rate?

What is Kinetics?

- Study of the rate at which chemical processes occur.
  - ✓ what factors affect the rate and to what degree
- Kinetics will then provide information on the reaction mechanism
  - ✓ exactly *how* the reaction occurs.
- At the nano- level, the rate of the reaction depends on the frequency of collisions.
- However not all collisions are productive, the collision must have
  - ✓ sufficient energy
  - ✓ suitable orientation



to get over the
"energy hump"

the higher the activation energy hump and/or the more complicated the orientation, the slower the reaction.

Which of the following affect reaction rate?

(Select all that apply.)

1. physical state (or phase) of reactants
2. form of the reactants: crushed vs chunky
3. concentration of reactants
4. pressure and/or volume for gases
5. temperature
6. presence of a catalyst
7. None of the above affect reaction rate

Which of the following affect reaction rate? *(Select all that apply.)*

1. physical state (or phase) of reactants
2. form of the reactants: crushed vs chunky
3. concentration of reactants
4. pressure and/or volume for gases
5. temperature
6. presence of a catalyst
7. None of the above affect reaction rate

Physical State: solid, liquid, gas

- In order to react, molecules must collide.

- The quicker the reactants can collide, the faster the reaction can occur.
- Thus gas mixtures or solutions react faster.
- Solids will react more slowly since collisions can not happen with the solid at once - there is a surface to collide with.
- thus surface area of solids matters ..... next slide

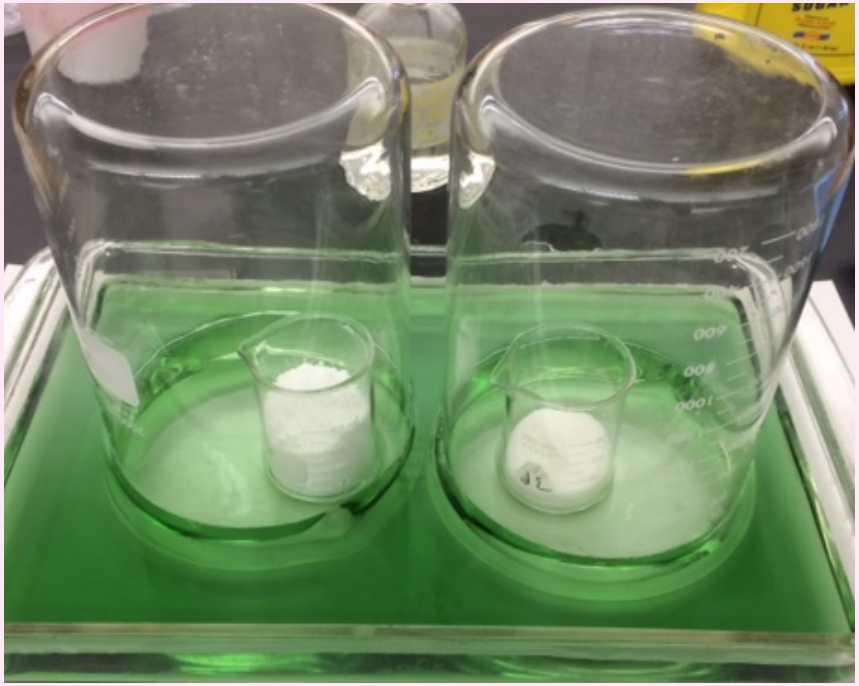
Changing Particle Size

- Particle size demonstrations with corn starch
- Sparks are a huge hazard in dusty grain elevators
- Turn to your mate and make a statement about crushed vs chunky and reaction rate....don't forget to use the word collision.
- "The smaller the particle size and more surface area, the more quickly reactants can come in in contact, making atoms collide more often, which will increase the reaction rate."

Sugar & Sulfuric Acid

- What’s the difference between granulated sugar and confectioner’s sugar?

- Particle size



Just what was that sugar reaction?

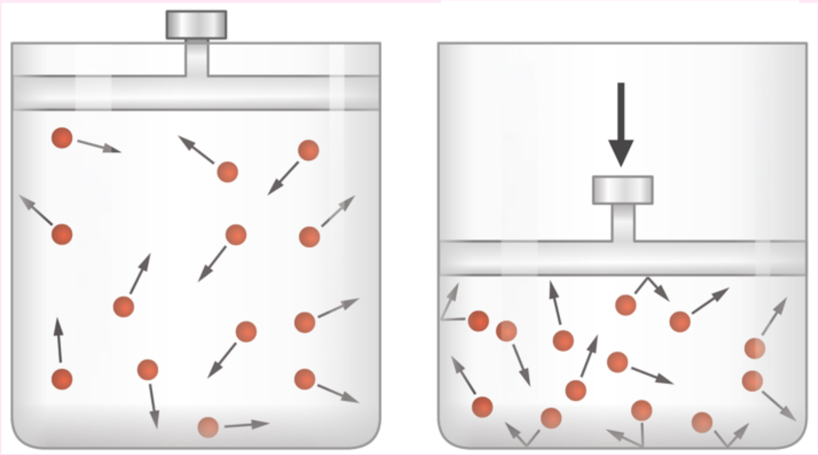
- Sucrose or common table sugar was mixed with concentrated sulfuric acid. Soon an *exothermic* reaction takes places during which a column of carbon rises from the beaker and a cloud of steam is produced. Concentrated sulfuric acid acts as a catalyst to dehydrate sucrose to produce carbon and water. The heat of the reaction vaporizes the water, and the gas causing the column of carbon puff up, just like gases during cooking cause a cake to rise.
- The name carbo*hydrate* derives from the formula of sugars such as sucrose, $C_{12}H_{22}O_{11}$ (notice the 2:1 H:O ratio $C_{12}(H_2O)_{11}$) in which the formula appears to be a hydrate of carbon.
- $C_{12}H_{22}O_{11(s)} \xrightarrow{\text{acid catalyst}} 11H_2O_{(g)} + 12C_{(s)}$

Concentration

- Hydrogen Peroxide, H_2O_2 demo
- Which test tube would have higher concentration?

- Turn to your mate and make a statement about concentration and reaction rate....don’t forget to use the word collision.
- “A higher the concentration, means more atoms, which means atoms collide more often, which will increase the reaction rate.”

Volume & Pressure of Gases



- What happens as we reduce the volume of a gas?
- Yes, pressure increases (holding temperature and # moles constant)

- Turn to your mate and make a statement about gas, volume (pressure) and reaction rate....don't forget to use the word collision.

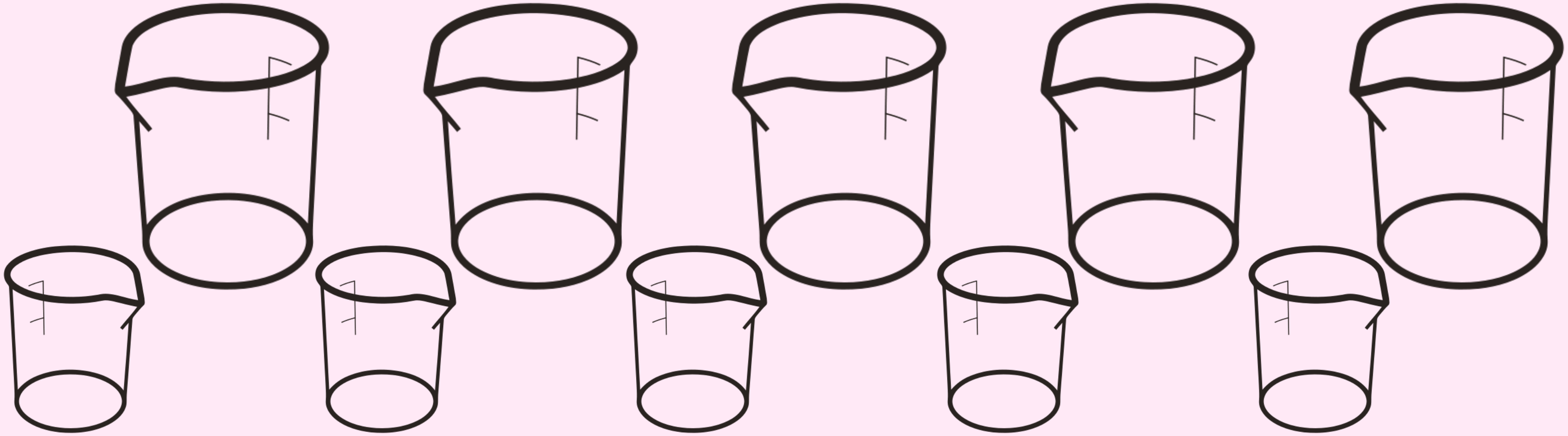
- "Reducing the volume of a gas, will cause the atoms (or molecules) to collide more often, increasing the reaction rate"

More Factors that Affect Rate

- Temperature
  - ✓ At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.
- Presence of a Catalyst
  - ✓ Catalysts speed up reactions by changing the mechanism of the reaction.
  - ✓ Provide the reaction with an allternative pathway.
  - ✓ Catalysts are not consumed during the course of the reaction.

- We’ll take a look at these factors as we proceed in this unit.
- *How can chemists measure rates of reaction?*

The Landolt “Clock Reaction” Method of Timing a Reaction



- Help me.
- I pour, you count; 1, 2, 3, 4, 5
- I pour again, you count; 1, 2, 3, 4, 5
- etc

The Landolt Clock
a very complex set of redox reactions

- $IO_3^- + 3HSO_3^- \rightarrow I^- + 3SO_4^{2-} + 3H^+$ *a slow step that chugs along starting with colorless and producing colorless...*

- $IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O$ *since there is lots of IO_3^- around as the first reaction is chugging along, the IO_3^- has a second option and will quickly react with I^- formed to produce I_3^-…which is yellow.*

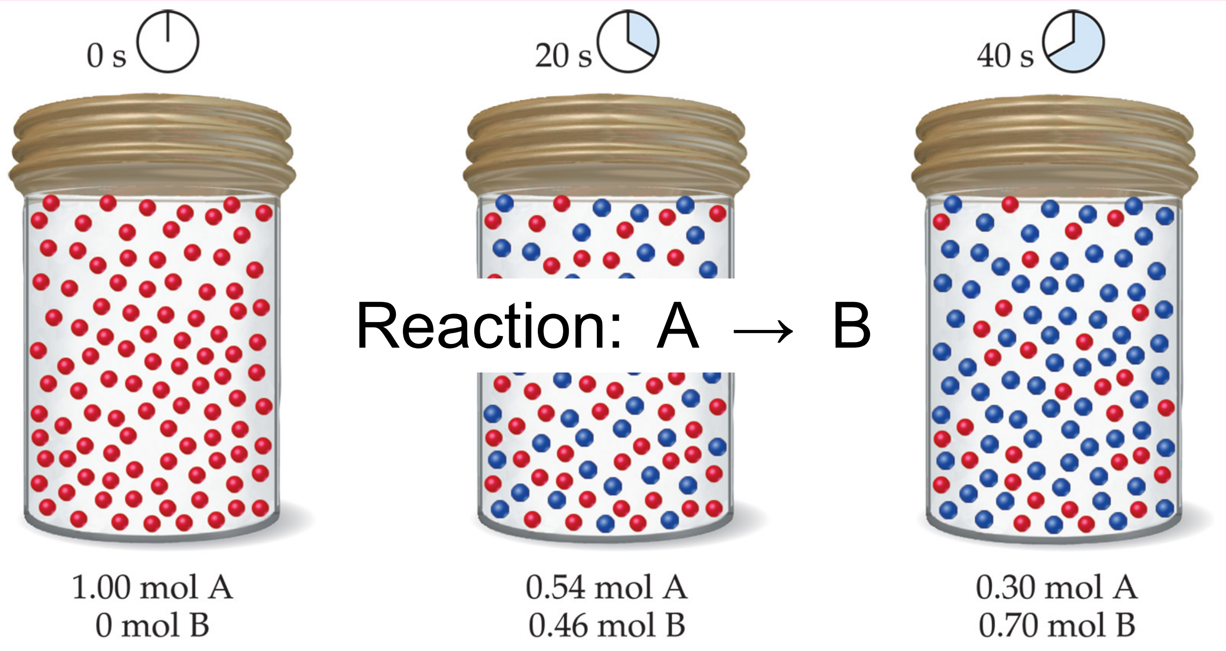
  but as long as there is some HSO_3^- present, while the first reaction is still chugging along, the I_3^- will quickly convert back to I^- because of the presence of HSO_3^-

★ $I_3^- + HSO_3^- + H_2O \rightarrow 3I^- + SO_4^{2-} + 3H^+$ *this is a very this is a fast step and will keep any I_3^- from hanging around until all of the bisulfite ion is completely used up, and then the I_3^- persists, which allows for….*

- $2I_3^- + \text{starch} \leftrightharpoons \text{starch}{-}I_5^- \text{ complex} + I^-$

How Will We Study Reaction Rates?

- Rates of reactions can be determined by monitoring the change in concentration as a function of time
- We can *watch* the decrease of reactants
- Or we can *watch* the increase of products.

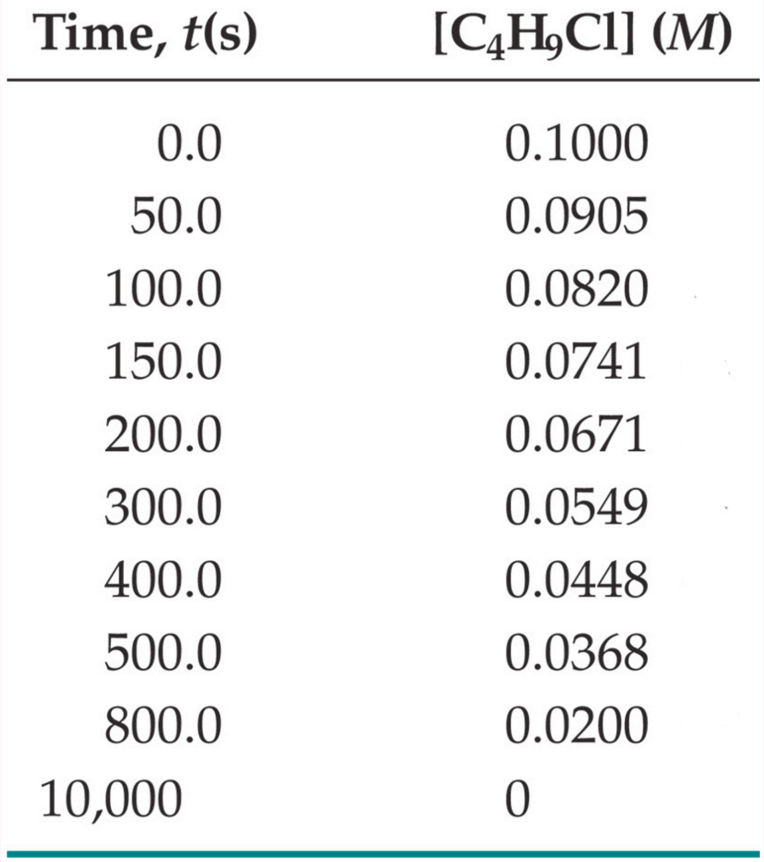


Reaction: A → B

- Any method of measuring relative amounts of reactants and products possible is acceptable.

Understanding the Details

$$C_4H_9Cl_{(aq)} + H_2O_{(L)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$$



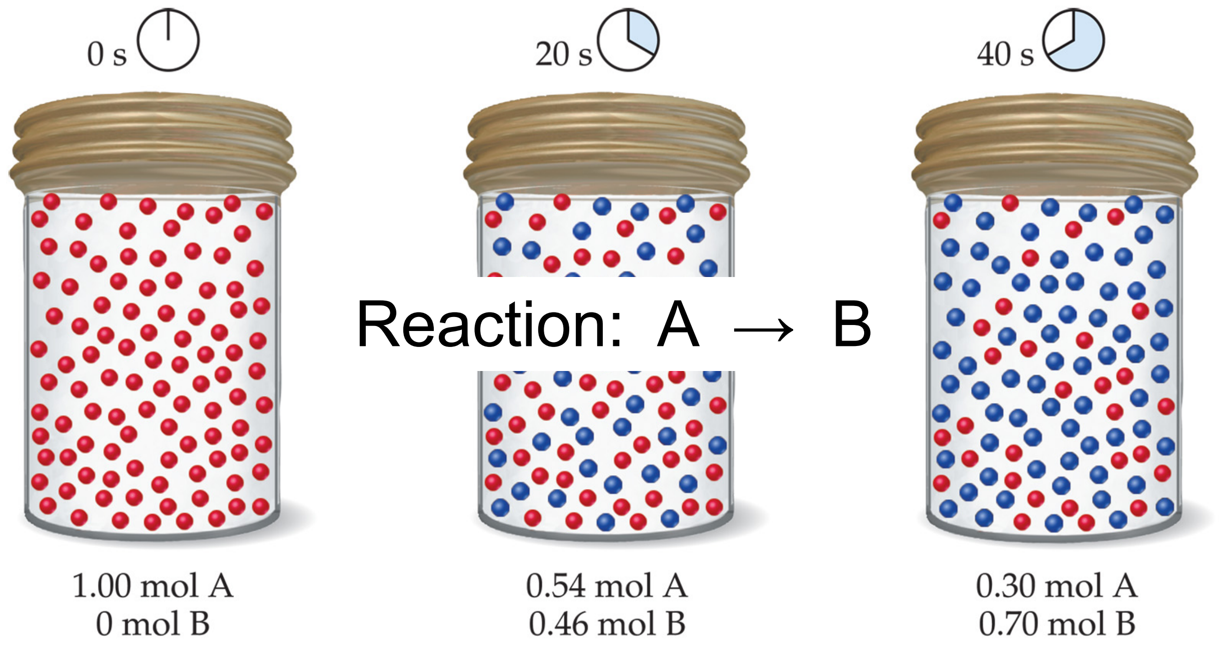
Time, t(s)	[C_4H_9Cl] (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

- The concentration of butyl chloride, C_4H_9Cl, was measured at various times as the reaction was allowed to proceed.
- The square brackets [C_4H_9Cl] mean “the concentration of C_4H_9Cl”
- The substance inside the brackets is measured in M (molarity = moles/L)

- We will usually measure concentration in molarity
- But any concentration units would work.

Measuring the Chemicals

- For gases, if we can measure their partial pressures, the quantities of A and B could be measured in pressure units (any pressure units will do)
  - ✓ 1 atm = 760 mmHg = 760 torr = 101.3 kPa = 14.7 psi
- Measuring pressure of a gas in a sealed container is valid because pressure is directly proportional to the quantity of the gas present.



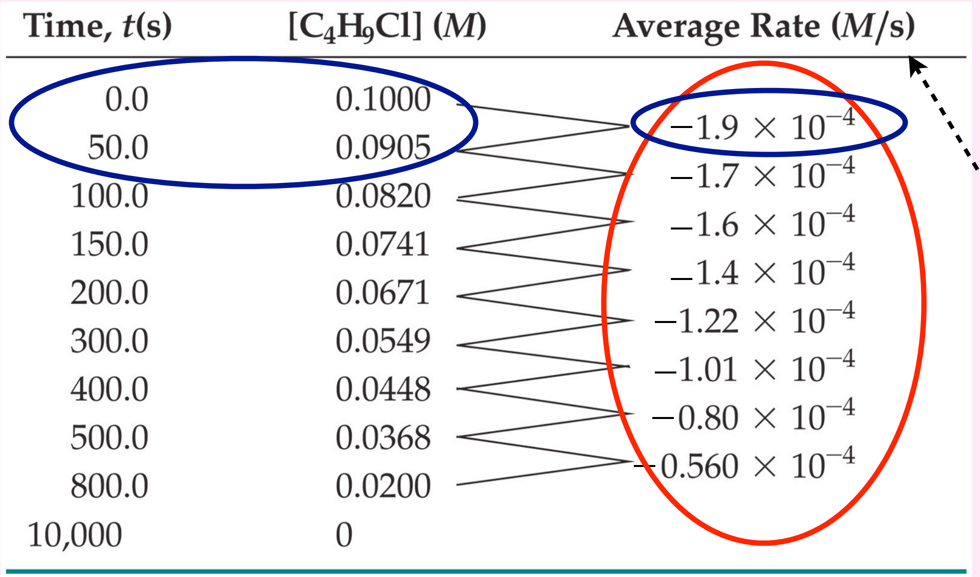
Reaction: A → B

The challenge in kinetics chemistry is finding effective methods of measure either reactants or products during the progress of a reaction.

Average Rate

- $C_4H_9Cl_{(aq)} + H_2O_{(L)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$

Consider this data collected for the reaction above.



Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	-1.9×10^{-4}
50.0	0.0905	-1.7×10^{-4}
100.0	0.0820	-1.6×10^{-4}
150.0	0.0741	-1.4×10^{-4}
200.0	0.0671	-1.22×10^{-4}
300.0	0.0549	-1.01×10^{-4}
400.0	0.0448	-0.80×10^{-4}
500.0	0.0368	-0.560×10^{-4}
800.0	0.0200	
10,000	0	

- What is Average Rate?
- The change in concentration divided by the change in time:
  - ✓ $\frac{[0.0905\,M - 0.1000\,M]}{50\,\text{sec}} = -1.9 \times 10^{-4}\,M/\text{sec}$
  - ✓ check out the units
  - ✓ M/s or mol/L s or mol $L^{-1}s^{-1}$

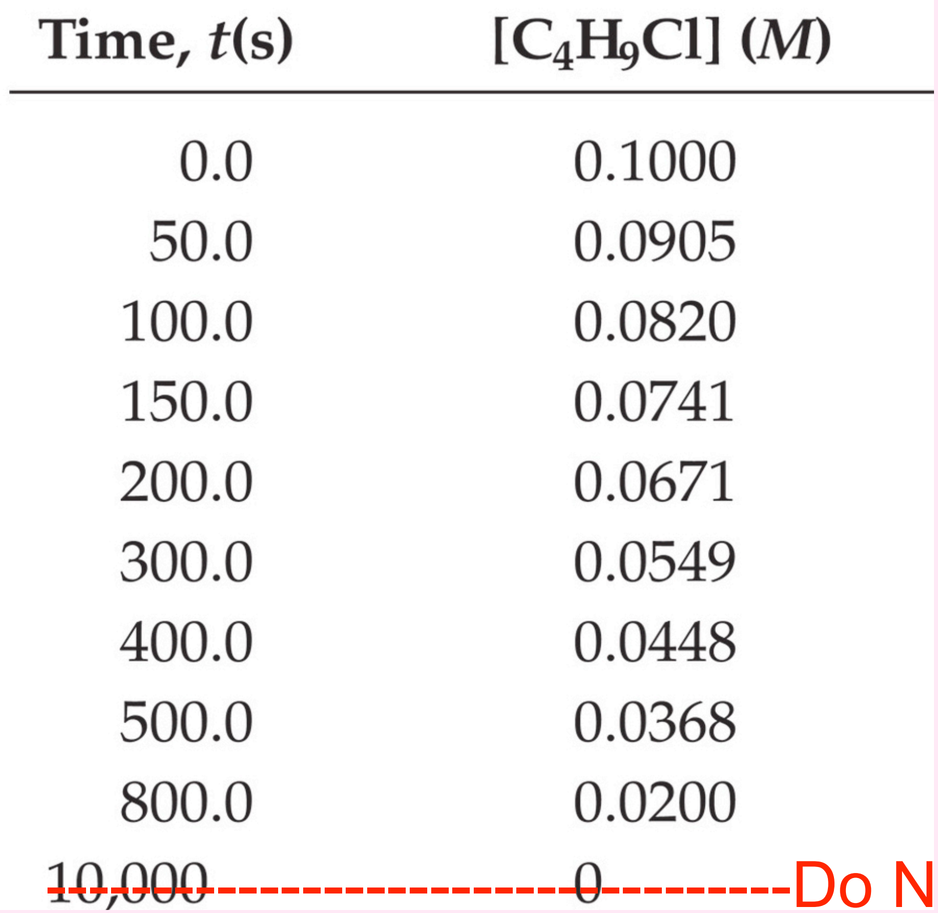
$$Average\ Rate = -\frac{\Delta[C_4H_9Cl]}{\Delta time}$$

- Note that the average rate decreases as the reaction proceeds.
- Why?

- As the reaction goes forward, there will be fewer collisions between reactant molecules.

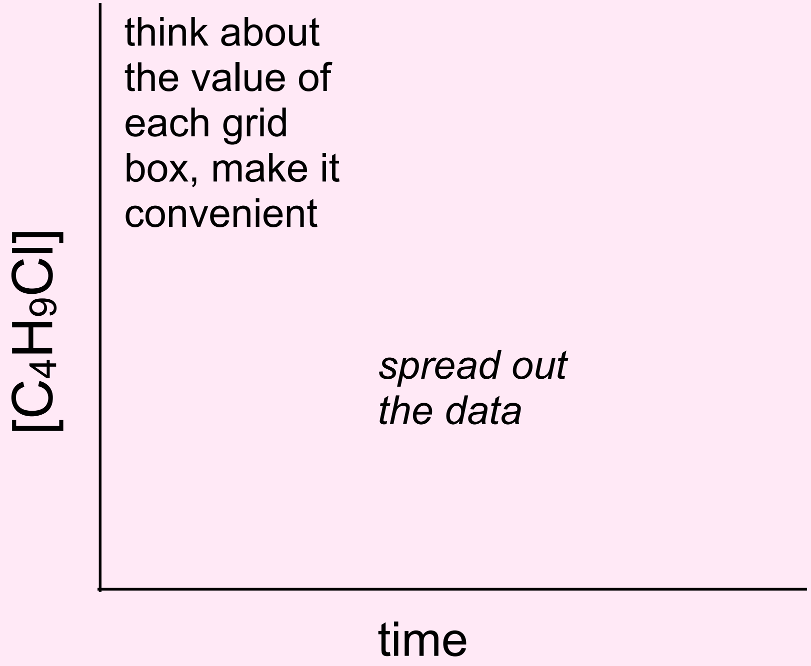
Concentration vs Time Plots

- $C_4H_9Cl_{(aq)} + H_2O_{(L)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$



Time, t(s)	$[C_4H_9Cl]$ (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
~~10,000~~	~~0~~

Do NOT include this data



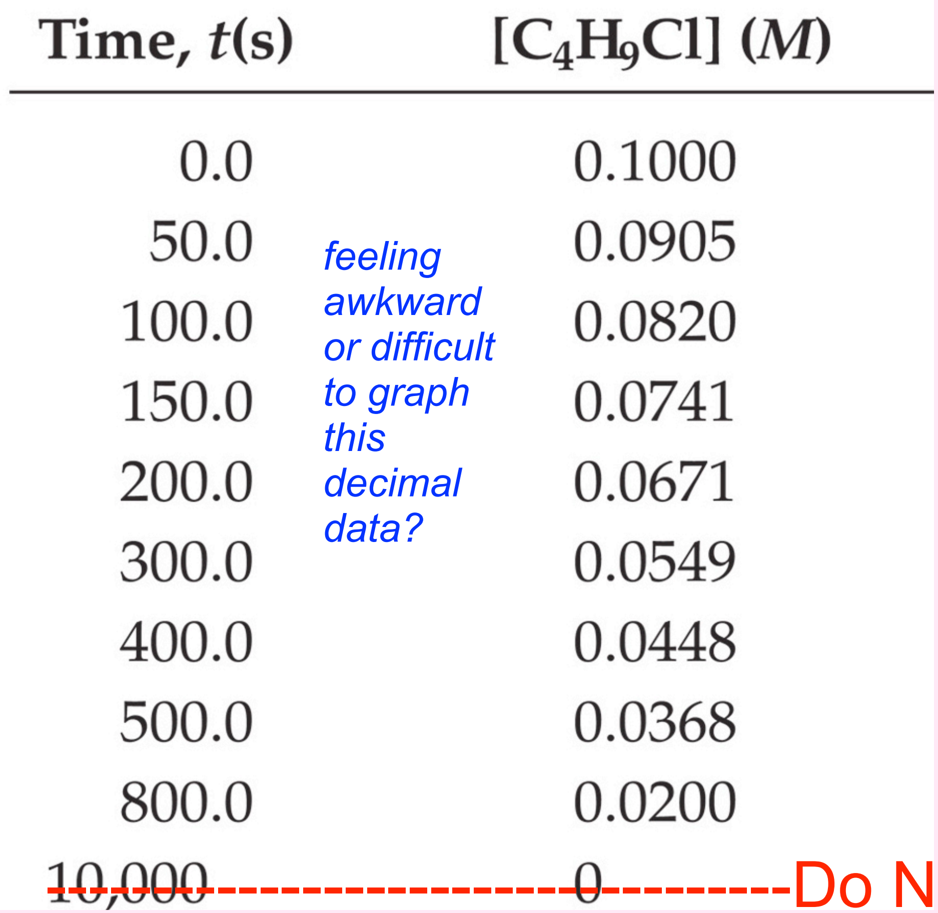
think about the value of each grid box, make it convenient

spread out the data

- Let's sketch the graph of Concentration vs Time

Concentration vs Time Plots

- $C_4H_9Cl_{(aq)} + H_2O_{(L)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$



Time, t(s)	$[C_4H_9Cl]$ (M)
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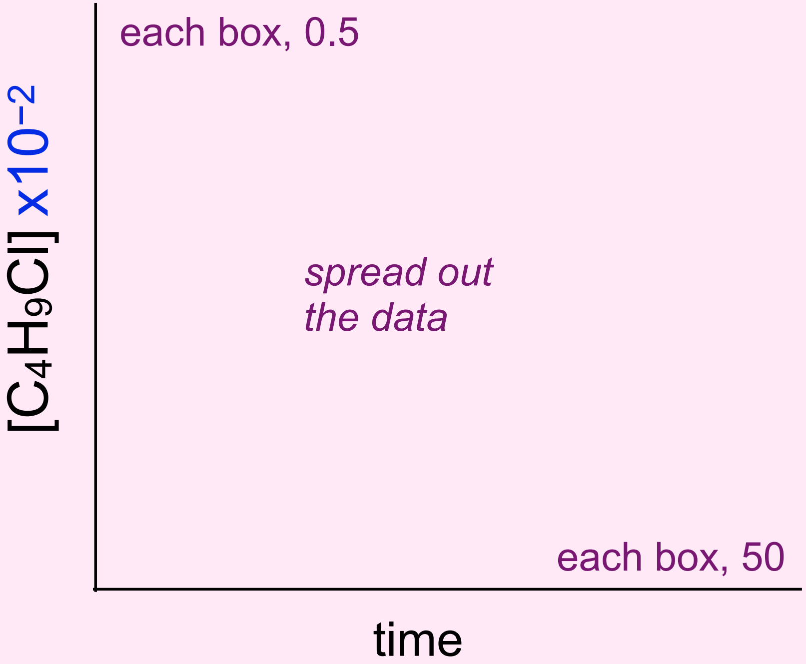
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
~~10,000~~	~~0~~

feeling awkward or difficult to graph this decimal data?

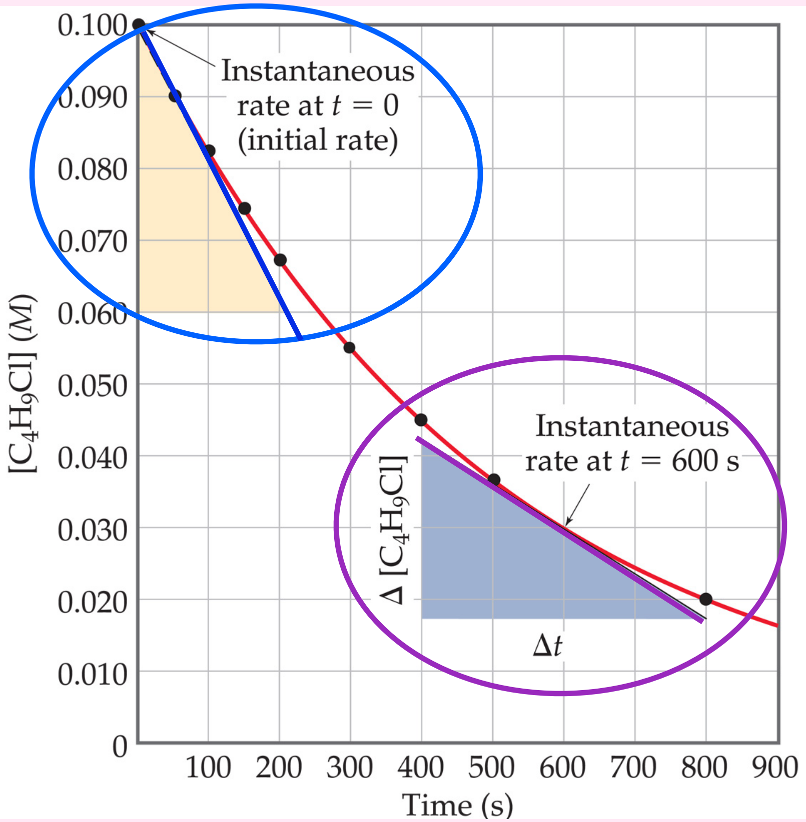
Do NOT include this data



- Let’s sketch the graph of Concentration vs Time

Instantaneous Rates

$C_4H_9Cl_{(aq)} + H_2O_{(L)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$



- A plot of concentration vs. time for the data on the previous slide yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.
  - ✓ Slope $t = 0$ is -1.9 x 10^{-4} M/s
  - ✓ Slope at $t = 600$ is -6.2 x 10^{-5} M/s
- All reactions slow down over time.

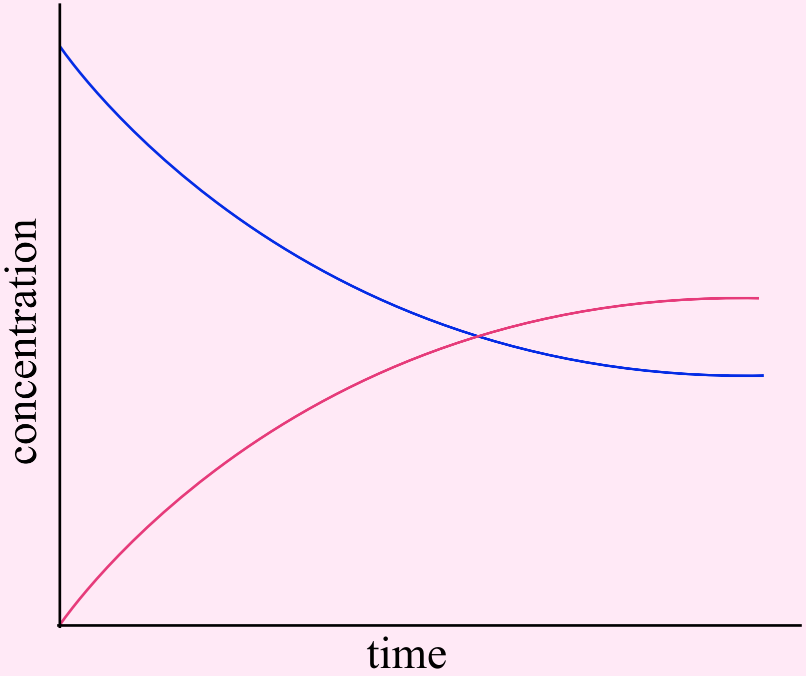
- The tangent line is less steep at a later time.
- Therefore, the best indicator of the “rate” of a reaction is the instantaneous rate near the beginning.

Rate: Instantaneous vs Average

- Imagine your drive to school is 6 miles in 15 minutes
  - ✓ Your average rate would be 24 mi/hr
  - ✓ Your instantaneous rate would be whatever the speedometer might read at any given moment which could be 0, 15, 24, 50, or anything else.
- When a chemist says "rate" they mean instantaneous rate unless otherwise indicated.
- The rate at $t = 0$, the moment the reaction starts is called the initial rate, and this is an instantaneous rate, and it is the rate that is most useful for chemists to measure.
- Of course you can't really measure at $t = 0$, so chemists measure for a short time, and use that as the initial instantaneous rate.

Reaction Rate and Stoichiometry

- $C_4H_9Cl_{(aq)} + H_2O_{(L)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$

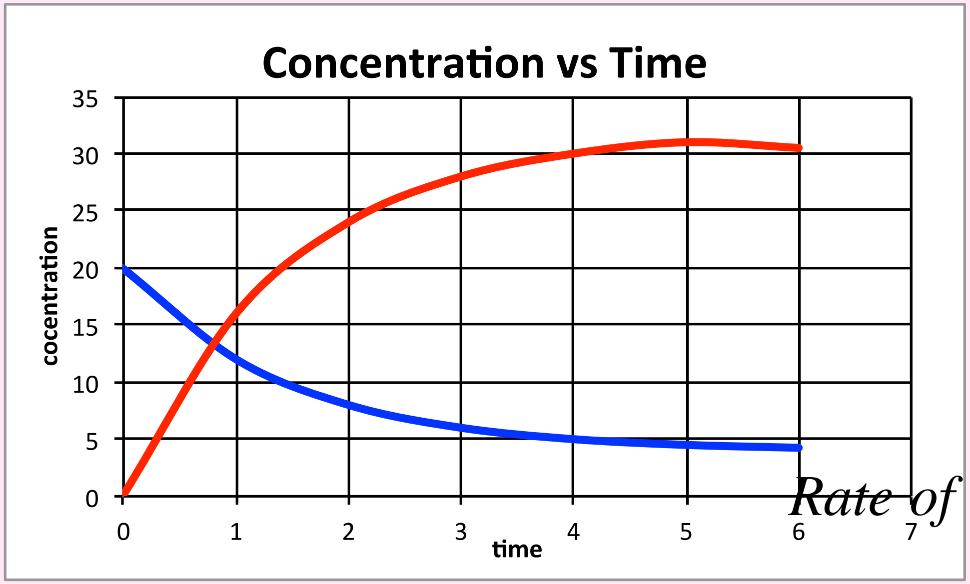


- Thus, the rate of disappearance of C_4H_9Cl
- is the same, though represented as opposite in sign, as the rate of appearance of C_4H_9OH.

$$Rate = -\frac{\Delta[C_4H_9Cl]}{\Delta time} = \frac{\Delta[C_4H_9OH]}{\Delta time}$$

What if the stoichiometry is not 1:1 ??

- $H_{2(g)} + I_{2(g)} \rightarrow 2\ HI_{(g)}$
- The rate of the change in concentration of the products (gaining products = +)
- is stoichiometrically related to the change in concentration of the reactants (losing them −)
- Check out the graph



Since HI rate is twice H_2 and I_2, to set the rates equal to each other, and to get a “generic” rate of reaction, we “normalize” the rates by dividing each rate by it’s stoichiometry. cut HI in half to match the rate of the H_2 and I_2.

$$Rate\ of\ Rxn = \frac{1}{2}\frac{\Delta[HI]}{\Delta time} = -\frac{\Delta[H_2]}{\Delta time} = -\frac{\Delta[I_2]}{\Delta time}$$

Let's Generalize the Stoichiometry

- For: $a\,A + b\,B \rightarrow c\,C + d\,D$
- The rate of formation and depletion can be "normalized" and compared as a single rate, which we might call the "rate of the reaction."

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

- Reactants are assigned a negative sign, since they are being depleted
- Products are positive, since they are increasing.

The reaction $3O_2 \rightarrow 2O_3$ is proceeding with a rate of change of O_2 equal to −0.60 M/s. What is the rate of change of O_3?

No calculator

1. 0.60 M/s
2. 0.90 M/s
3. 0.40 M/s
4. 1.20 M/s
5. -0.60 M/s
6. -0.90 M/s
7. -0.40 M/s
8. -1.20 M/s

The reaction $3O_2 \rightarrow 2O_3$ is proceeding with a rate of change of O_2 equal to -0.60 M/s. What is the rate of change of O_3?

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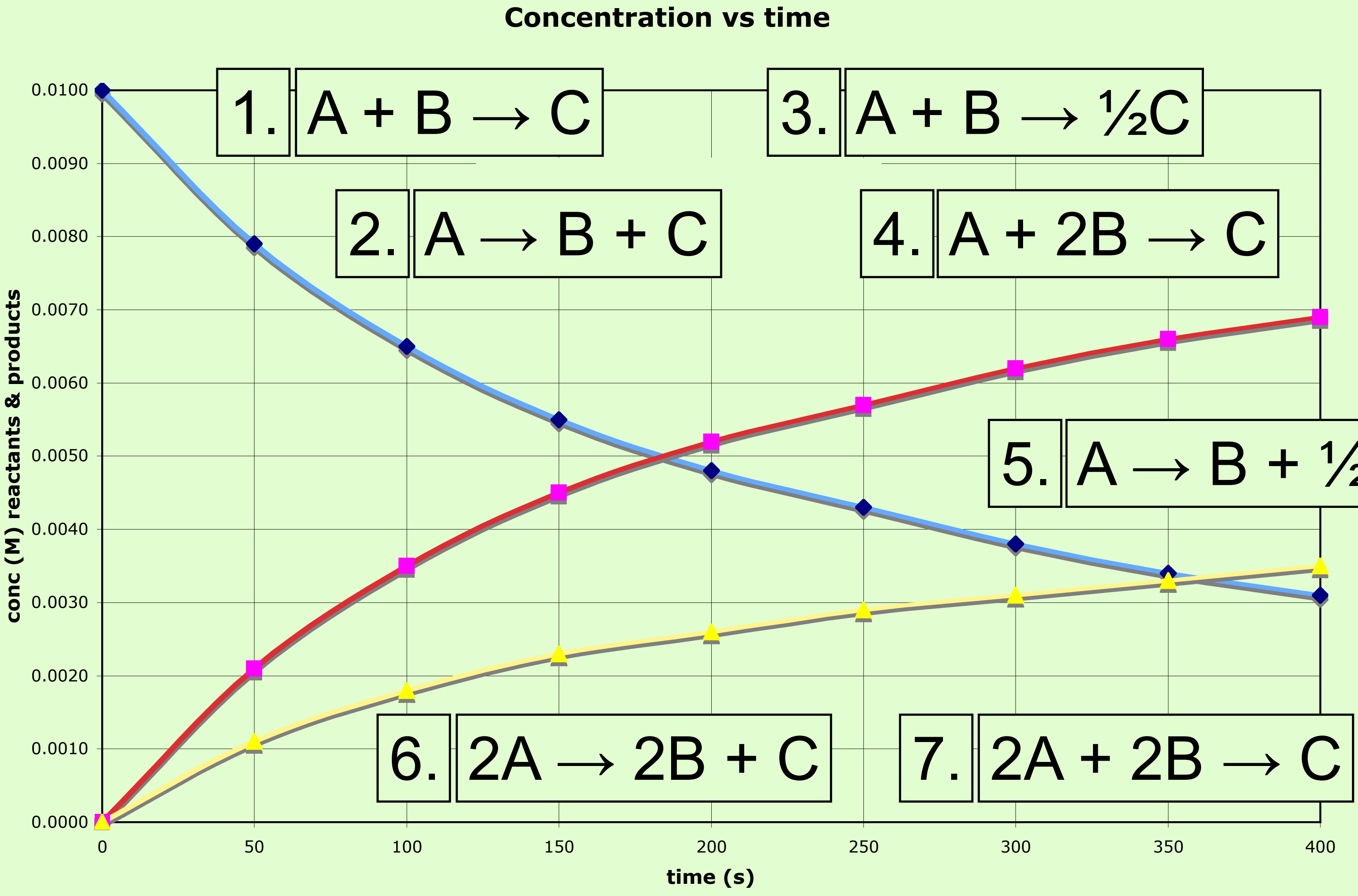
3. 0.40 M/s
4. 1.20 M/s
5. -0.60 M/s
6. -0.90 M/s
7. -0.40 M/s
8. -1.20 M/s

$$-0.60\,Ms^{-1}\frac{2O_3}{3O_2}$$

Each letter represents a reactant or product (A, B, C). Each line follows the changing concentration of a single reactant or product. Which of the following balanced equations could represent a reaction represented by the three lines on kinetics graph below.



1. $A + B \rightarrow C$

2. $A \rightarrow B + C$

3. $A + B \rightarrow \frac{1}{2}C$

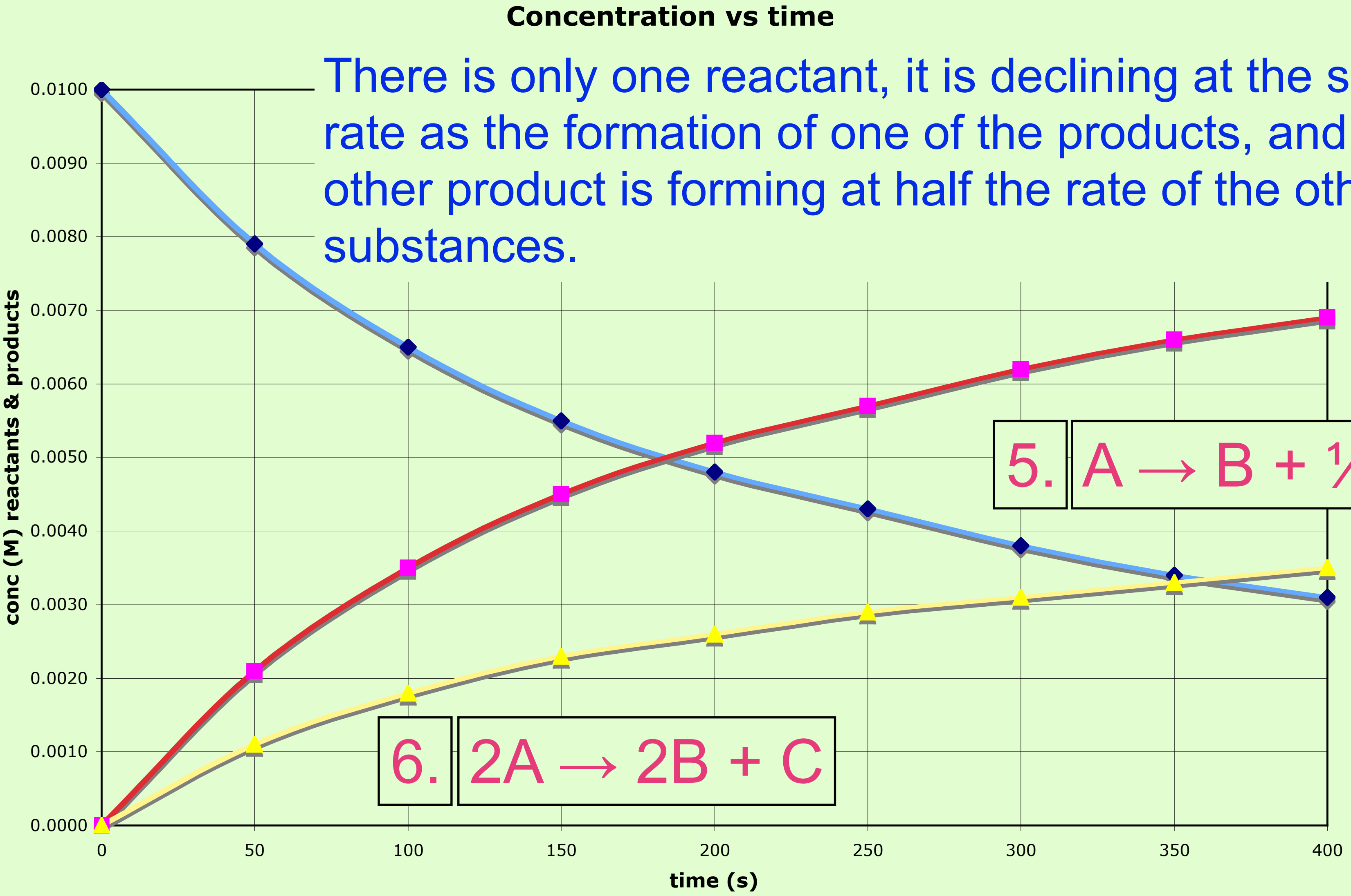
4. $A + 2B \rightarrow C$

5. $A \rightarrow B + \frac{1}{2}C$

6. $2A \rightarrow 2B + C$

7. $2A + 2B \rightarrow C$

Using generic letters (A, B, C), which of the following balanced equations could represent a reaction represented by the kinetics graph below.



There is only one reactant, it is declining at the same rate as the formation of one of the products, and the other product is forming at half the rate of the other two substances.

5. A → B + ½C

6. 2A → 2B + C

Reaction Rate and Concentration

(instantaneous rate)

- $Br_{2(g)} + 2\ NO_{(g)} \rightarrow 2\ NOBr_{(g)}$
- Comparing reaction rates with concentrations gives us information about the reactions.
- When comparing exp 1 & 2
  - ✓doubling the conc of Br_2 , while holding NO constant
  - ✓doubles the initial rate.

Trial 1	$[Br_2]_0$	$[NO]_0$	Initial Rate M/sec
1	0.1	0.1	1.4×10^{-7}
2	0.2	0.1	2.8×10^{-7}
3	0.4	0.1	5.7×10^{-7}
4	0.2	0.2	11.2×10^{-7}
5	0.2	0.4	44.8×10^{-7}
6	0.2	0.8	179×10^{-7}

Reaction Rate and Concentration

- $Br_{2(g)} + 2\ NO_{(g)} \rightarrow 2\ NOBr_{(g)}$
- Likewise, when comparing exp 4 & 5
  - ✓ doubling the conc of NO
  - ✓ quadrupled the reaction rate.
- And when comparing exp 5 & 6
  - ✓ increase the conc of NO by 3
  - ✓ increases the reaction rate by 9

Trial 1	$[Br_2]_0$	$[NO]_0$	Initial Rate M/sec
1	0.1	0.1	1.4×10^{-7}
2	0.2	0.1	2.8×10^{-7}
3	0.4	0.1	5.7×10^{-7}
4	0.2	0.2	11.2×10^{-7}
5	0.2	0.4	44.8×10^{-7}
6	0.2	1.2	403×10^{-7}

Rate Law

- The data we just looked at tells us
  - ✓ Rate $\propto [Br_2]$ and Rate $\propto [NO]^2$
- So we can write: rate $\propto [Br_2]\,[NO]^2$
- but who likes proportions...we'd like an equality, so we need a proportionality constant, k since...

Trial 1 data
$[.1][.1]^2 \neq 1.4\text{x}10^{-7}$

- so we rewrite: $\boxed{\text{Rate} = k\,[Br_2]\;[NO]^2}$
- This equation is called the rate law, *k* is the rate constant, and the exponents are the reaction orders.
  - ✓ first order with respect to Br_2
  - ✓ second order with respect to NO
  - ✓ The overall reaction order can be found by adding the exponents on the reactants in the rate law.
  - ✓ Thus we say, this reaction is (1+2) third−order overall.

A reaction has the rate law: rate = k [A] [B]^2 What is the overall order of the reaction?

1. first
2. second
3. third
4. fourth
5. impossible to determine without rate data or concentration vs time graphs.

A reaction has the rate law: rate = k [A] [B]^2 What is the overall order of the reaction?

1. first
2. second
3. third
4. fourth
5. impossible to determine without rate data or concentration vs time graphs.

- Simply add the exponents

Determining Rate Laws

Using Concentration & Rate Data
“Table Logic”

Working with Rate & Concentration Data

- Let's practice determining the order of reactions with respect to each reactant
- Writing the rate law
- Calculating the rate constant
- Determining the units on k

Break out Practice E1

Practice E.1 Determining the *order* $rate = k[A]_o^x[B]_o^y$

- For reaction A + B → C
- Let's compare two trials to see how the rate changes when concentration changes.

trial	$[A]_0$ (mol/L)	$[B]_0$ (mol/L)	Initial Rate (mole/L hour)
1	4	6	20
2	4	3	10
3	2	6	5

- Set up a ratio of the rate law of one trial to a second trial − Select carefully. *Hold one reactant constant, and larger numbers on top.*

$$\frac{rate1 = k[A]_o^x[B]_o^y}{rate2 = k[A]_o^x[B]_o^y} \qquad \frac{20}{10} = \left[\frac{4}{4}\right]^x \left[\frac{6}{3}\right]^y \qquad 2 = [2]^y \qquad \mathrm{y} = 1$$

- y = 1 tells us, first order with respect to B.

- Compare another set of trials to test for the order of A.

$$\frac{rate1 = k[A]_o^x[B]_o^y}{rate3 = k[A]_o^x[B]_o^y} \qquad \frac{20}{5} = \left[\frac{4}{2}\right]^x \left[\frac{6}{6}\right]^1 \qquad 4 = [2]^x \qquad \mathrm{x} = 2$$

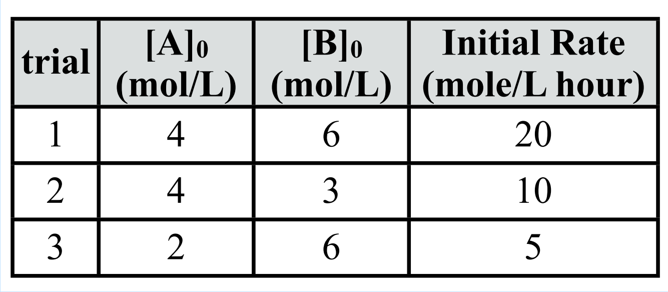
- x = 2 tells us second order with respect to A.

Practice E.1 Determining the *rate constant*

- Now that we know the order with respect to each reactant, we can write the rate law.

$$rate = k[A]^2[B]^1$$

- Choose any single set of data and insert values into the rate law to determine the rate constant.



trial	$[A]_0$ (mol/L)	$[B]_0$ (mol/L)	Initial Rate (mole/L hour)
1	4	6	20
2	4	3	10
3	2	6	5

$$20 = k[4]^2[6]^1 \qquad k = \frac{20}{16 \times 6} \qquad k = 2.7 \times 10^{-4}$$

- Units?
  - ✓ Since reaction is 3rd order overall, units must be reciprocal time and reciprocal Molarity^2.

$$\frac{M}{hour} = \frac{1}{M^2 hour}[M]^2[M]^1 \qquad k = 2.7 \times 10^{-4}\, L^2 mol^{-2} hour^{-1}$$

Break out Practice E.1

- Let’s try #’s 1 & 2
- remember…orders will appear more obvious if you set the ratio with the larger values on top of the smaller values.
- What to do if one reactant is never held constant - as is the case with #2 ?
  - ✓ determine the order for reactant that you can
  - ✓ then that reactant won’t cancel out when you set up your ratio, but you can use algebra to move it to the other side of the equation and solve as you otherwise would.

P E.1 Let's compare the rate law with the reaction stoichiometry

1. $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O_{(L)}$ $\text{rate} = k\,[NH_4^+]\,[NO_2^-]$
2. $I^- + OCl^- \rightarrow IO^- + Cl^-$ $\text{rate} = k\,[I^-]\,[OCl^-]$

- After the first two problems, you might think that the order of the reaction can be determined by the stoichiometry of the overall reaction.

- Unfortunately, the stoichiometry of the overall equation does always indicate the order of the reaction....let's continue with more….

Continue with Practice E.1

- and now move on to #’s 3, 4 & 5

P E.1 Let's compare the rate law with the reaction stoichiometry

1. $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O_{(L)}$ $\quad$ rate = k $[NH_4^+][NO_2^-]$
2. $I^- + OCl^- \rightarrow IO^- + Cl^-$ $\quad$ rate = k $[I^-][OCl^-]$
3. $2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$ $\quad$ rate = k $[ClO_2]^2[OH^-]$
4. $BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$ $\quad$ rate = k $[BrO_3^-][Br^-][H^+]^2$
5. $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$ $\quad$ rate = k $[NO]^2[Cl_2]$
6. $2\,NO + 2\,H_2 \rightarrow N_2 + 2H_2O$ $\quad$ rate = k $[NO]^2[H_2]$

- We can not predict rate laws from the stoichiometry of the overall equation.
- *Experimental data must be used.*

Algebra 2 Public Announcement

Handy Log Rule

(to help with challenge probs 11-14 and LAD E1 Process Data Parts 4 & 5)

- rate = $[A]^m$
- log both sides: log(rate) = $\log([A]^m)$
  - ✓ $\log([A]^m)$ => $m\log[A]$
  - ✓ log(rate) = $m\log[A]$ solve for *m* $\frac{\log(rate)}{\log[A]} = m$
- If the calculating the order from [conc] vs rate data, doesn't seem easily obvious (zero, first , or second order) we can use handy log rules to help us determine the order of the reaction.

Determining

Units on Rate Constants

The unit canceling game.

IMHO this is a silly excercise, but this concept could be worth 1 or 2 points on your AP exam.

I personally think we should just say the units are whatever they need to be, and leave it at that.

Since I am not in charge of the AP exam, so in the hopes of scraping out a couple of extra points, let's take a few minutes to learn to play the rate constant units game!

Units on Rates

- The units of rate will always be amount per time
- You already know this….

✓ rate of driving your car $\frac{miles}{hour}$

✓ rate of your heart $\frac{beats}{minute}$

✓ In this course, we will usually use $\frac{concentration}{time}$

$\frac{molarity}{minute}$ $\frac{molarity}{second}$ $\frac{molarity}{hour}$

$M^{-2}time^{-1}$

Units of the Rate Constant (3rd order)

- The units on the rate constant are whatever they need to be to cancel with the molarity units in the rate law to end up with rate units.
  - ✓ $\frac{M}{time}$ or $\frac{mol}{L \bullet time}$ or $mol\ L^{-1}\ time^{-1}$
- For a third order overll rate law, what need be the units on k to cancel with the molarity units to give appropriate rate units?
  - ✓ $\frac{M}{time} = k[M][M]^2$
  - ✓ Thus *k* units must be $\frac{M}{time} = \frac{1}{M^2 time}[M][M]^2$
  - ✓ which can be written in many variations!

$$\frac{1}{M^2 time} \qquad M^{-2}time^{-1} \qquad \frac{1}{\left(\frac{mol}{L}\right)^2 \bullet time} \qquad \frac{L^2}{mol^2 \bullet time} \qquad L^2\ mol^{-2}time^{-1}$$

- The molarity units will have one exponent less than the overall order.

Units of the Rate Constant for 2nd Order

- Rate = *k* [A] [B] $\frac{M}{time} = k[M][M]$

- For the hypothetical rate law above, what are the units on k ?

  - ✓ Thus *k* units must be $\frac{M}{time} = \frac{1}{M \bullet time}[M][M]$

  - ✓ & many variations!

$$\frac{1}{M \bullet time} \qquad M^{-1}time^{-1} \qquad \frac{1}{\frac{mol}{L} \bullet time} \qquad \frac{L}{mol \bullet time} \qquad L\ mol^{-1}time^{-1}$$

- Again, the molarity units are one less than the overall order of the reaction.

What could be the units for the rate constant for a reaction that is first order overall?

(Select all that apply.)

1. s^{-1}
2. M/s
3. L mol^{-1} s^{-1}
4. $M^{-2}s^{-1}$
5. $M^{-1}s^{-1}$
6. s/M
7. L/(mol s)
8. 1/days
9. L^2 mol^{-2} s^{-1}

A → products

$$rate = k\left[A\right]$$

What are the units for the rate constant for a reaction that is first order overall?

(Select all that apply.)

1. s^{-1}
2. M/s
3. L mol^{-1} s^{-1}
4. $M^{-2}s^{-1}$
5. $M^{-1}s^{-1}$
6. s/M
7. L/(mol s)
8. 1/days
9. L^2 mol^{-2} s^{-1}

A → products

$$\frac{M}{time} = \frac{1}{time}\left[M\right]$$

What are the units for the rate constant for a reaction that is zero order with respect to Y? *(Select all that apply.)*

$Y \rightarrow$ products

1. s^{-1}
2. $L^0\ mol^0\ s^{-1}$
3. M/s
4. $L\ mol^{-1}\ s^{-1}$
5. Ms^{-1}
6. $M^{-1}s^{-1}$
7. s/M
8. L/(mol s)
9. $mol\ L^{-1}\ s^{-1}$

At this point in time, it may be hard to understand how a reaction can be zero order.

Hold on....we'll get to that later in this unit.

What are the units for the rate constant for a reaction that is zero order with respect to Y? *(Select all that apply.)*

Y → products

1. s^{-1}
2. $L^0\ mol^0\ s^{-1}$
3. M/s
4. $L\ mol^{-1}\ s^{-1}$
5. Ms^{-1}
6. $M^{-1}s^{-1}$
7. s/M
8. L/(mol s)
9. $mol\ L^{-1}\ s^{-1}$

- The units on rate are: M/time = k[M]
- The k must always have a 1/time unit *and* with zero order overall, there is no concentration unit thus the rate constant must provide what is needed for the resulting rate unit.

LAD E1

Determining Rate Laws

Using Concentration & Rate Data

“Table Logic”

LAD E.1 Decomposition of H_2O_2 Collecting concentration and rate data

- Let stop and do “Elephant Toothpaste.”

  https://youtu.be/p1eG2y2mn54?t=2m58s

- Write the reaction for the decomposition of hydrogen peroxide.

LAD E.1 Decomposition of H_2O_2 Collecting concentration and rate data

- $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$
  - ✓ Bubbles will form
- We can measure the formation of bubbles as a measure of the amount of O_2 gas being formed.
- Check out the clever apparatus for measuring bubbles.

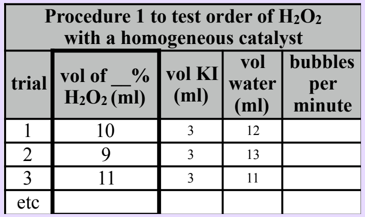
Let’s test it out...

- Communicate with a nearby group about something you will vary that will make your trial different than theirs.
  - ✓ add different amounts of water to vary the concentration of H_2O_2
  - ✓ Use different quantities of KI to vary the catalyst
  - ✓ Compare solid MnO_2 vs KI
- We will not test temperature

LAD E.1 Decomposition of H_2O_2

Collecting concentration and rate data

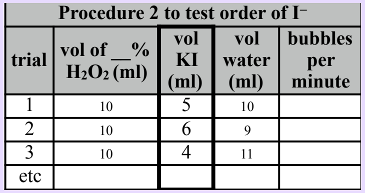
1. Varying H_2O_2 while holding catalyst KI constant to determine the order with respect to H_2O_2.



Procedure 1 to test order of H_2O_2 with a homogeneous catalyst

trial	vol of __% H_2O_2 (ml)	vol KI (ml)	vol water (ml)	bubbles per minute
1	10	3	12	
2	9	3	13	
3	11	3	11	
etc				

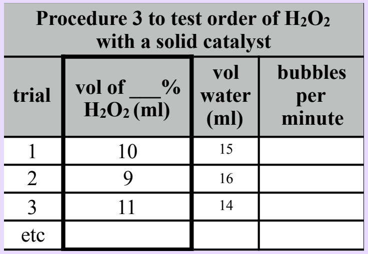
2. Varying catalyst I^- while holding H_2O_2 constant to determine the order with respect to I^-



Procedure 2 to test order of I^-

trial	vol of __% H_2O_2 (ml)	vol KI (ml)	vol water (ml)	bubbles per minute
1	10	5	10	
2	10	6	9	
3	10	4	11	
etc				

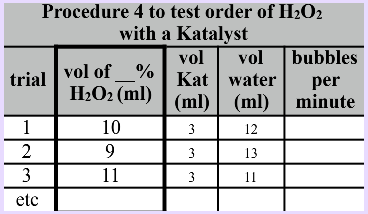
3. Varying H_2O_2 using the same solid catalyst to determine the order with respect to H_2O_2.



Procedure 3 to test order of H_2O_2 with a solid catalyst

trial	vol of ___% H_2O_2 (ml)	vol water (ml)	bubbles per minute
1	10	15	
2	9	16	
3	11	14	
etc			

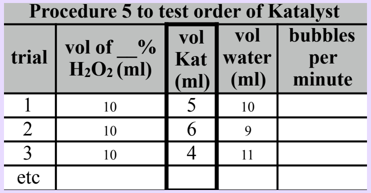
4. Varying H_2O_2 while holding catalyst “Kat” constant to determine the order with respect to H_2O_2.



Procedure 4 to test order of H_2O_2 with a Katalyst

trial	vol of __% H_2O_2 (ml)	vol Kat (ml)	vol water (ml)	bubbles per minute
1	10	3	12	
2	9	3	13	
3	11	3	11	
etc				

5. Varying catalyst “Kat” while holding H_2O_2 constant to determine the order with respect to “Kat.”



Procedure 5 to test order of Katalyst

trial	vol of __% H_2O_2 (ml)	vol Kat (ml)	vol water (ml)	bubbles per minute
1	10	5	10	
2	10	6	9	
3	10	4	11	
etc				

Algebra 2 Public Announcement

Handy Log Rule

(to help with LAD E1 Process Data Parts 4 & 5)

- rate = $[A]^m$
- log both sides: log(rate) = $\log([A]^m)$
  - ✓ $\log([A]^m)$ => $m\log[A]$
  - ✓ log(rate) = $m\log[A]$ solve for *m* $\frac{\log(rate)}{\log[A]} = m$
- If the calculating the order from [conc] vs rate data, doesn't seem easily obvious (zero, first , or second order) we can use handy log rules to help us determine the order of the reaction.

Using Handy Log Rules with Rate Data

if the order of the reaction is not so obvious

Trial	$[X]_o$	$[Y]_o$	rate
1	3.5	6.1	26
2	2.6	6.1	19.3
3	3.5	10.1	71.4

- Chose to determine order of [X]

$$\frac{\#1}{\#2}\frac{26}{19.3}=\left[\frac{3.5}{2.6}\right]^x\left[\frac{6.1}{6.1}\right]^y \quad 1.35=\left[1.35\right]^x \quad x=1$$

- Chose to determine order of [Y]

$$\frac{\#3}{\#1}\frac{71.4}{26.0}=\left[\frac{3.5}{3.5}\right]^1\left[\frac{10.1}{6.1}\right]^y \quad 2.75=\left[1.66\right]^y \quad y=?$$

- Not so obvious? Log both sides

$$\log[RateRatio]=\log[ConcRatio]^y \qquad \log[RateRatio]=y\log[ConcRatio]$$

$$\frac{\log[RateRatio]}{\log[ConcRatio]}=y \qquad \frac{\log[2.75]}{\log[1.66]}=y \quad y=1.99 \quad \sim 2$$

- *This would not likely be necessary on the AP Exam. But you may need this tool for some of the problems #7-10 on Practice E.1 and for LAD E1 Process Data Parts 4 & 5*

The Rate Constant

Just how constant is k?

What does *k* depend on?

- It is important to remember that the rate of a reaction depends on concentration, however the rate constant does NOT. k is a constant (well… mostly constant)
  - ✓ k is dependent on
    - The nature of the reactants
    - Presence of a catalyst
    - Temperature

More Practice?

Just how constant is k?

The reaction: $I^- + OCl^- \rightarrow IO^- + Cl^-$ is first order with respect to both reactants. The rate law constant is 0.061 $M^{-1}s^{-1}$. What is the rate of the reaction when $[I^-]$=0.10M and $[OCl^-]$=0.20 M?

no calculator

1. 2.4×10^{-4} M/s
2. 1.2×10^{-4} M/s
3. 1.2×10^{-3} M/s
4. 2.4×10^{-5} M/s
5. 6.1×10^{-3} M/s

The reaction: $I^- + OCl^- \rightarrow IO^- + Cl^-$
is first order with respect to both reactants. The rate law constant is 0.061 $M^{-1}s^{-1}$. What is the rate of the reaction when $[I^-]=0.10M$ and $[OCl^-]=0.20\ M$?

no calculator

1. 2.4×10^{-4} M/s
2. 1.2×10^{-4} M/s
3. 1.2×10^{-3} M/s

- substitute into the rate law
- rate = k $[I^-]\ [OCl^-]$
- rate = $0.061 M^{-1}s^{-1}[0.10M][0.20M]$

4. 2.4×10^{-5} M/s
5. 6.1×10^{-3} M/s

The rate law for the reaction: A + B → C
This reaction is second order with respect to A and first order with respect to B. What happens to the rate when the concentration of A is doubled?

1. the rate is halved
2. the rate doubles
3. the rate triples
4. the rate quadruples
5. impossible to determine

The rate law for the reaction: A + B → C
This reaction is second order with respect to A and first order with respect to B. What happens to the rate when the concentration of A is doubled?

1. the rate is halved
2. the rate doubles
3. the rate triples
4. the rate quadruples
   - Assuming that the concentration of B is held constant.
5. impossible to determine
   - If you did not make the previous assumption, this would be the appropriate answer.

The table below provides rate data for the reaction: $2A + B \rightarrow C$. What is the rate law for this reaction?

1. rate = $k\,[A]^2$
2. rate = $k\,[B]^2$
3. rate = $k\,[A]\,[B]$
4. rate = $k\,[A]^2[B]^2$
5. rate = $k\,[A]^2[B]$
6. rate = $k\,[A]\,[B]^2$
7. rate = $k\,[A]^0[B]^2$
8. rate = $k\,[A]^2[B]^0$

	[A]	[B]	rate M/s
1	2	1	0.1
2	2	2	0.4
3	4	4	1.6

no calculator

The table below provides rate data for the reaction: $2A + B \rightarrow C$. What is the rate law for this reaction?

	[A]	[B]	rate M/s
1	2	1	0.1
2	2	2	0.4
3	4	4	1.6

1. rate = $k\,[A]^2$
2. rate = $k\,[B]^2$
3. rate = $k\,[A]\,[B]$
4. rate = $k\,[A]^2[B]^2$
5. rate = $k\,[A]^2[B]$
6. rate = $k\,[A]\,[B]^2$

- comparing exp 1 to 2: as B is doubled (while A held constant) the rate is quadrupled, thus second order.
- comparing exp 3 to 2: as B is doubled, and A is doubled, the rate only quadruples, thus A must be having no effect.
- The only possible solution for x is 0

$$\frac{\text{exp 3:} \qquad 1.6 = k[4]^x[4]^2}{\text{exp 2:} \qquad 0.40 = k[2]^x[2]^2}$$

no calculator

The table below provides rate data for the reaction: A + B → C. What is the rate law for this reaction?

1. rate = $k\,[A]^{1/2}$
2. rate = $k\,[B]^2$
3. rate = $k\,[A]\,[B]$
4. rate = $k\,[A]^2[B]^{1/2}$
5. rate = $k\,[A]^0[B]$
6. rate = $k\,[A]\,[B]^3$
7. rate = $k\,[A]\,[B]^4$
8. rate = $k\,[A]^0[B]^3$

trial	[A]	[B]	rate M/s
X	1	1	0.1
Y	2	2	1.6
Z	3	1	0.3

no calculator

The table below provides rate data for the reaction: A + B → C. What is the rate law for this reaction?

trial	[A]	[B]	rate M/s
X	1	1	0.1
Y	2	2	1.6
Z	3	1	0.3

no calculator

6. rate = *k* [A] [B]^3

- comparing trial Z to X: as A is tripled (while B held constant) the rate is triples, thus first order.
- compare trial Y to X: as A doubles and B doubles, the rate increases by a factor of 16.
  - ✓ This means that 2x of the 16 factor is caused by the change in A, thus the other

Let’s summarize.

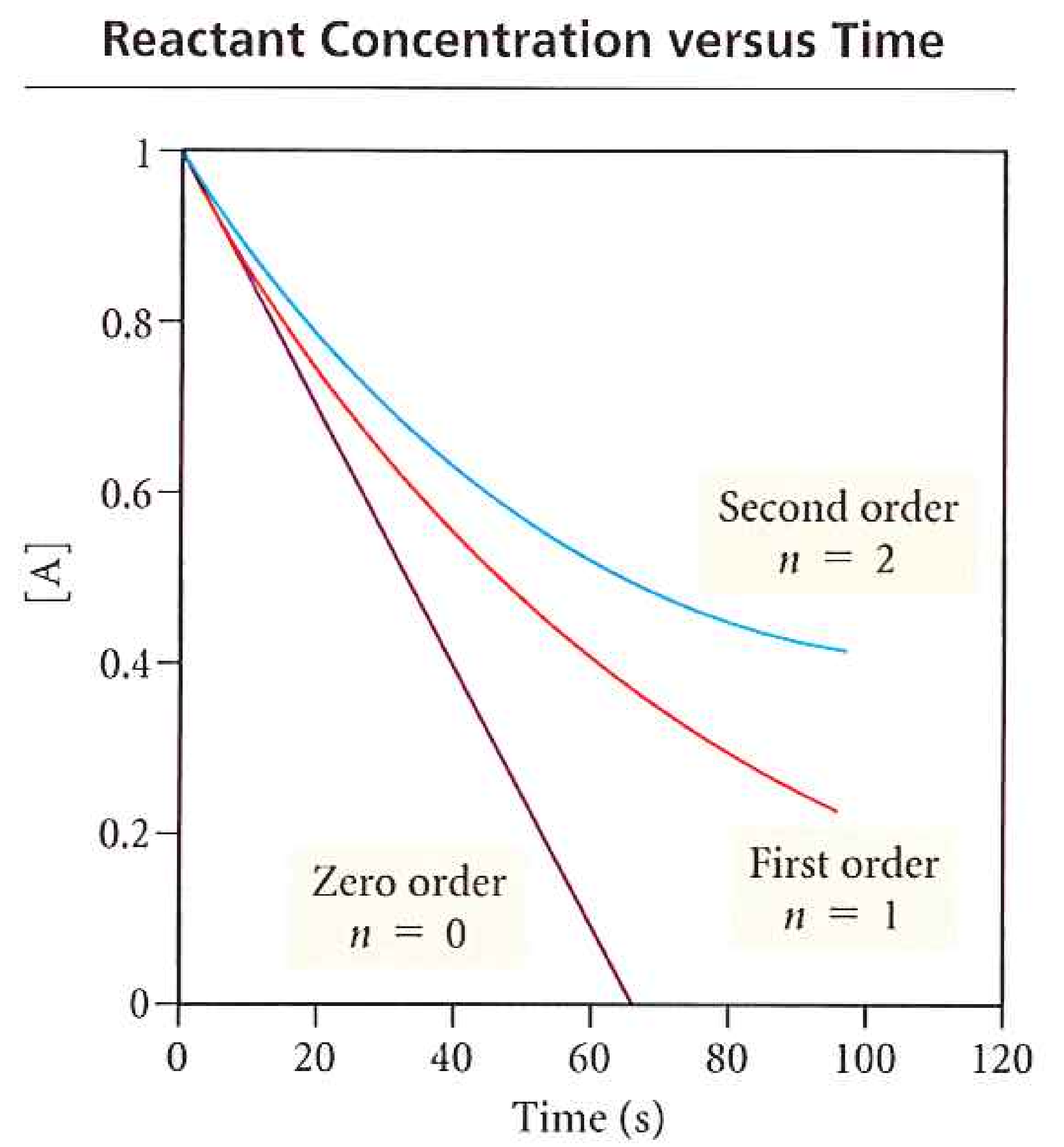
We can measure
Concentration and Rates
or
Concentration and time

Rate Laws - Summary

- You can NOT look at the stoichiometry of a chemical equation and know its rate law.
- Rate laws MUST be determined experimentally.
- Rate laws can be determined by observing the effect on rate when changing initial concentration.
- The exponents in rate laws are *usually* 0, 1, or 2, but they can be higher, or fractional or even negative.
- The (differential) rate law tells us how the rate of a reaction varies with the concentration of the reactants.
- But at other times we might be more interested in how the concentrations of reactants change over time.
  - ✓ Let's look at concentration vs time graphs again

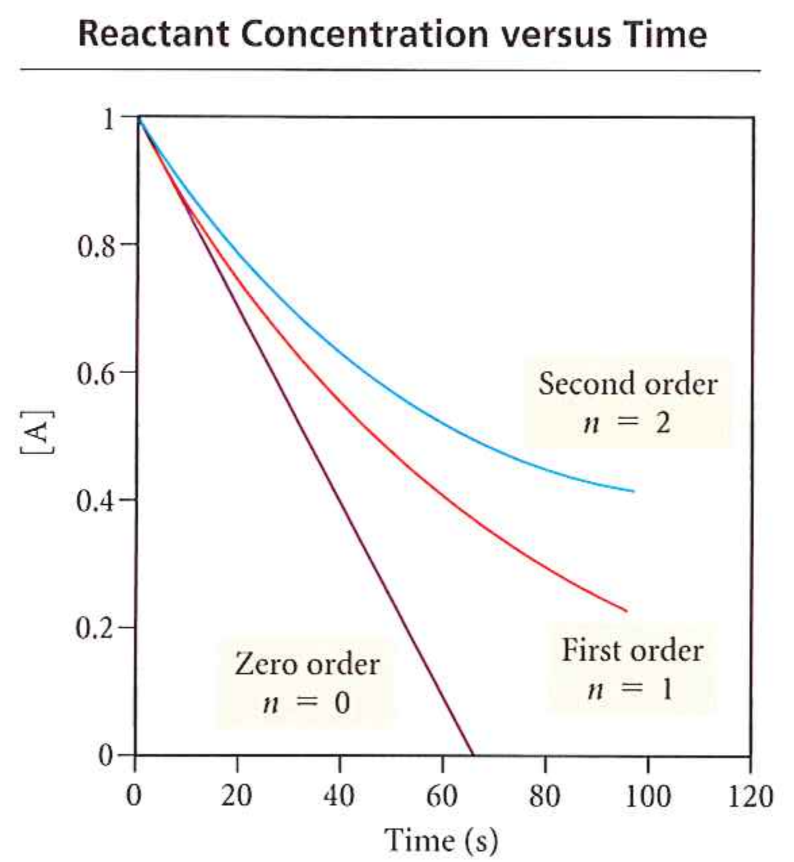
Conc vs Time Graph

- Turn to your mate, and discuss the differences and similarities between these three lines.
- Why?



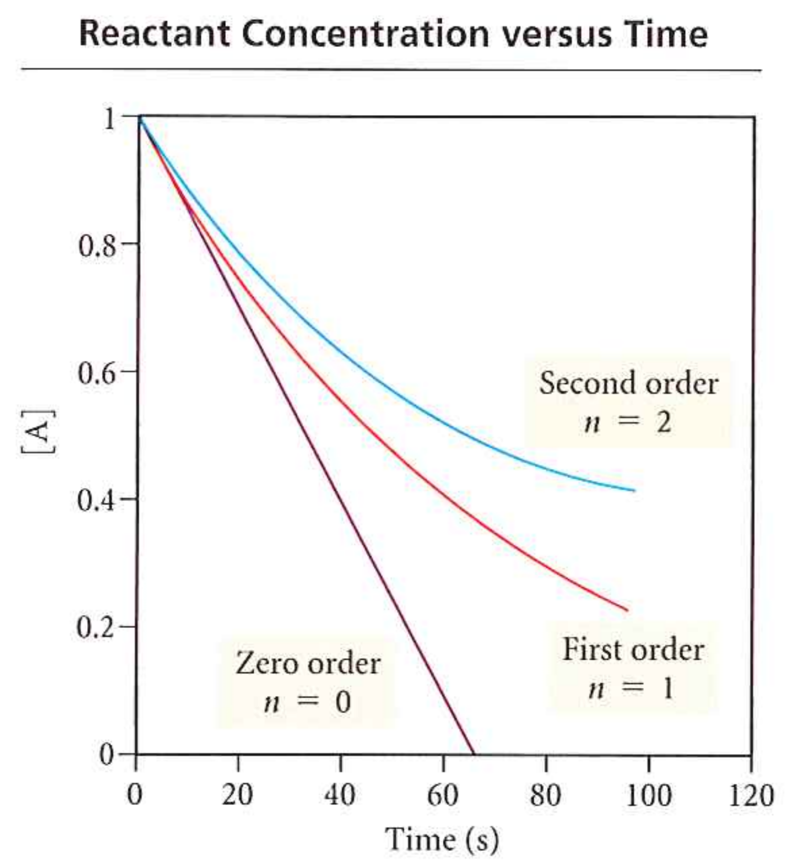
Conc vs Time Graph

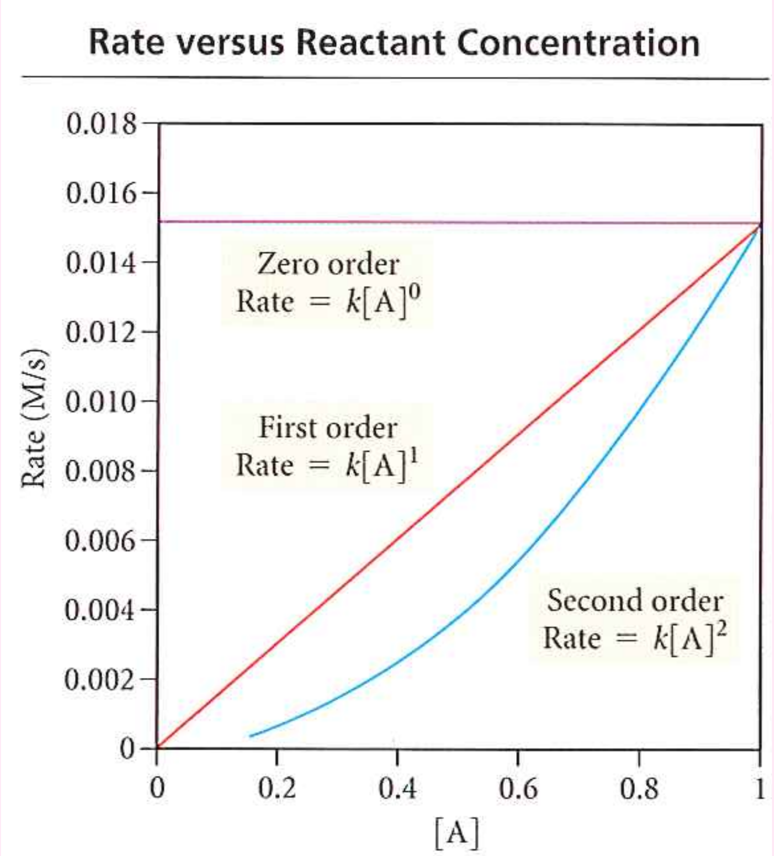
- zeroth order
  - ✓ rate = k
- first order
  - ✓ rate = k [A]
  - ✓ the reaction slows down as the reaction proceeds because concentration of the reactant decreases



- second order
  - ✓ rate = k $[A]^2$
  - ✓ the reaction is even more sensitive to the reactant concentration and flattens sooner since the rate is proportional to the square of the concentration

Compare: Conc vs Time Graph with Rate vs Conc Graph

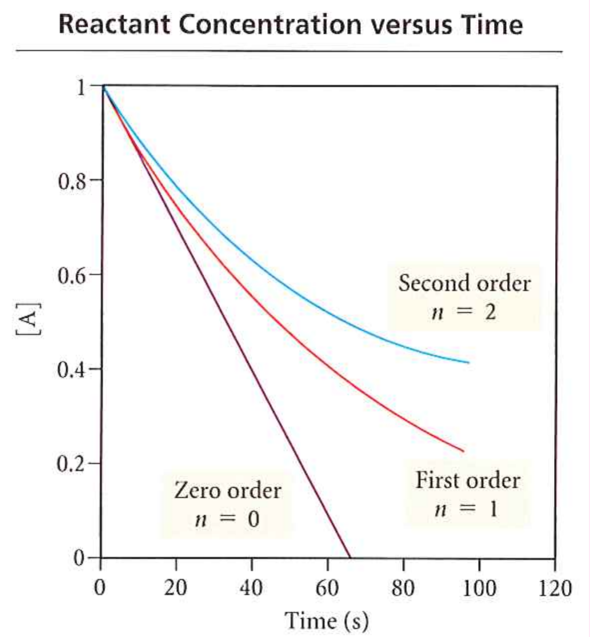

Reactant Concentration versus Time

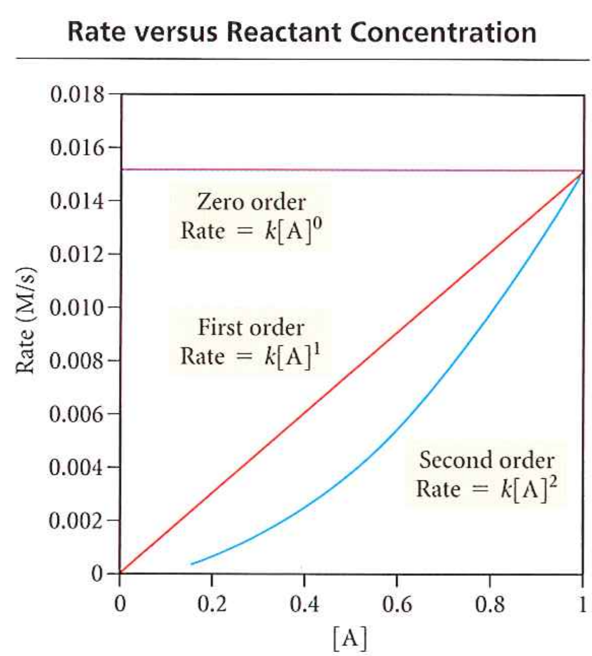

Rate versus Reactant Concentration

- Turn to your mate, and discuss why the graphs on the right are the shape that they are.

Compare: Conc vs Time Graph with Rate vs Conc Graph

- The rate for zero order is constant and is unaffected by concentration.
- The rate for first order is directly proportional to the concentration.
  - ✓ What does the slope tell us?
- The rate for second order is proportional to the square of the concentration, thus a curve.

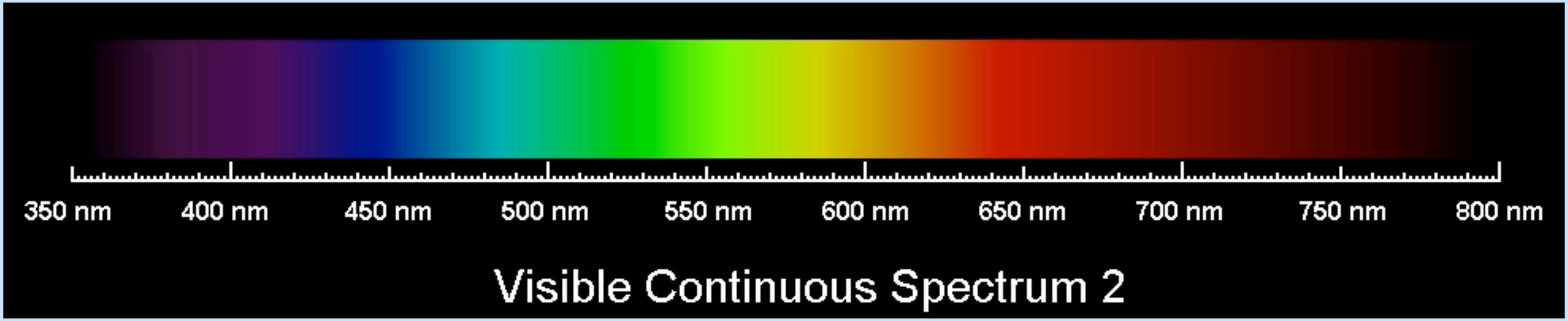




Using the Spectrophotometer to collect data: concentration vs time

LAD E.2
Crystal Violet

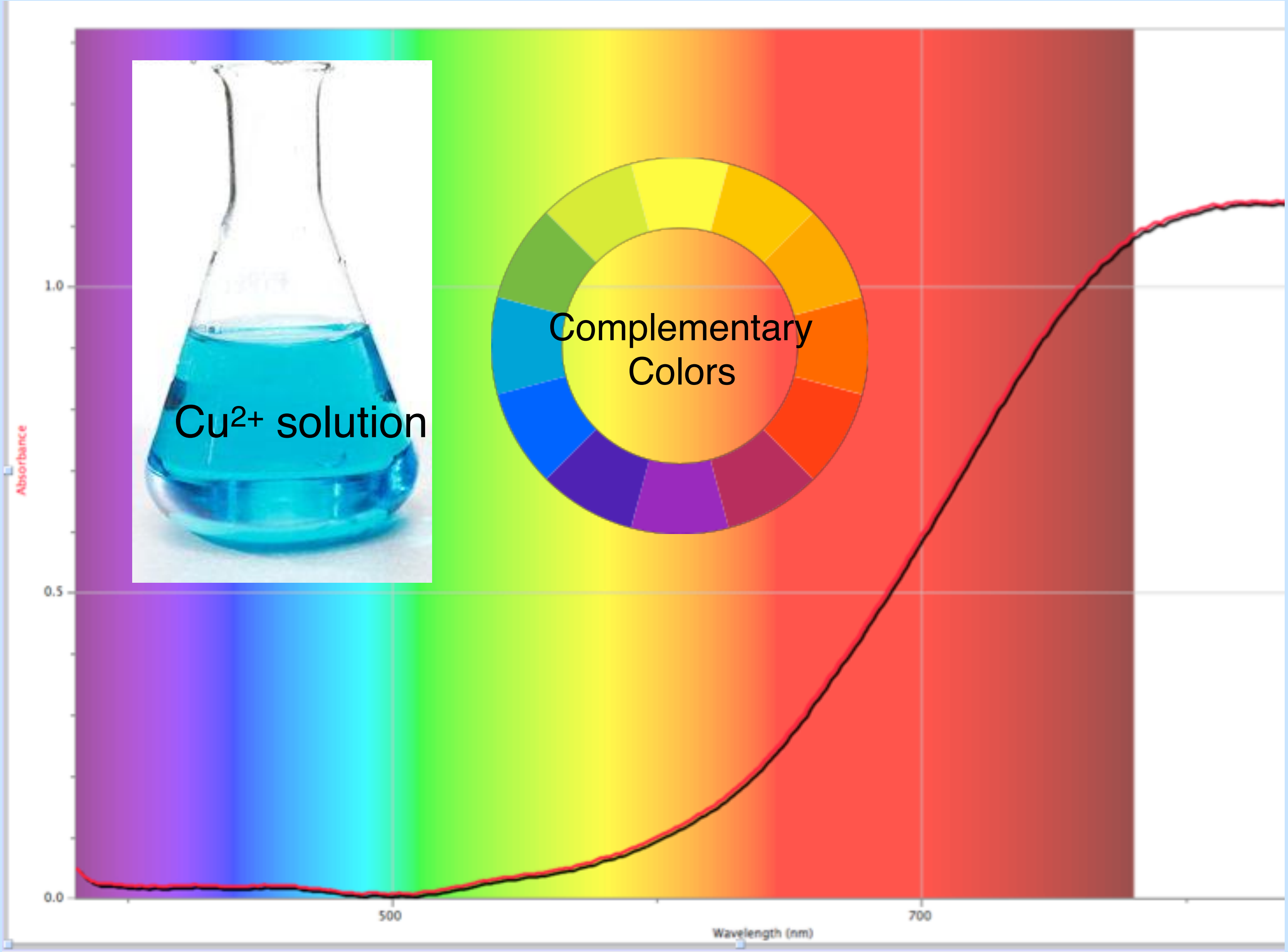
Color as a function of wavelengths of Light



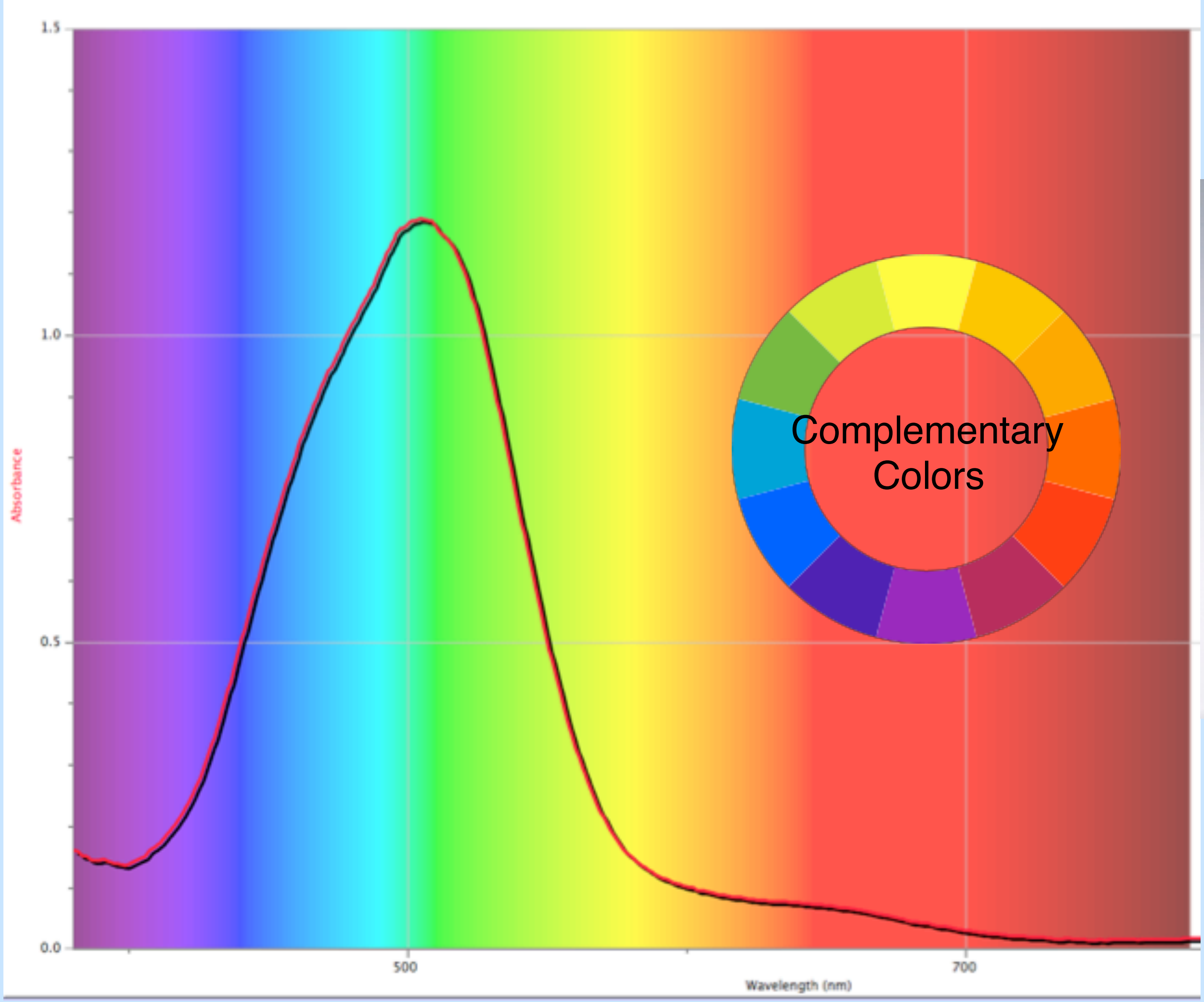
Visible Continuous Spectrum 2

- Color in a visible spectrum and color wheel on your lab sheet.

Copper(II) nitrate

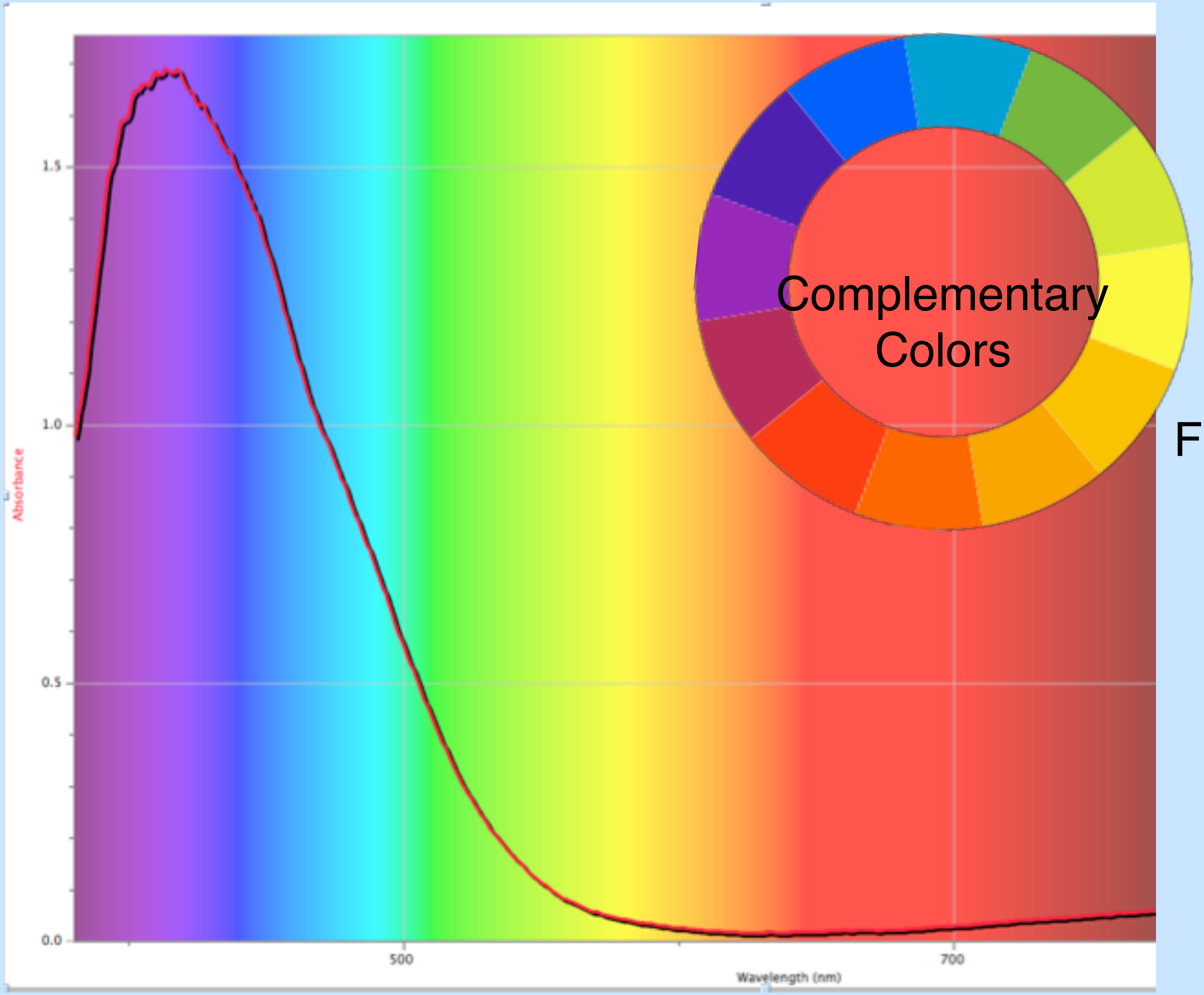


Cobalt(II) nitrate



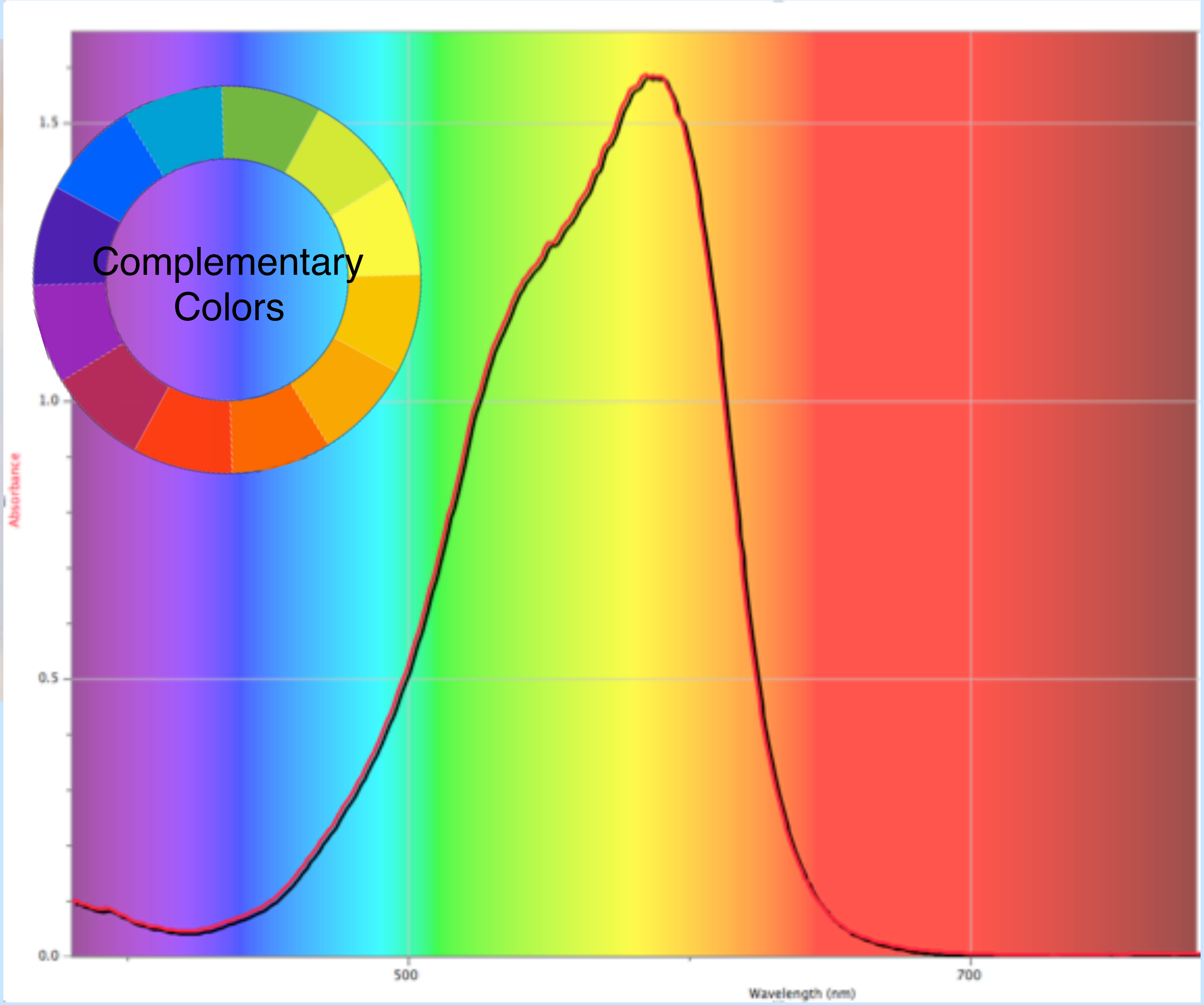
Co^{2+} solution

Iron(II) chloride



Fe^{2+} solution

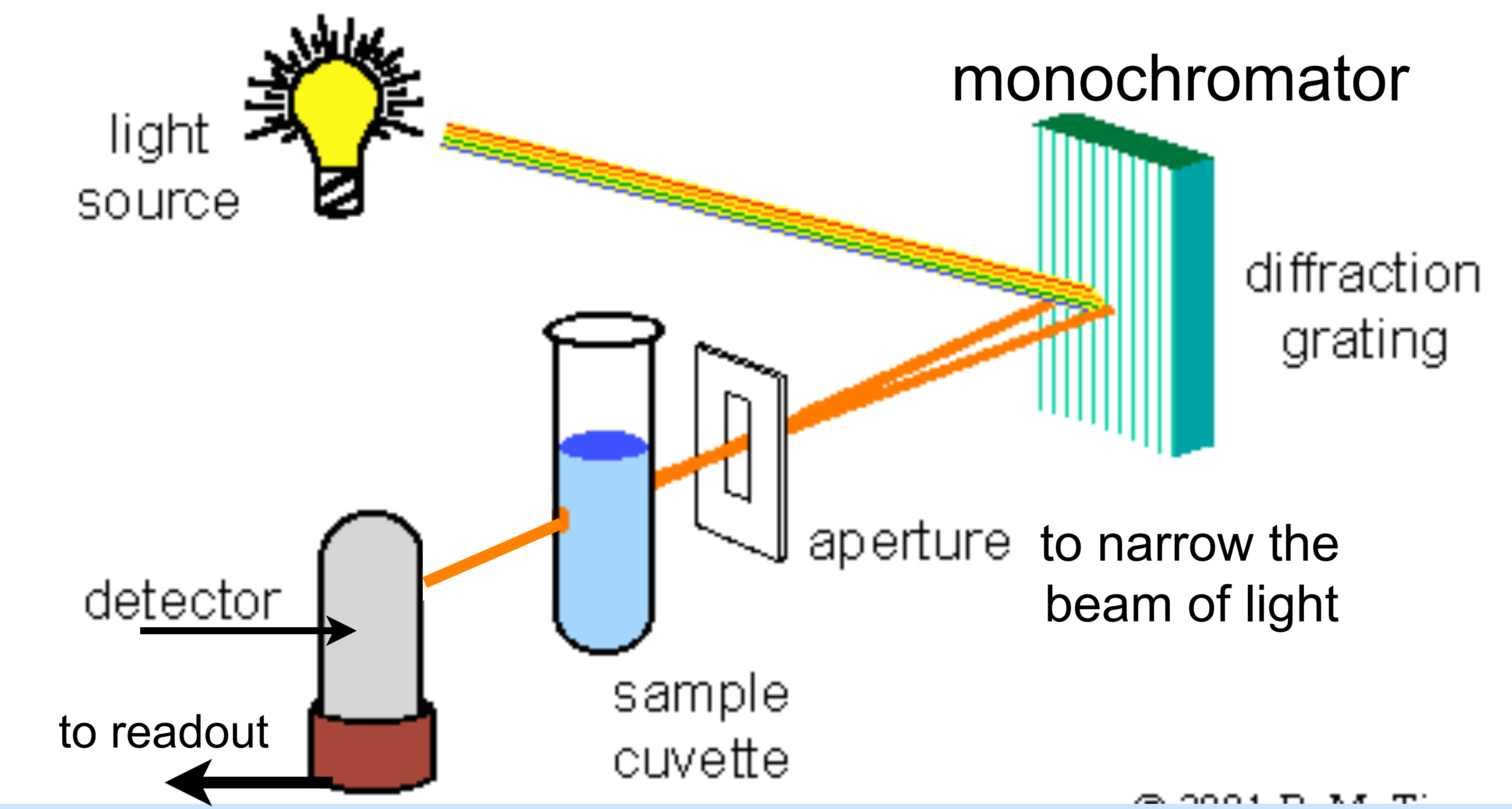
Crystal Violet



Gathering Concentration vs Time Data

- We can use the spectrophotometer to measure absorbance over time.
- Remember from LAD B1 and F1, absorbance is proportional to concentration.
  - ✓ $A = abc$
    - A = Absorbance (a unitless number)
    - a = absorptivity (a constant unique to each compound)
    - b = path length (a constant since we use the same cuvettes for any given trial)
    - c = concentration

Spectrophotometer schematic



monochromator

to narrow the beam of light

to readout

Gathering Concentration vs Time Data

- Using the spectrophotometer to measure concentration of a reaction over time, as the reaction proceeds.
- Crystal Violet + NaOH → colorless
- *Let's try it…. and gather some data*

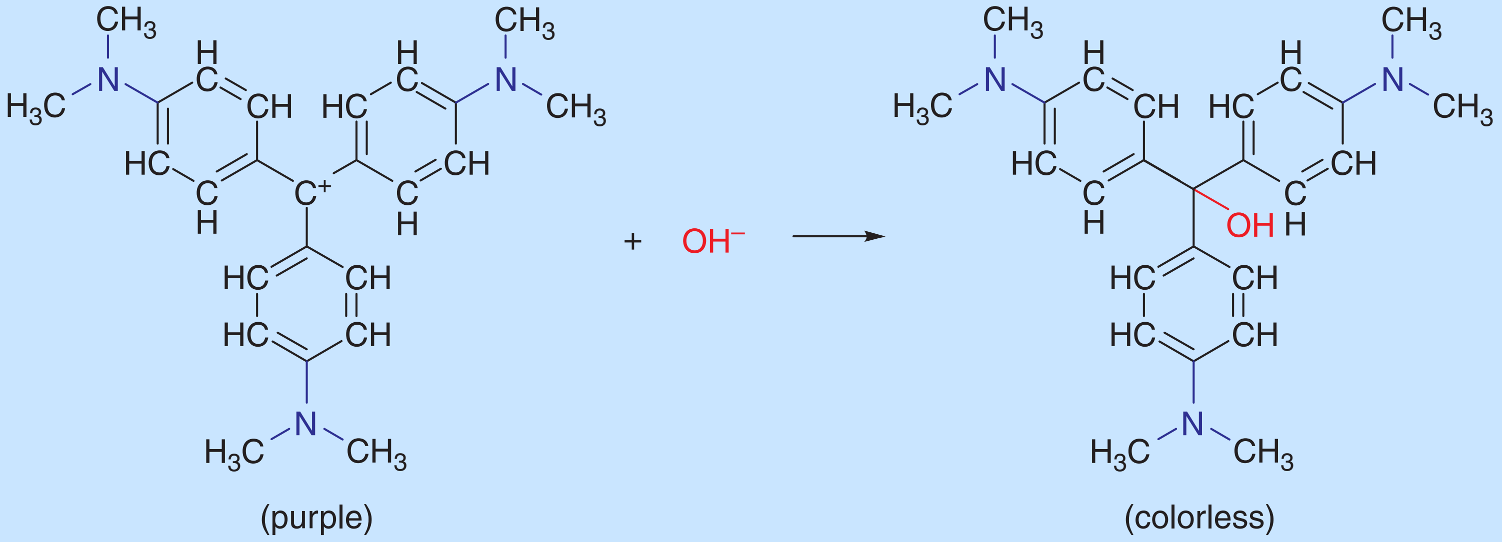


Figure 2. Chemical structures in the reaction in this laboratory activity

What Does the Graphed Data Tell Us?

Collecting Concentration vs Time Data

Differential vs Integrated

- The differential rate law (what we have been using so far) came from analyzing concentration and rate data.
- Using calculus to integrate these differential rate laws will help us analyze concentration and time data.
- No matter which method or data we choose to analyze a reaction, the order of the reaction will be the same for any one particular reaction, and k will be the same constant (for any particular temperature and same catalyst if used).
- The order of the reaction must be determined experimentally.
  - ✓ Which rate law you choose to work with depends on the type of data that is easiest to collect:
  - ✓ concentration & rate OR concentration & time

differential *integrated*

Δ in concentration vs time for 1st Order

- For: A → products
- If experimental data determined the rate law to be:
  - ✓ Rate = k [A]
- This law can be integrated with calculus to yield:
  - ✓ $\ln[A]_t - \ln[A]_0 = -kt$ (look for this on the formula sheets)
- We can use this equation to
  - ✓ Solve for any one of the four variables given the other three
    - Determine the concentration of some reactant remaining at any time after the reaction proceeds for some time.
    - Calculate the time required for a reactant to drop to a particular level.
    - etc….

Graphing 1st Order Reactions

- We could rewrite the first order integrated rate equation ($\ln[A]_t - \ln[A]_0 = -kt$) in a number of ways by manipulating it with algebra

  - ✓ $\ln[A]_t = -kt + \ln[A]_0$

- Notice that for the equation written this way,
- $\ln[A]_t = -kt + \ln[A]_0$
- $y = mx + b$ is the equation for a straight line.

- Thus the graph of $\ln[A]_t$ vs t will give a straight line with a slope of $-k$ and a y intercept = $\ln[A]_0$

Δ in concentration vs time for 2nd Order

- For: B → products
- If the experimental data determined the rate law to be:
  - ✓ Rate = k $[B]^2$
- Using calculus the law can be integrated to yield:
- $\frac{1}{[B]_t} - \frac{1}{[B]_o} = kt$ which can be algebraically manipulated to:
- $\frac{1}{[B]_t} = k\,t + \frac{1}{[B]_o}$
- This also is the equation for a straight line
- $y = mx + b$
- So the graph of $\frac{1}{[B]_t}$ vs t will give a straight line with a slope of k and a y intercept = $\frac{1}{[B]_o}$

Δ in concentration vs time for 0 Order

- For: C → products
- If the experimental data determined the rate law to be:
  - ✓ Rate = k $[C]^0$ or rate = k
- The law can be integrated to yield: $[C]_t + [C]_0 = -kt$

Not on the formula sheets, but exactly the same as 1st order without the natural log.

- $[C]_t = -kt + [C]_0$
- This also is the equation for a straight line
- $y = mx + b$
- So the graph of $[C]_t$ vs t will give a straight line with a slope of −k and a y intercept = $[C]_0$

The catalyzed decomposition of hydrogen peroxide is a *first* order reaction with the rate constant given below.

For an experiment in which the starting concentration of hydrogen peroxide is 0.110 M, what is the concentration of H_2O_2 450 minutes after the reaction begins?

$2\ H_2O_2 \rightarrow 2H_2O + O_2$ $k = 1.33 \times 10^{-4}\ \text{min}^{-1}$

1. 0.0961 M
2. 0.00658 M
3. 0.104 M
4. 0.0156 M
5. 0.117 M

yes, calculator

The catalyzed decomposition of hydrogen peroxide is a *first* order reaction with the rate constant given below.

For an experiment in which the starting concentration of hydrogen peroxide is 0.110 M, what is the concentration of H_2O_2 450 minutes after the reaction begins?

$2\ H_2O_2 \rightarrow 2H_2O + O_2$ $\qquad$ $k = 1.33 \times 10^{-4}\ \text{min}^{-1}$

You may use a calculator for this problem.

1. 0.0961 M
2. 0.00658 M
3. 0.104 M
4. 0.0156 M
5. 0.117 M

- Use the integrated rate law and solve for $[H_2O_2]_t$

✓ $\ln[H_2O_2]_t = -kt + \ln[H_2O_2]_0$

✓ $\ln[H_2O_2]_t = -1.33\text{x}10^{-4}\text{min}^{-1}(450\ \text{min}) + \ln[0.110\text{M}]$

Collecting Conc vs Time data

- If the graph of [A] vs time is linear
  - ✓ the reaction is zero order with repect to A
- If you the graph of ln[A] vs time is linear
  - ✓ the reaction is first order with repect to A
- If you the graph of $\frac{1}{[A]}$ vs time is linear
  - ✓ the reaction is second order with repect to A

Half Life

The time required for the concentration of a reactant to decrease to half of that reactant’s initial concentration.

Half-Life

- Half life – symbolized $t_{½}$
- The time required for the concentration to drop to half of its previous value.
- Half life is a convenient way to describe how fast or slow a reaction occurs.
  - ✓ Fast reactions will have a short half life.

Deriving Half-life Equations

- Zero order

just watch, don't write

- Almost the formula sheets: $[A]_t - [A]_o = -kt$
- Algebra: $[A]_o - [A]_t = kt$
- After a half life we would have half the starting concentration $[A]_t = \frac{1}{2}[A]_o$
- Substitute: $[A]_o - \frac{1}{2}[A]_o = kt_{1/2}$
- Subtract: $\frac{1}{2}[A]_o = kt_{1/2}$
- so……….. $\frac{[A]_o}{2k} = t_{1/2}$
- Thus the half life of a zero order reaction is always changing because it is dependent on the concentration at any given moment.

Deriving Half-life Equations

just watch, don't write

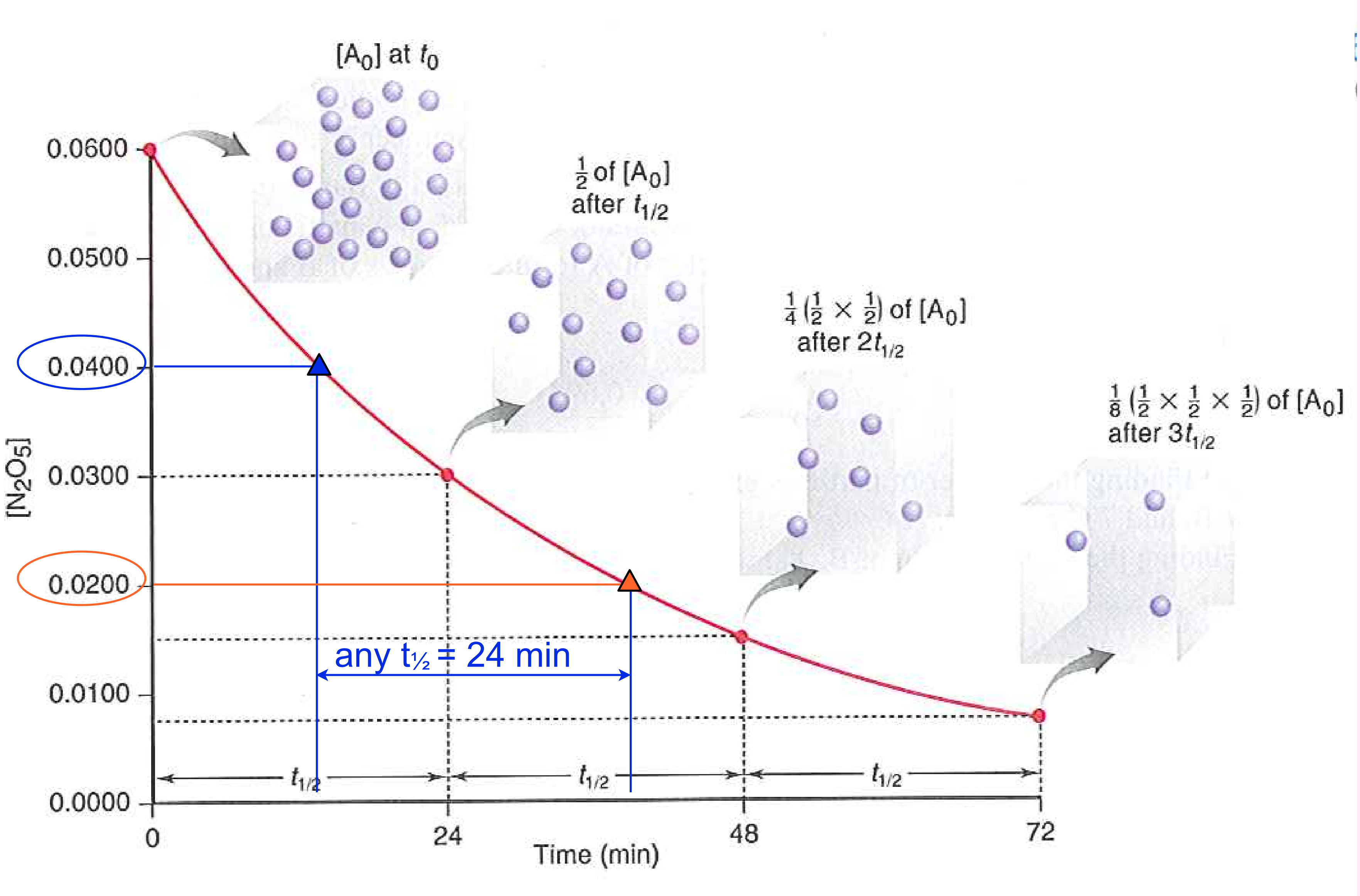
- Second order
- From the formula sheets: $\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$
- After a half life we would have half the starting concentration $[A]_t = \frac{1}{2}[A]_o$
- Substitute: $\frac{1}{\frac{1}{2}[A]_o} - \frac{1}{[A]_o} = kt_{1/2}$
- $\xrightarrow{\hspace{6em}}$ Algebra: $\frac{2}{[A]_o} - \frac{1}{[A]_o} = kt_{1/2}$
- Subtract: $\frac{1}{[A]_o} = kt_{1/2}$
- Voila $\frac{1}{k[A]_o} = t_{1/2}$
- Thus the half life of a second order reaction is always changing because it is dependent on the concentration at any given moment.

Deriving Half-life Equations

just watch, don't write

- First order
- From the formula sheets: $\ln[A]_t - \ln[A]_o = -kt$
- Handy Log Rule: $\ln\left(\frac{[A]_t}{[A]_o}\right) = -kt$
- After a half life we would have half the starting concentration $[A]_t = \frac{1}{2}[A]_o$
- Substitute: $\dashrightarrow \ln\left(\frac{\frac{1}{2}[A]_o}{[A]_o}\right) = -kt_{1/2} \dashrightarrow \ln\left(\frac{1[A]_o}{2[A]_o}\right) = -kt_{1/2}$
- Cancel: $\ln\left(\frac{1}{2}\right) = -kt_{1/2} \dashrightarrow$ then solve: $-0.693 = -kt_{1/2}$
- Voila $\frac{0.693}{k} = t_{1/2}$
- Thus the half life of a first order reaction is a constant for any particular reaction because it is independent of the concentration.

Determining half life from a [conc] vs time graph for a first order reaction.



any t½ = 24 min

93.75 % of some radioactive isotope has decayed after 8 hours.
What is the half life of this isotope?

No Calculator

1. 0.5 hour
2. 1 hour
3. 1.6 hours
4. 2 hours
5. 4 hours
6. 7.5 hours
7. 8 hours

93.75 % of some radioactive isotope has decayed after 8 hours.
What is the half life of this isotope?

No Calculator

1. 0.5 hour
2. 1 hour
3. 1.6 hours
4. 2 hours
   - 100% > 50% > 25% > 12.5% > 6.25% left, is 93.75% decayed.
   - 4 half lives for 8 hours is 2 hours per half life.
5. 4 hours
6. 7.5 hours
7. 8 hours

What is the rate constant for a first–order reaction in which the half life is 3 hours?

1. $4.33\ h^{-1}$
2. $3\ h^{-1}$
3. $2.08\ h^{-1}$
4. $0.231\ h^{-1}$

No calculator

What is the rate constant for a first-order reaction in which the half life is 3 hours?

You may use a calculator for this problem.

- Use the first order half-life equation which is *not* concentration dependent and solve for k.

1. 4.33 h^{-1}
2. 3 h^{-1}
3. 2.08 h^{-1}
4. 0.231 h^{-1}

$$\frac{0.693}{t_{1/2}} = k$$

What fraction of a reactant remains after 3 half-lives of a first order reaction?

1. ½
2. ⅛
3. ⅓
4. ¹⁄₁₆
5. ⅙

no calculator

What fraction of a reactant remains after 3 half-lives of a first order reaction?

1. ½
2. ⅛
   - Regardless of the amount present, for a first-order reaction, after one half-life, ½ remains, after a second half-life, ¼ remains, and after a third half-life, ⅛th remains.
3. ⅓
4. ⅟16
5. ⅙

The decay of some iodine isotope has a half life of 10 days. After 40 days, there is 1.5 g of that iodine isotope are present. What was the original mass of the radioactive isotope present?

1. 6
2. 5
3. 4.5
4. 12
5. 24

no calculator

The decay of some iodine isotope has a half life of 10 days. What percentage of iodine has decayed after 40 days, there is 1.5 g of that iodine isotope are present. What was the original mass of the radioactive isotope present?

1. 6
2. 5
3. 4.5
4. 12
5. 24

no calculator

Reaction Mechanism

Just how does the reaction happen? What molecules are actually bumping into each other, and in what order do these crashes occur?

Reaction Mechanism

- Most chemical reactions do not occur in a single step as the balanced equation implies, but through a series of individual steps (like Hess' Law).
- We call these steps the reaction mechanism
  - ✓ each individual reaction is called an *elementary step* or elementary reaction
  - ✓ Each step describes an actual *individual molecular event*
  - ✓ An elementary step is *not* made up of simpler steps
  - ✓ The rate law of an **elementary step** (unlike an overall balanced equation) can be deduced from the reaction stoichiometry of that elementary step.

Hydrogen Gas + Iodine Monochloride

- For this reaction: $H_2 + 2\ ICl \rightarrow 2\ HCl + I_2$
- A two step mechanism has been proposed.
  - ✓ $H_2 + ICl \rightarrow HI + HCl$
  - ✓ $HI + ICl \rightarrow HCl + I_2$
- The two elementary steps will sum to the overall reaction. (Just like Hess' Law)
- HI would be an *intermediate*.
  - ✓ A molecule that forms in one step and is consumed in a subsequent step.

Molecularity

- Since the steps of a mechanism are the real story of which particles are actually crashing together, it is important that the number of particles in any step is small so it the crash is a reasonable possibility.
- The rate law of an elementary step is deducible from the stoichiometry!
  - ✓ Unimolecular
    - $A \rightarrow$ product   rate = $k[A]$
  - ✓ Bimolecular
    - $2A \rightarrow$ product   rate = $k[A]^2$
    - $A + B \rightarrow$ product   rate = $k[A][B]$
  - ✓ Termolecular − *this is not so likely*
    - $2A + B \rightarrow$ product   rate = $k[A]^2[B]$

A Mechanism is a Hypothesis

- A chemist *proposes* a mechanism and then determines if the mechanism fits the experimentally observed rate law.
- It is very difficult to *prove* that a mechanism represents the actual chemical steps, only that it is *consistent with the data*.
- To be valid, three criteria must be met
  - ✓ The elementary steps must add up to the overall balanced equation (just like Hess' Law)
  - ✓ The elementary steps must be reasonable. They should be unimolecular or bimolecular (termolecular only very rarely).
  - ✓ The mechanism must correlate with the observed rate law.

Slow Steps….Fast Steps

- It stands to reason that the steps would proceed at different rates.
- Remember that the two factors that affect the productivity of reaction collisions would likely be different for the different steps
    - ✓ sufficient energy to weaken bonds
    - ✓ favorable orientation of molecules

together these cause the activation energy

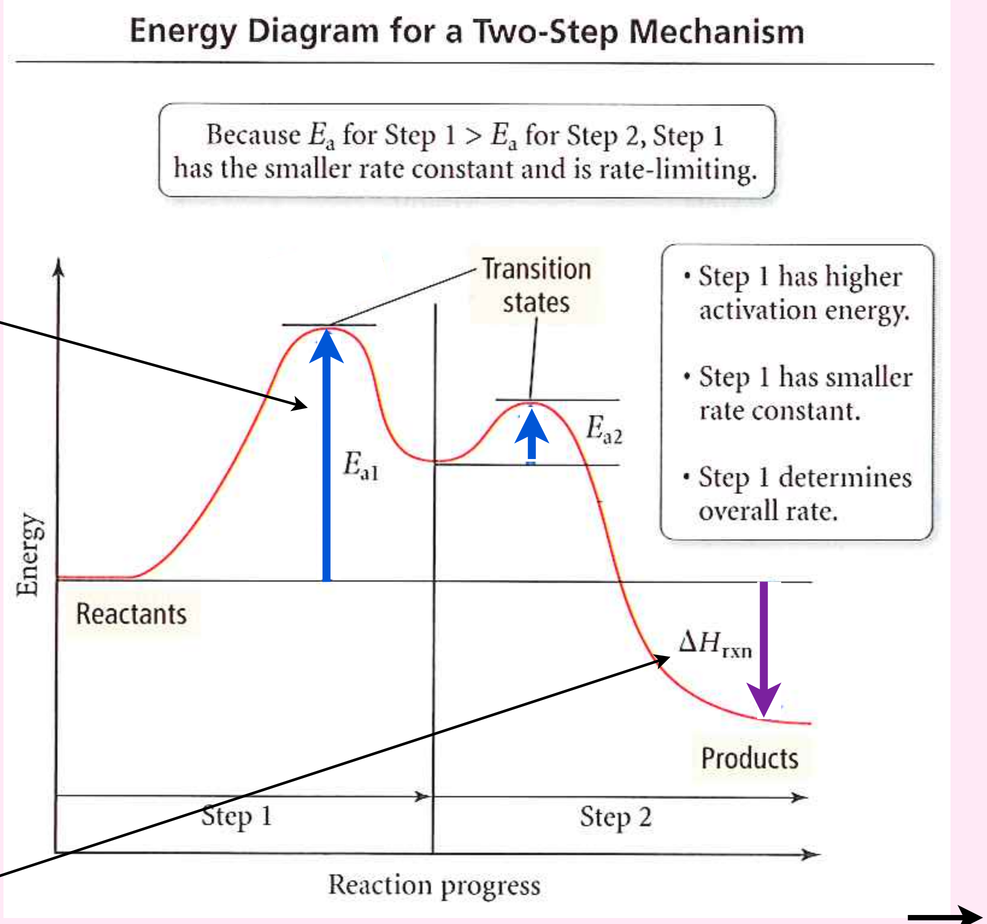
- One step has to be the slowest, and that step will be the *rate-determining* step.
- The slow step limits the overall reaction and determines the rate law for the overall reaction.

Hydrogen Gas + Iodine Monochloride

- For this reaction: $H_2 + 2ICl \rightarrow 2HCl + I_2$
- If this reaction proceeded in a single elementary step, the rate law would be ~~$\text{rate} = k[H_2]\,[ICl]^2$~~
- But it is not. The experimentally determined rate law is
  - ✓ $\text{rate} = k[H_2]\,[ICl]$
- So we know that there must be more than one step.
- The rate laws for elementary steps **after** the slow step do not play any role in the overall rate law
- If the first elementary step of the proposed mechanism is the slow step,
  - ✓ $\boxed{H_2 + ICl} \rightarrow HI + HCl$ *slow* $\text{rate} = k[H_2]\,[ICl]$
  - ✓ $HI + ICl \rightarrow HCl + I_2$ *fast* $\text{rate} = k[HI]\,[ICl]$
- The rate law for the mechanism will be consistent with the experimentally determined rate law.

Hydrogen Gas + Iodine Monochloride

- For this reaction: $H_2 + 2ICl \rightarrow 2HCl + I_2$
  - ✓ $H_2 + ICl \rightarrow HI + HCl$ *slow* rate = $k[H_2]\,[ICl]$
  - ✓ $HI + ICl \rightarrow HCl + I_2$ *fast* rate = $k[HI]\,[ICl]$
- Rate Law
  - ✓ rate = $k[H_2]\,[ICl]$
- The higher activation energy of the first step makes that step slower than the second step.
- ΔH_{rxn} is exothermic



Energy Diagram for a Two-Step Mechanism

Because E_a for Step 1 > E_a for Step 2, Step 1 has the smaller rate constant and is rate-limiting.

- Step 1 has higher activation energy.
- Step 1 has smaller rate constant.
- Step 1 determines overall rate.

How do rate laws tell us about reaction mechanisms?

- $NO_2 + CO \rightarrow NO + CO_2 \quad \Delta H < 0$
- Given the reaction above, *if* the actual mechanism of the reaction was NO_2 bumping into CO
- You would expect the rate law to be
  - ✓ rate = $k [NO_2] [CO]$
- Experimental evidence indicates that in fact the rate law is
  - ✓ rate = $k [NO_2]^2$
- How can this be? What really might be going on at the molecular level?

Elementary steps of multi-step Rx's

when the first step is the slow step

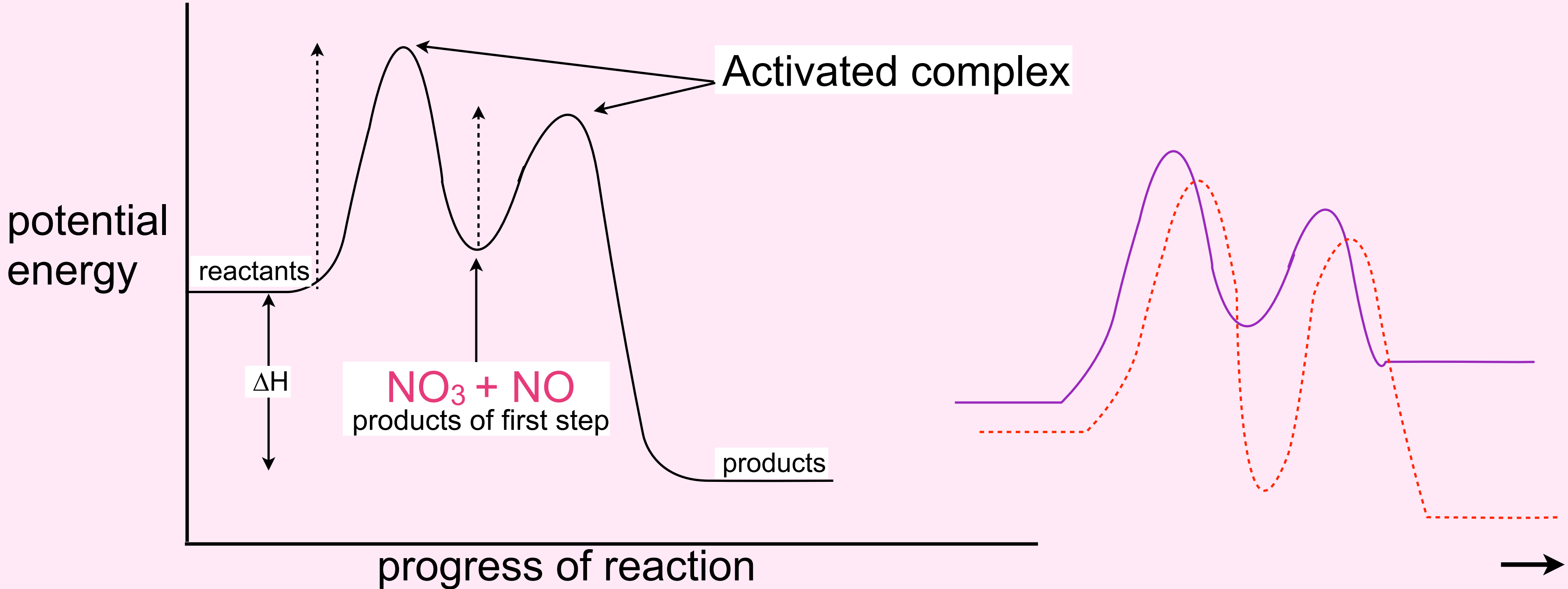
- $NO_2 + CO \rightarrow NO + CO_2 \quad \Delta H < 0$
  - ✓ Experimentally determined rate = $k\,[NO_2]^2$
  - ✓ How can this be? What really might be going on at the molecule level?
- Scientists have proposed the following mechanism which supports the experimentally determined rate law above:
  - ✓ $NO_2 + NO_2 \rightarrow NO_3 + NO$ *slow*
  - ✓ $NO_3 + CO \rightarrow NO_2 + CO_2$ *fast*
- Since the slow step is the first step, the rate law of this step is the rate law of the reaction.
- Since CO appears *after* the rate determining step, it does not appear in the rate law and thus, this reaction would be zero order with respect to CO.

rate = k $[NO_2]^2$

- Mechanism as proposed in previous slide:
  $NO_2 + CO \rightarrow NO + CO_2$ $\Delta H < 0$
  - ✓ $NO_2 + NO_2 \rightarrow NO_3 + NO$ slow
  - ✓ $NO_3 + CO \rightarrow NO_2 + CO_2$ fast
- NO_3 is an *intermediate*.
  - ✓ a substance that is formed and subsequently used up during a reaction.
  - ✓ intermediates are less stable than reactants and products,
  - ✓ but intermediates are much more stable than the very unstable transition state (or activated complex),
  - ✓ intermediates have “normal” bonds and can sometimes be isolated and collected.

rate = k $[NO_2]^2$

- Mechanism as proposed in previous slide:
  $NO_2 + CO \rightarrow NO + CO_2$ $\Delta H < 0$
  - ✓ $NO_2 + NO_2 \rightarrow NO_3 + NO$ slow
  - ✓ $NO_3 + CO \rightarrow NO_2 + CO_2$ fast
- Let’s take a look at the potential energy diagram.



rate = k $[NO_2]^2$

- Mechanism for: $NO_2 + CO \rightarrow NO + CO_2$
  - ✓ $NO_2 + NO_2 \rightarrow NO_3 + NO$ slow
  - ✓ $NO_3 + CO \rightarrow NO_2 + CO_2$ fast
- Is this mechanism valid?
- Remember, three criteria must be met:
  - ✓ The elementary steps must add up to the overall balanced equation; they do.
  - ✓ The elementary steps must be reasonable. They should be unimolecular or bimolecular; they are.
  - ✓ The mechanism must correlate with the observed rate law; it does.

Consider: $2NO + Br_2 \rightarrow 2NOBr$

- The experimentally determined rate law for the reaction above is rate = $k [NO]^2 [Br_2]$
- This might lead you to believe that this means that the actual mechanism for this reaction is *termolecular*.
- But termolecular steps are extremely rare, and proceed very slowly, and the odds are not in their favor.
- It is likely that some other mechanism involving only bimolecular elementary steps results in the rate law.

Multi-step Rx

in which the *second* step is the *slow* step

- $2NO + Br_2 \rightarrow 2NOBr$
  - ✓ The experimentally determined rate law is
  - ✓ rate = $k[NO]^2 [Br_2]$
- Scientists might propose this mechanism:
  - ✓ $NO + Br_2 \rightarrow NOBr_2$ fast
  - ✓ $NOBr_2 + NO \rightarrow 2NOBr$ slow
- The slow step is the rate determining step which would give a rate law:
  - ✓ rate = $k[NOBr_2] [NO]$
- But this is not consistent with the experimentally determined rate law, *and* it involves an intrinsically less stable intermediate. We try to avoid intermediates in the rate law. Lets take a closer look...

$$2NO + Br_2 \rightarrow 2NOBr$$

experimentally determined rate = $k[NO]^2 [Br_2]$

- Using the *Quickie Method*, you can determine the rate law by crossing out intermediates
  - ✓ $NO + Br_2 \rightarrow$ ~~$NOBr_2$~~ fast
  - ✓ ~~$NOBr_2$~~ $+ NO \rightarrow 2NOBr$ slow
- and put any remaining reactants up to and including the slow step into the rate law.
  - ✓ which results in the experimentally observed
  - ✓ rate = $k [NO]^2 [Br_2]$
- but what's really going on here…..hold on...buckle your seat belts….here we go!

$2NO + Br_2 \rightarrow 2NOBr$ rate = $k[NO]^2[Br_2]$

- Write the rate law for each elementary step
  - ✓ $NO + Br_2 \rightarrow NOBr_2$ fast $rate_1 = k_1[NO][Br_2]$
  - ✓ $NOBr_2 + NO \rightarrow 2NOBr$ slow $rate_2 = k_2[NOBr_2][NO]$
- If the first step is not the rate determining step, the product of the initial fast step will start to build up, and start reversing back into reactant and the first reaction will reach equilibrium.
- Because of this equilibrium we can write a rate law for the reverse reaction: $rate_{1rev} = k_{1rev}[NOBr_2]$
  - ✓ since rate fwd = rate reverse, then $k_{1fwd}[NO][Br_2] = k_{1rev}[NOBr_2]$
  - ✓ isolate $[NOBr_2]$ $[NOBr_2] = \dfrac{k_{1fwd}[NO][Br_2]}{k_{1rev}}$
- then substitute into the slow step rate law to eliminate the intermediate

$$rate_2 = k_2[NOBr_2][NO]$$

$$rate_{rxn2} = k_2\left(\frac{k_{1fwd}}{k_{1rvs}}[Br_2][NO]\right)[NO]$$

$$rate = k_{observed}[Br_2][NO]^2$$

- This results in the experimentally observed rate law.

Another Mechanism Problem… What to do when AP says, "Justify."

- Write the overall reaction represented by the mechanism shown below.
- Determine the rate law for this mechanism *and justify.*
  - ✓ $NO_2 + O_3 \leftrightharpoons NO_3 + O_2$ fast
  - ✓ $NO_3 + NO_2 \rightarrow N_2O_5$ slow

$$2\,NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

- The Quickie Method
  - ✓ $NO_2 + O_3 \rightarrow \cancel{NO_3} + O_2$ fast
  - ✓ $\cancel{NO_3} + NO_2 \rightarrow N_2O_5$ slow
- Cross off the intermediates
- Include the reactants up to and including the slow step.
- Any products before the slow step show up in the denominator
  - ✓ which results in this rate law:

$$rate = k\left[NO_2\right]^2\left[O_3\right]\left[O_2\right]^{-1}$$

  - ✓ *but wait…what's really going on here….*

$2\,NO_2 + O_3 \rightarrow N_2O_5 + O_2$

- Write the rate law for each elementary step
  - ✓ $NO_2 + O_3 \rightarrow NO_3 + O_2$ fast $rate_1 = k_1[NO_2][O_3]$
  - ✓ $NO_3 + NO_2 \rightarrow N_2O_5$ slow $rate_2 = k_2[NO_3][NO_2]$
- If the first step is *not* the rate determining step, the product of the initial fast step will start to build up, and start reversing back into reactant and the first reaction will reach *equilibrium*.
- We can write a rate law for the reverse reaction:
  - ✓ $rate_{rev1} = k_{rev1}[NO_3][O_2]$
  - ✓ since rate fwd = rate reverse, write $k_{fwd1}[NO_2][O_3] = k_{rev1}[NO_3][O_2]$
  - ✓ isolate $[NO_3]$ = $\dfrac{k_{1fwd}}{k_{1rvs}}\dfrac{[NO_2][O_3]}{[O_2]}$
- then substitute into the slow step rate law to eliminate the intermediate
- $rate_2 = k_2[NO_3][NO_2]$ $rate_{rxn2} = k_2[NO_2]\left(\dfrac{k_{1fwd}}{k_{1rvs}}\dfrac{[NO_2][O_3]}{[O_2]}\right)$
  - ✓ which results in this rate law: $rate = k[NO_2]^2[O_3][O_2]^{-1}$
  - ✓ A negative order indicates that with increased O_2, the reaction slows down. O_2 acts as an inhibitor.

Consider the breakdown of ozone

- $2O_3 \rightarrow 3O_2$
- A two step mechanism has been proposed for this reaction
  - ✓ $O_3 \rightarrow O_2 + O$ slow
  - ✓ $O_3 + O \rightarrow 2O_2$ fast
- What is the rate law that corresponds to this mechanism?
- rate = $k[O_3]$

For some other hypothetical Rx: $2X_3 \rightarrow 3X_2$

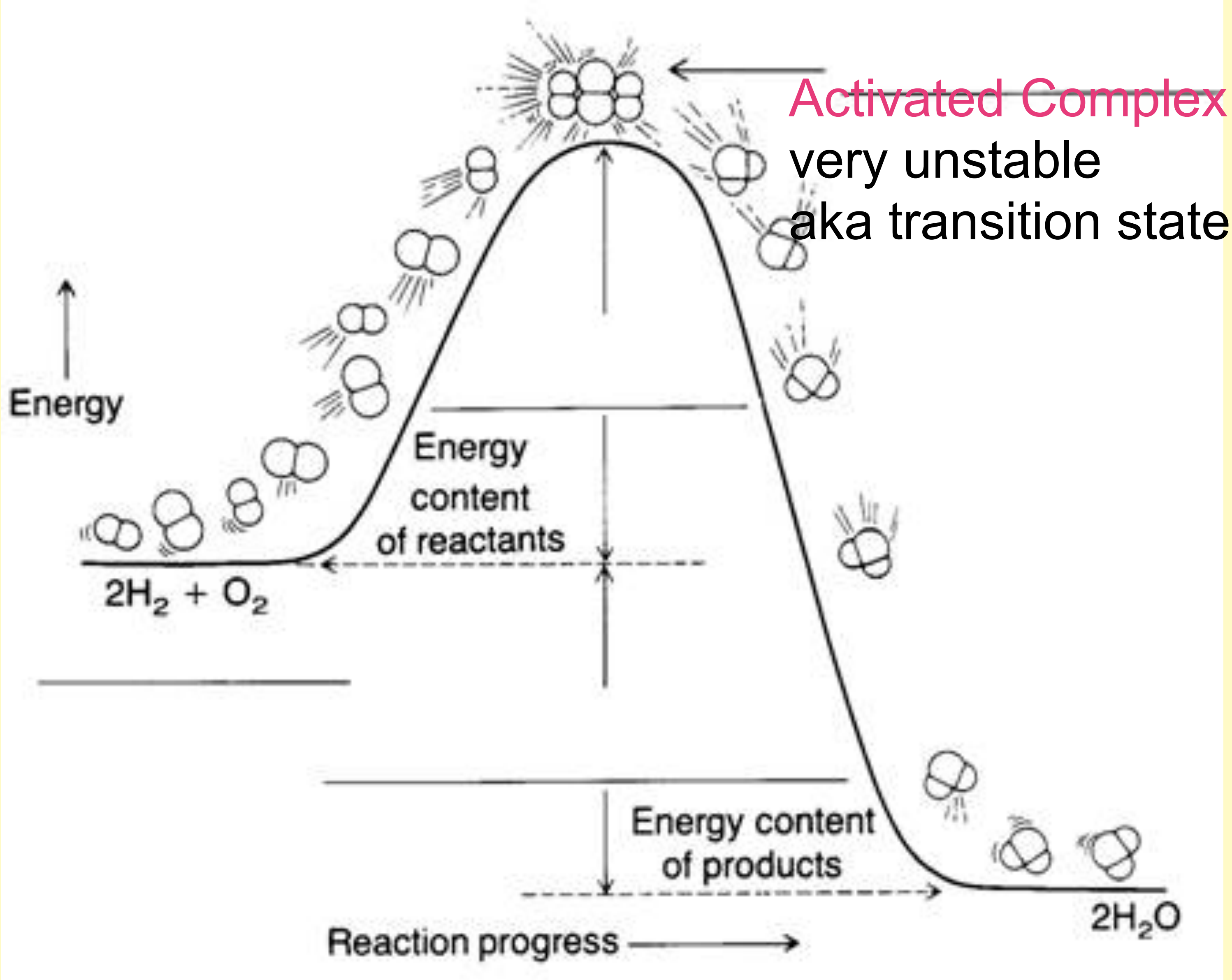
- Write the rate law for each elementary step
  - ✓ $X_3 \rightarrow X_2 + X$ *fast* $k_{1fwd} = [X_3]$
  - ✓ $X_3 + X \rightarrow 2X_2$ *slow* $k_{2fwd} = [X_3][X]$
- If the first step is NOT the rate determining step, the product of the initial fast step will start to build up, and start reversing back into reactant and the first reaction will reach equilibrium.
- We can write a rate law for the reverse reaction:
  - ✓ $k_{1rev} = [X_2][X]$
  - ✓ since rate fwd = rate reverse, then $[X_3] = [X_2][X]$
  - ✓ isolate [X] = $\frac{k_{1fwd}}{k_{1rvs}} \frac{[X_3]}{[X_2]}$
- then substitute into the slow step rate law to eliminate the intermediate
- $k_{2fwd} = [X_3][X]$ $rate_{rxn2} = k_2[X_3]\left(\frac{k_{1fwd}}{k_{1rvs}} \frac{[X_3]}{[X_2]}\right)$
  - ✓ which results in this rate law: $rate = k[X_3]^2[X_2]^{-1}$
  - ✓ A negative order indicates that with increased X_2, the reaction slows down. X_2 acts as an inhibitor.

$$2X_3 \rightarrow 3X_2$$

- Using the Quickie Method to determine the rate law...
  - ✓ $\boxed{X_3} \rightarrow \enclose{circle}{X_2} + \cancel{X}$ fast
  - ✓ $\boxed{X_3} + \cancel{X} \rightarrow 2X_2$ slow
- Cross off the intermediates
- Include the reactants up to and including the slow step.
- Put any products before the slow step in the denominator
  - ✓ which results in this rate law:

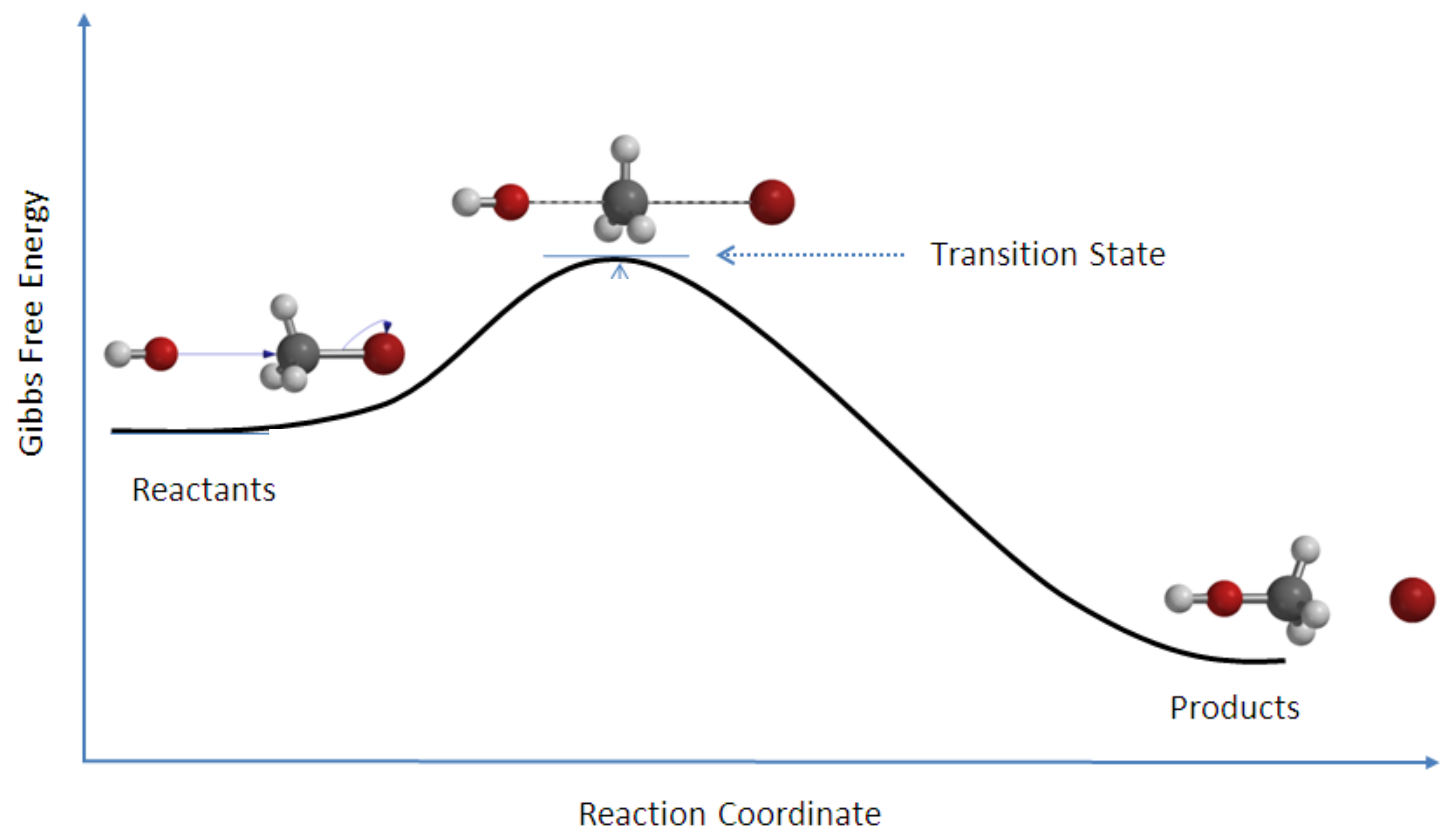
$$rate = k\left[X_3\right]^2\left[X_2\right]^{-1}$$

Reactants - Activated Complex - Products



Activated Complex
very unstable
aka transition state

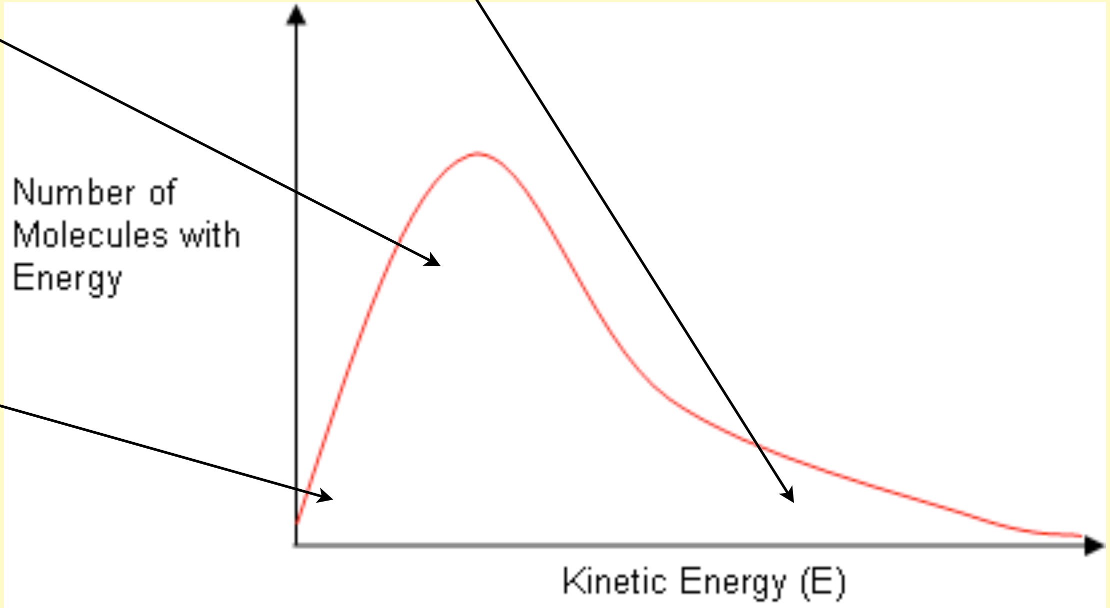
Reactants - Activated Complex - Products



Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$

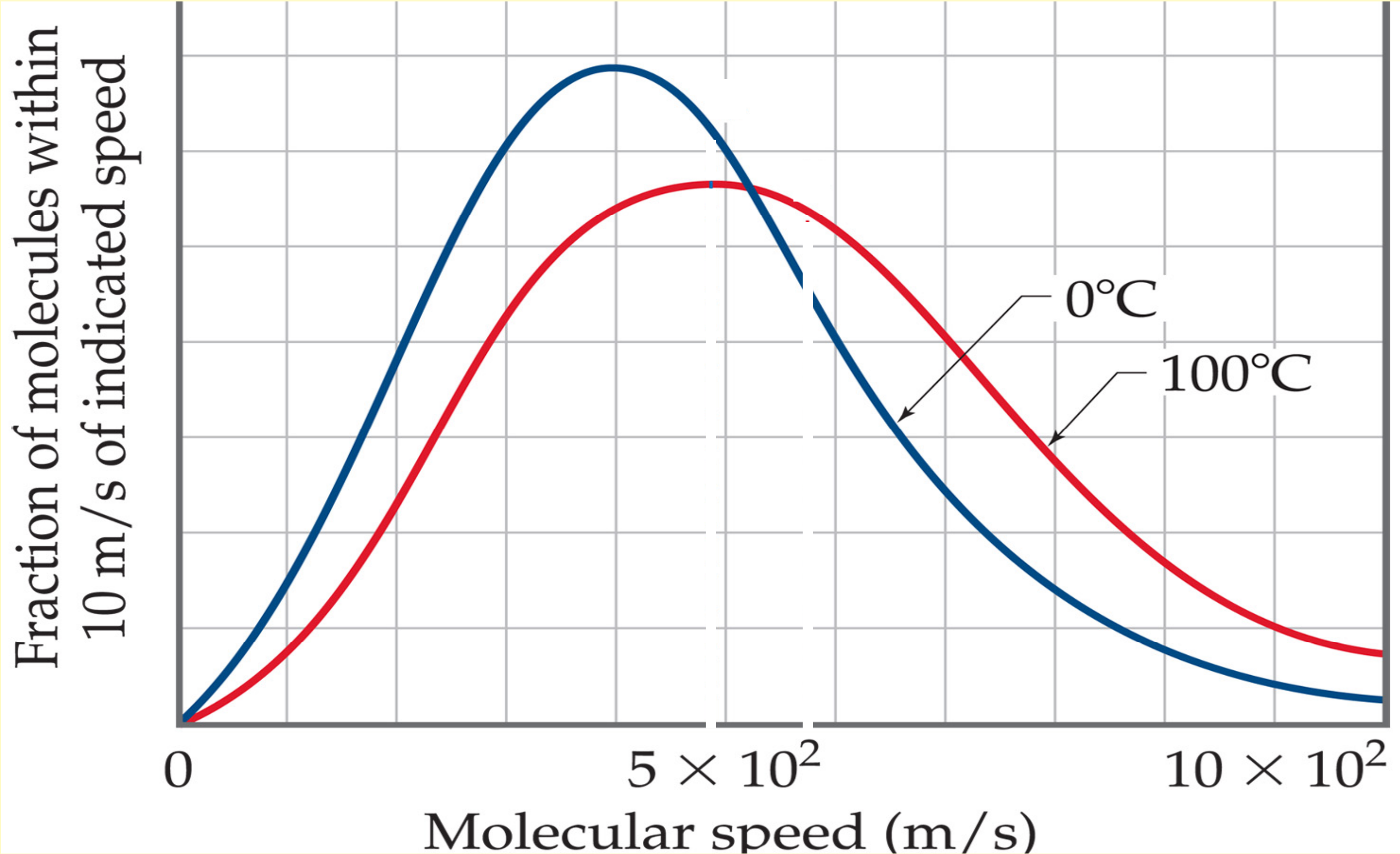
Boltzmann Distribution Curve

- The area under each curve represents all the molecules in the sample.
- A few molecules move faster.
- Lots of molecules move slower.
- A few molecules move very slowly



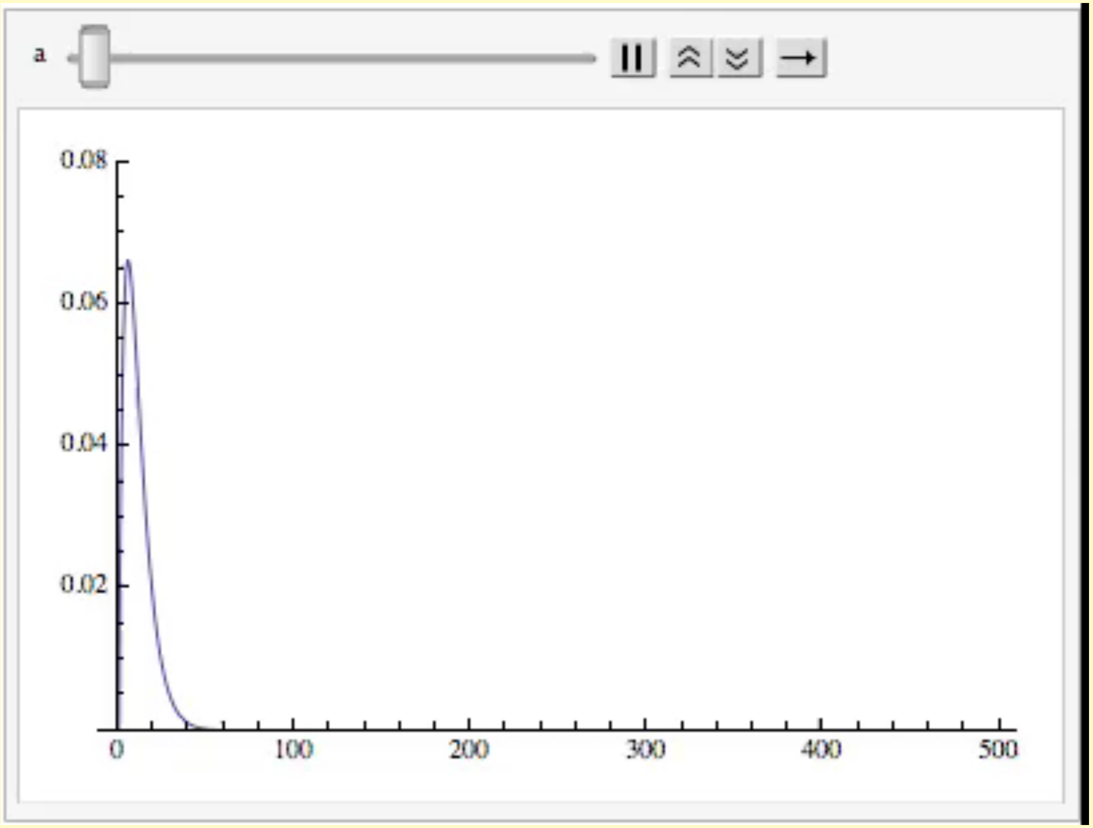
Boltzmann Distribution Curve

- When the temperature of the sample is increased,
  - ✓ the curve shifts right.
  - ✓ The curve drops lower because the number of molecules in the sample remains the same.



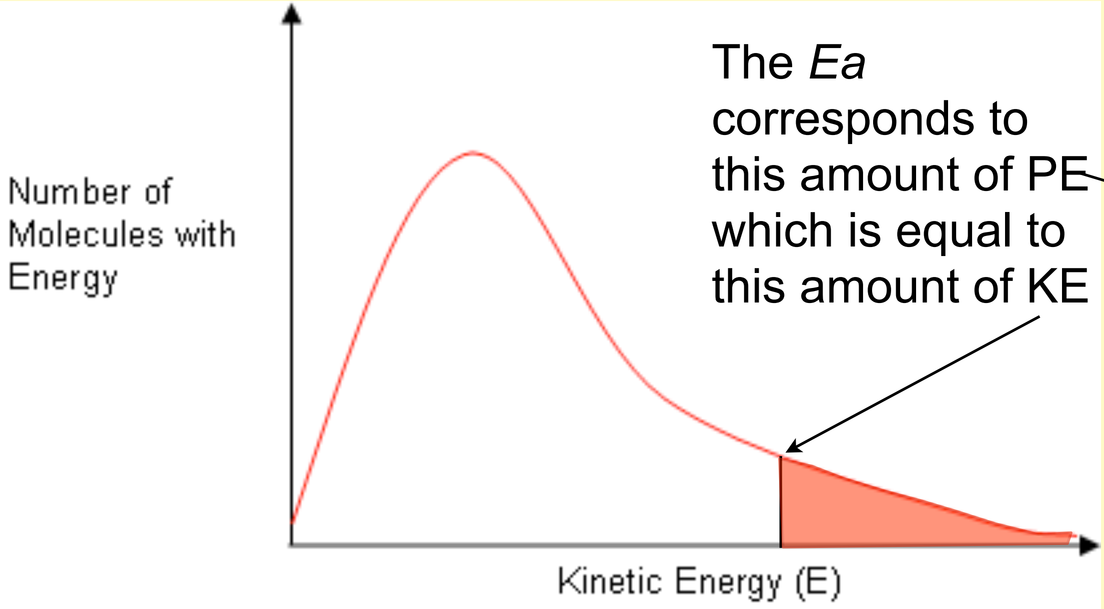
Boltzmann Distribution Curve

- Observe the shape of the curve at different temperatures.

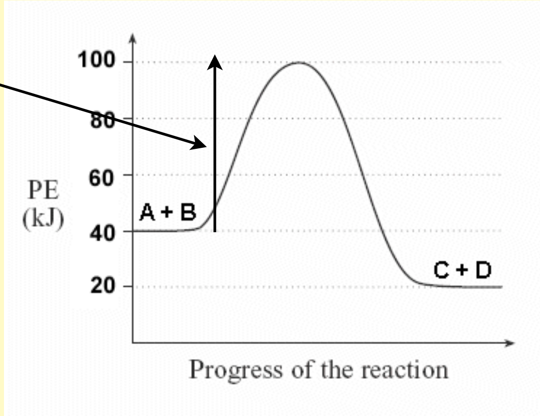


Boltzmann Distribution Curve as related to Potential Energy Curve

- The vertical lines represent the activation energy, E_a, required by the reaction.
- The area to the right of the E_a line represents the number of molecules with enough energy to make it over the energy hump.

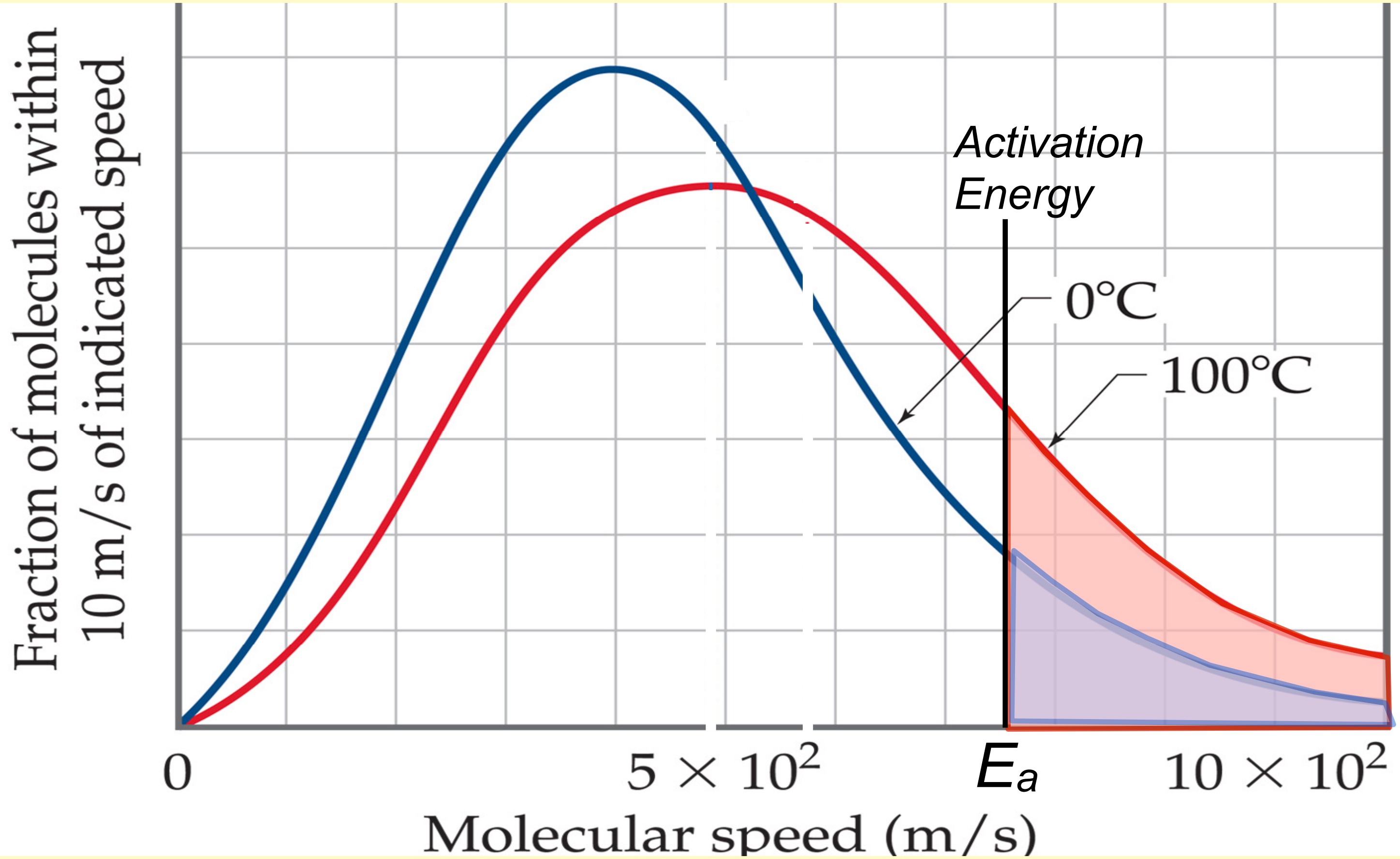


The *Ea* corresponds to this amount of PE which is equal to this amount of KE



Boltzmann Distribution Curve

- A particular activation energy is required for the reaction.
- All the crashes of a particular speed, KE will have enough energy to react.
- When the temperature of the sample is increased, more molecules meet the minimum temperature required for a successful reaction.



Whew...that’s all for now.

more tomorrow...

Let’s take a look at FR #3 part (e)

- Quickie method won’t work for this one!
- We end up with an intermediate still in the rate law

Step 1	Cl_2	→	$\cancel{2}\,Cl$	*fast equilibrium*
Step 2	$CH_4 + \cancel{Cl}$	→	$CH_3 + HCl$	*slow*
Step 3	$CH_3 + Cl_2$	→	$CH_3Cl + Cl$	*fast*
Step 4	$CH_3Cl + Cl$	→	$CH_2Cl_2 + H$	*fast*
Step 5	$H + Cl$	→	HCl	*fast*

- rate = $[Cl_2]\,[CH_4]\,[Cl]^{-1}$
- Leaving a intermediate in the rate law
- Try it, using the equilibrium method.

Let’s take a look at FR #4 part (e)

- Quickie method won’t work for this one!
  - ✓ We need to use the equilibrium method.
- Determine the order with respect to Cl_2 and CH_4

Step 1	Cl_2	→	2 Cl	*fast equilibrium*
Step 2	CH_4 + Cl	→	CH_3 + HCl	*slow*
Step 3	CH_3 + Cl_2	→	CH_3Cl + Cl	*fast*
Step 4	CH_3Cl + Cl	→	CH_2Cl_2 + H	*fast*
Step 5	H + Cl	→	HCl	*fast*

$$rate_{1fwd} = k_{1fwd}\left[Cl_2\right] \qquad rate_{1rvs} = k_{1rvs}\left[Cl\right]^2 \qquad k_{1fwd}\left[Cl_2\right] = k_{1rvs}\left[Cl\right]^2 \qquad \left[Cl\right] = \left(\frac{k_{1fwd}}{k_{1rvs}}\left[Cl_2\right]\right)^{\frac{1}{2}}$$

substitute

$$rate = k_{2fwd}\left[CH_4\right]\left[Cl\right]$$

$$rate = k_{2fwd}\left[CH_4\right]\left[\left(\frac{k_{1fwd}}{k_{1rvs}}\left[Cl_2\right]\right)^{\frac{1}{2}}\right] \qquad rate = k\left[CH_4\right]\left[Cl_2\right]^{\frac{1}{2}}$$

Assume a reaction occurs by the mechanism given below. What is the rate law for the reaction?

$A + B \rightleftarrows C$ fast

$C + B \rightarrow D$ slow

1. Rate = k [A] [B] [C]
2. Rate = k $[A]^2$
3. Rate = k [A] $[B]^2$
4. Rate = k [A] [B]
5. Rate = k [A] [B] / [D]
6. Rate = k [A]
7. Rate = k [C]

Assume a reaction occurs by the mechanism given below. What is the rate law for the reaction? *(Select all that apply.)*

$A + B \rightleftarrows C$ fast
$C + B \rightarrow D$ slow

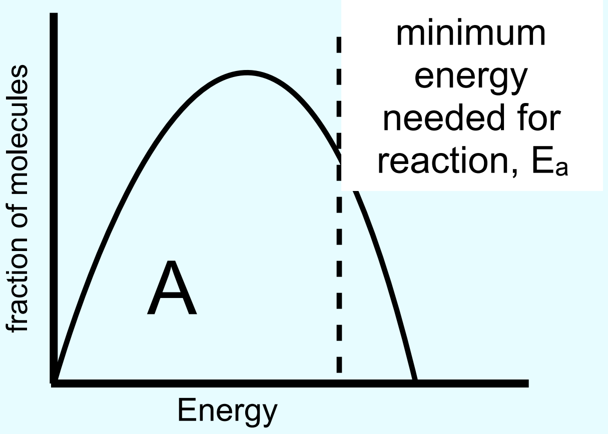
1. Remember, the slow step is the rate determining step. rate = $k_s[C][B]$
2. But we would prefer not to have intermediates in the rate law.
3. *ANSWER - Rate = $k\,[A]\,[B]^2$*

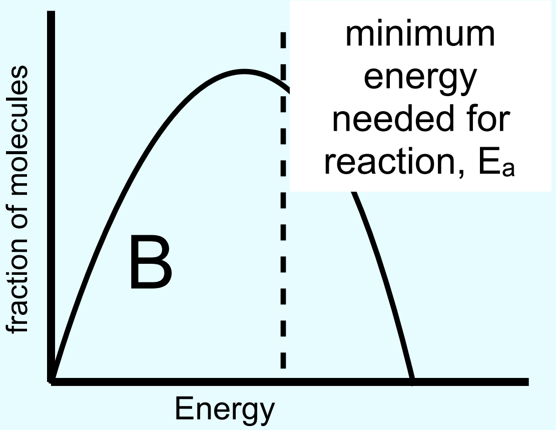
- $A + B \rightleftarrows \cancel{C}$ fast
- $\cancel{C} + B \rightarrow D$ slow

Cancel out the intermediates, then gather what's left.

- so $\text{rate}_{\text{overall}} = k[A][B]^2$

What could cause the change from A to B in the kinetic energy diagram shown? aka Boltzmann Distribution Curve *(Select all that apply.)*

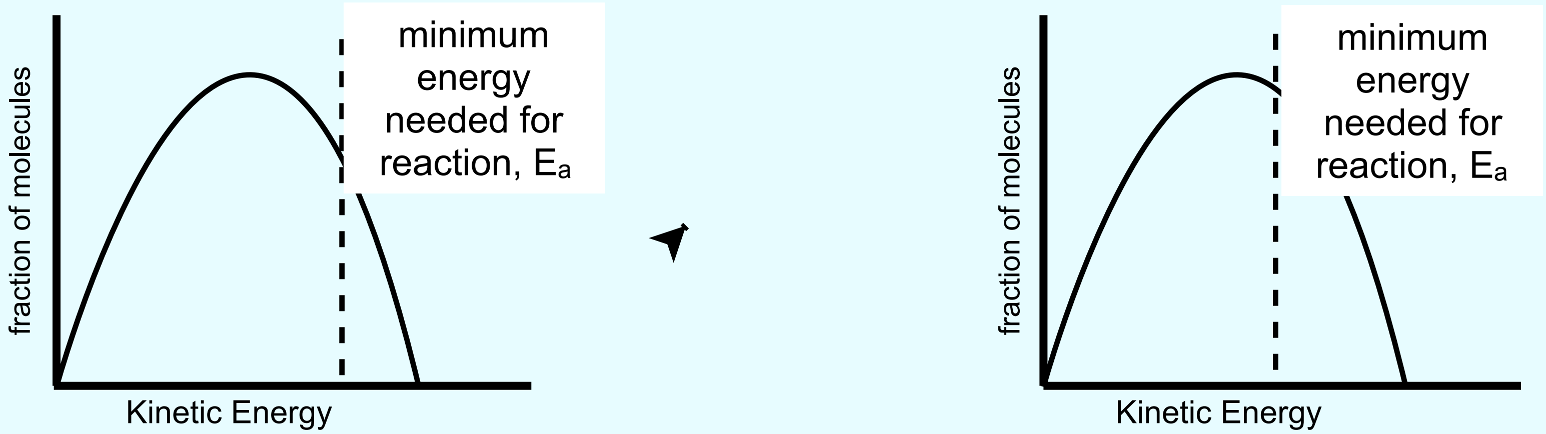




1. increasing the temperature
2. increasing the surface area of the reactants
3. addition of a catalyst
4. removal of a catalyst
5. increasing the concentration of a reactant
6. none of the above could cause this change

What could cause the change from A to B in the kinetic energy diagram shown?

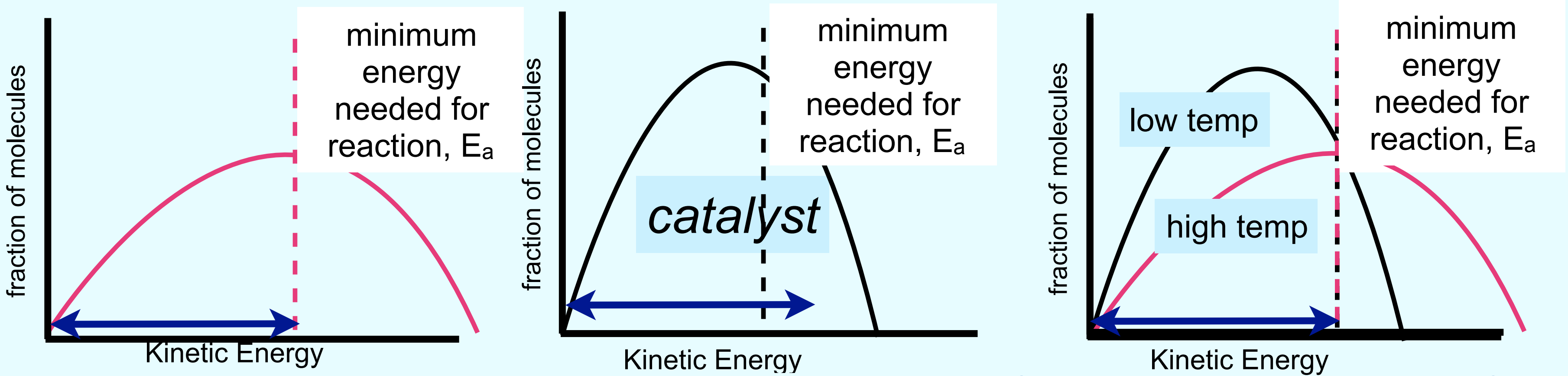
(Select all that apply.)



1. decreasing the temperature
2. increasing the surface area of the reactants
3. addition of a catalyst
4. removal of a catalyst
5. increasing the concentration of a reactant
6. none of the above could cause this change

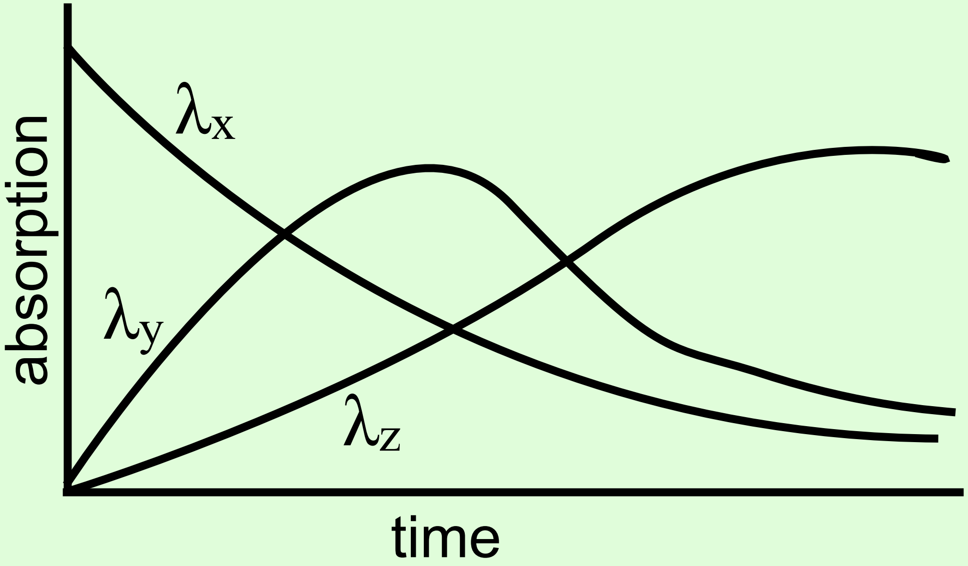
- The presence of a catalyst is the only factor that actually changes the E_a.
- What role does temp play?....see next slide

What could cause the change in the kinetic energy diagram shown? *(Select all that apply.)*



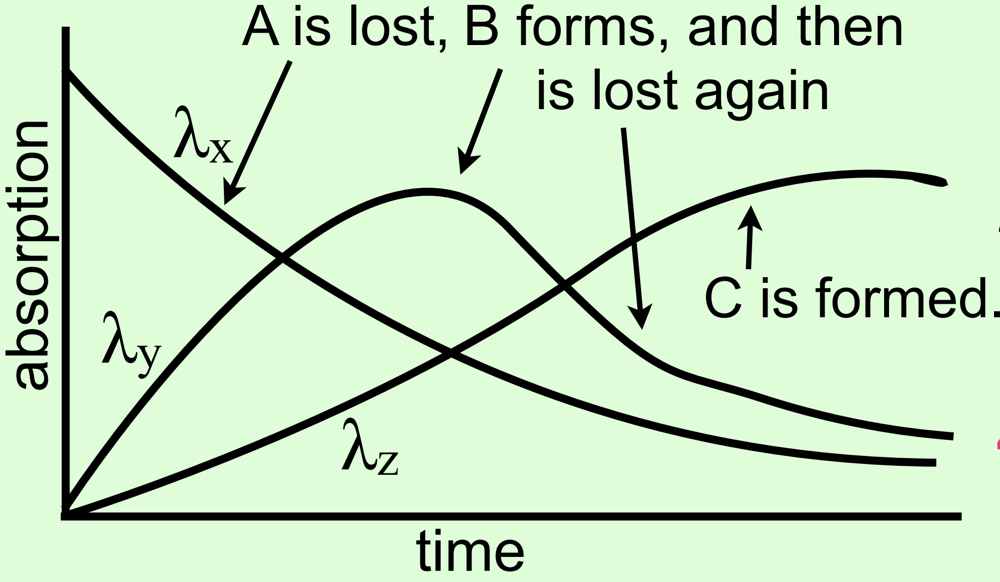
- *Increasing* temp would cause the line to *appear* as if the activation energy shifts as in the second graph, but temp does not change the value of E_a.
- At higher temperatures, the curve to elongates and flattens resulting in more molecules able to achieve the minimum E_a.
- In the second graph, the E_a value is incorrectly represented as shifted left (smaller) as evidenced by the blue arrow, which is the same length in the first graph to show the lower E_a
- In the third graph, the high temp change graph is overlaid a low temp graph to show its effect.
- So increasing temperature will increase the *number* of molecules that have the minimum activation energy, but not actually change the value of E_a.

Different molecules each absorb at particular wavelengths. The rate of a reaction was followed by the absorption of light by the reactants and products at each of their absorbing wavelengths (λ_x, λ_y, λ_z) as time progresses. Which of the following mechanisms is consistent with the experimental absorption data?



1. $A \rightarrow B$, $A \rightarrow C$
2. $A \rightarrow B + C$
3. $A \rightarrow B$, $B \rightarrow C + D$
4. $A \rightarrow B$, $B \rightarrow C$

Different molecules each absorb at particular wavelengths. The rate of a reaction was followed by the absorption of light by the reactants and products at each their absorbing wavelengths (λ_x, λ_y, λ_z) as time progresses. Which of the following mechanisms is consistent with the experimental absorption data?



1. $A \rightarrow B$, $A \rightarrow C$
2. $A \rightarrow B + C$
3. $A \rightarrow B$, $B \rightarrow C + D$
4. $A \rightarrow B$, $B \rightarrow C$

Which of the following increase the rate of reaction involving a solid *(Select all that apply.)*

1. adding more of the solid
2. increasing the temperature
3. adding a catalyst
4. increasing the surface area of the solid

Which of the following increase the rate of reaction involving a solid

1. adding more of the solid
2. increasing the temperature
3. adding a catalyst
4. increasing the surface area of the solid

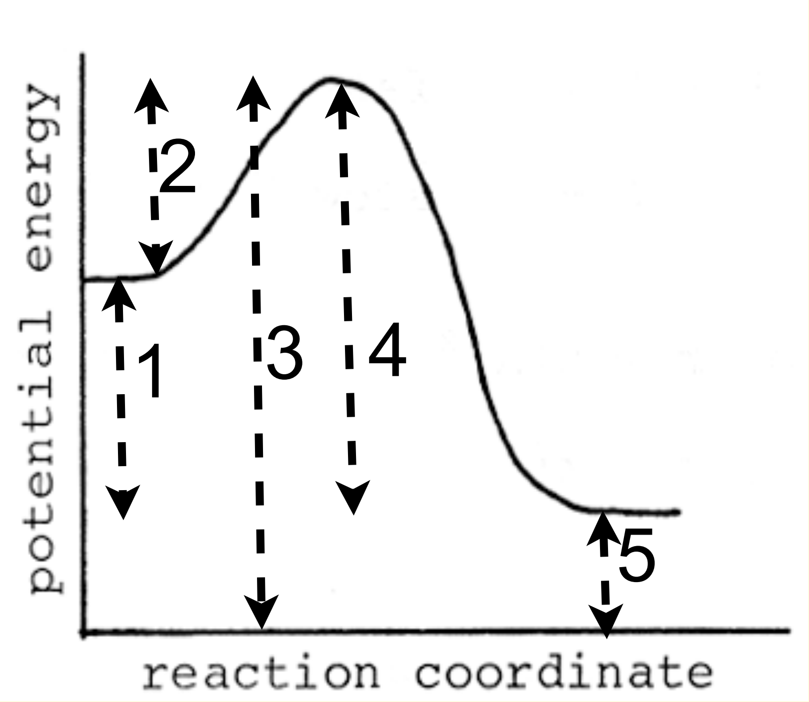
Which of the following is true about a catalyst? *(Select all that apply.)*

1. It speeds up the forward reaction
2. It lowers the activation energy
3. It provides a different mechanism for the reaction
4. It can act as an inhibitor
5. It speeds up the reverse reaction
6. Can be homogeneous or heterogeneous
7. It does not get used up over the course of the reaction.
8. It can also be called an enzyme
9. Helps the formation of intermediates.

Which of the following is true about a catalyst? *(Select all that apply.)*

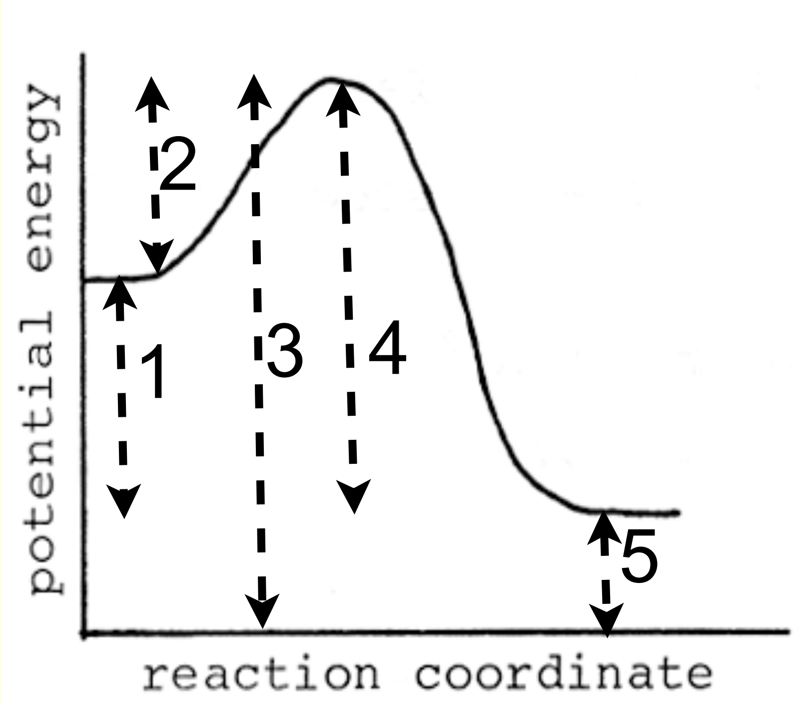
1. It speeds up the forward reaction
2. It lowers the activation energy
3. It provides a completely different mechanism for the reaction
4. It can act as an inhibitor
    - I suppose this could be true if such a large excess amount were present, and began to disrupt the reaction
5. It speeds up the reverse reaction
6. Can be homogeneous or heterogeneous
7. It does not get used up over the course of the reaction.
8. It can also be called an enzyme
    - for a biological reaction
9. Helps the formation of intermediates.

What number corresponds to the activation energy for the reaction: X → Y

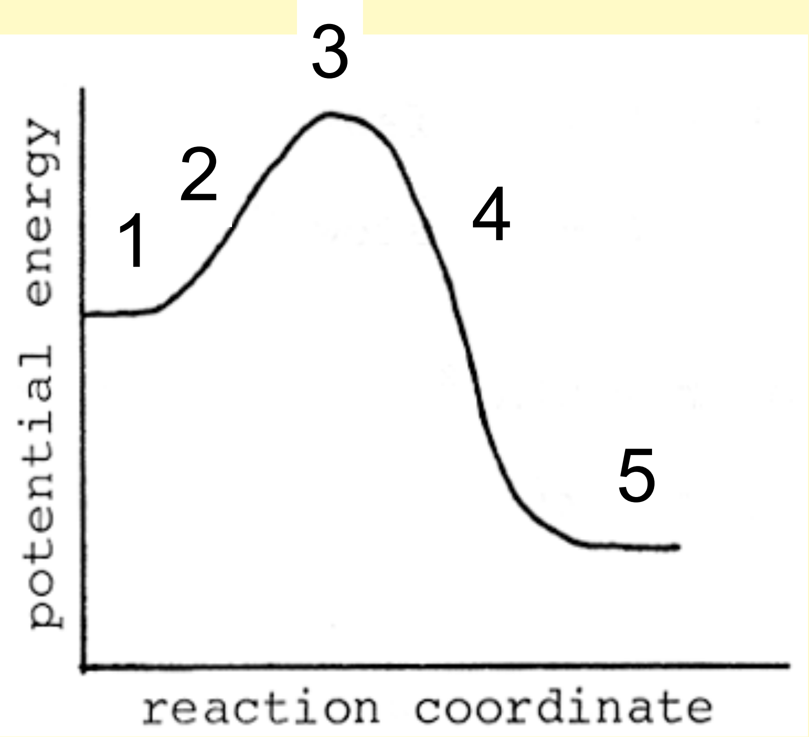


What number corresponds to the activation energy for the reaction: X → Y

- #2
- The activation energy is the difference between the reactant energy and the top of the curve.

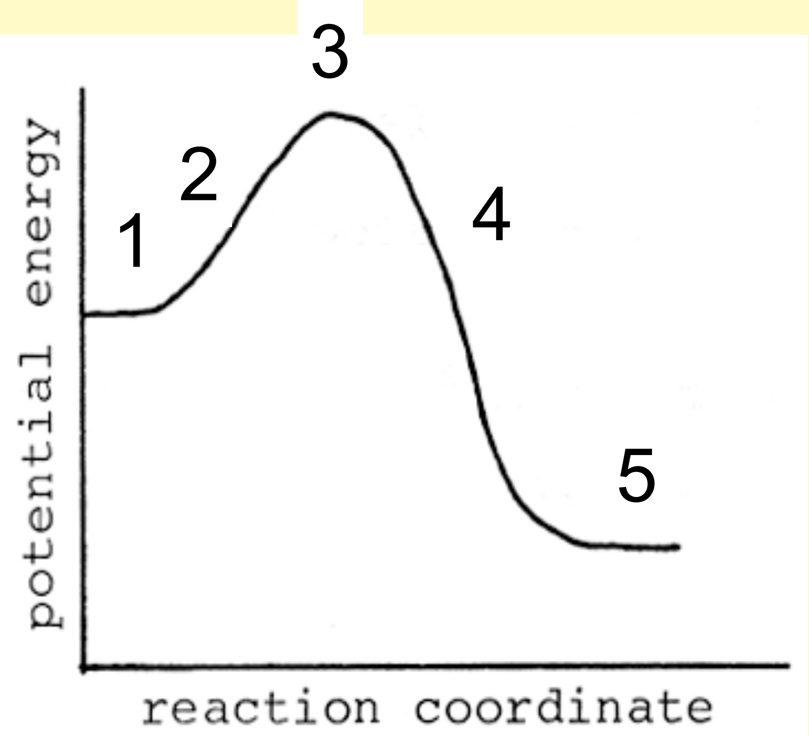


At what point on the potential energy diagram does the activated complex occur?

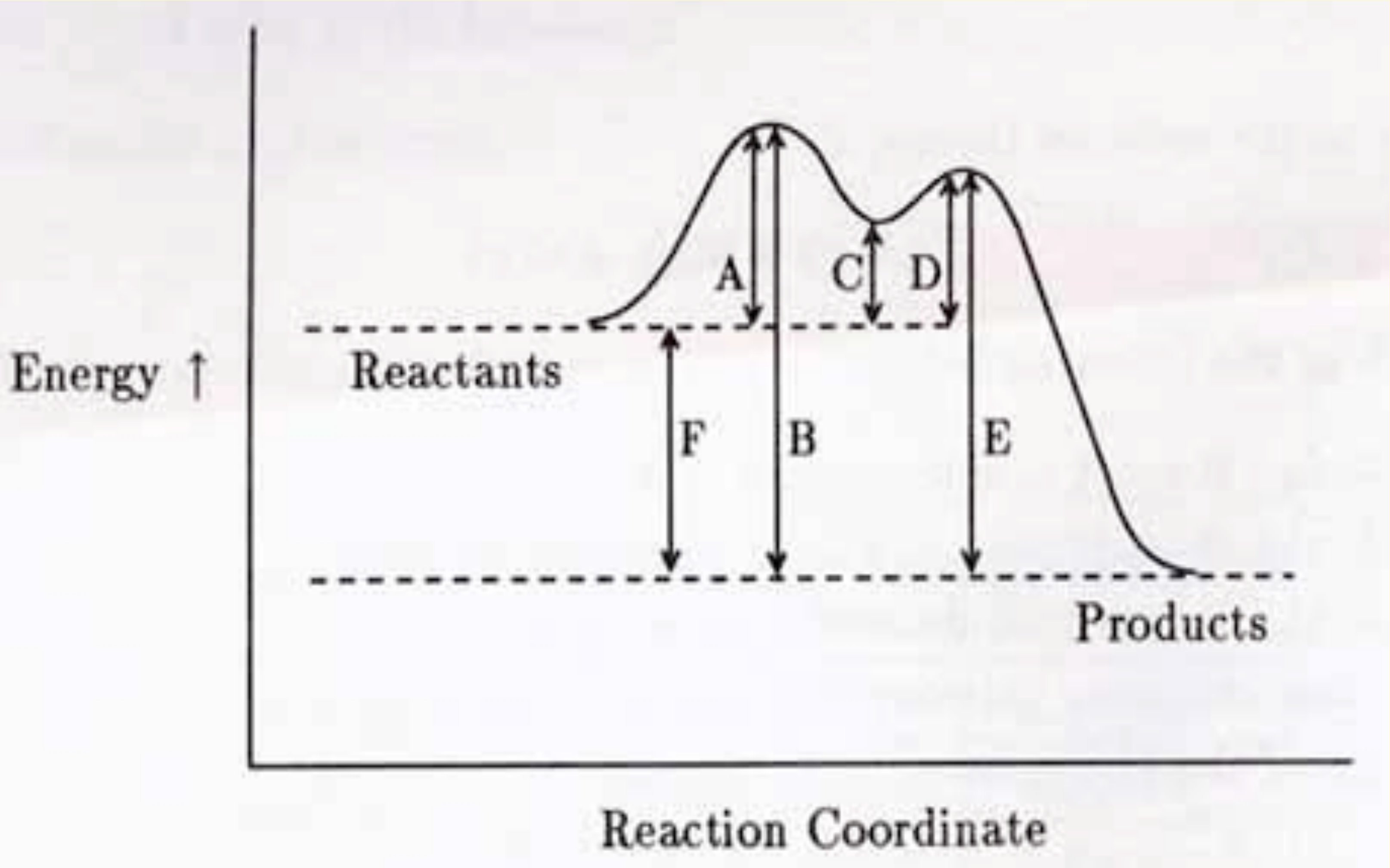


At what point on the potential energy diagram does the activated complex occur?

- # 3
- The transition state that occurs at the top of the energy barrier in between the reactants and products is called the activated complex.

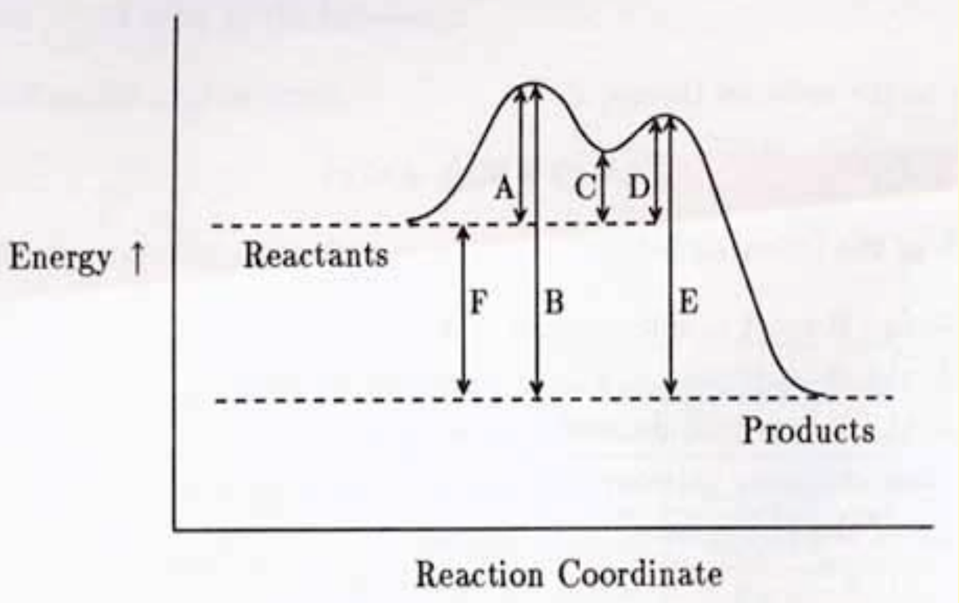


How many steps are involved in the reaction mechanism for the reaction indicated by the energy diagram below.



How many steps are involved in the reaction mechanism for this reaction indicated by the energy diagram below.

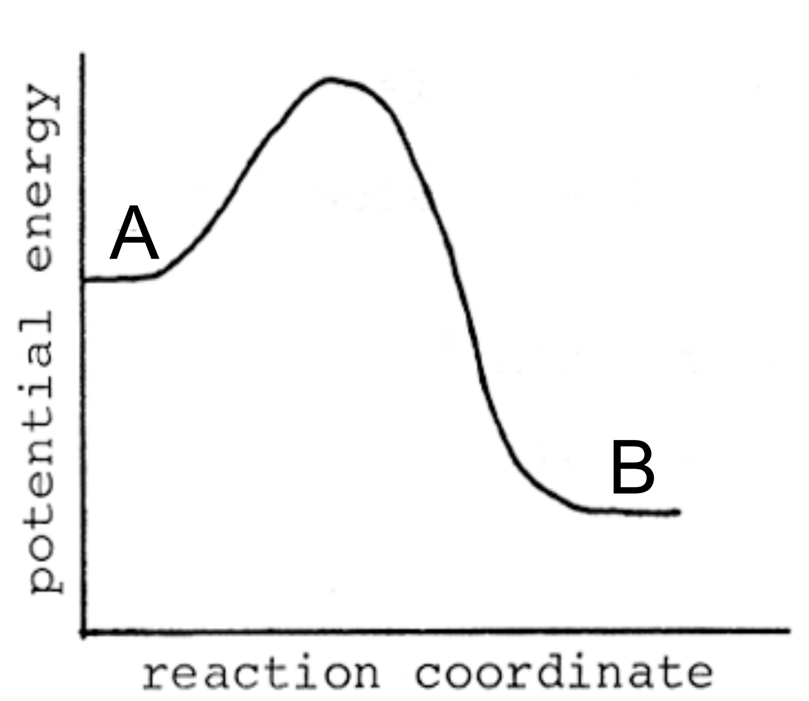
- 2 steps
- The presence of two peaks on the graph that represents the reaction mechanism indicates a two step process.



Addition of a catalyst that speeds the forward reaction will also speed the reverse reaction.

1. True
2. False
3. can not be determined

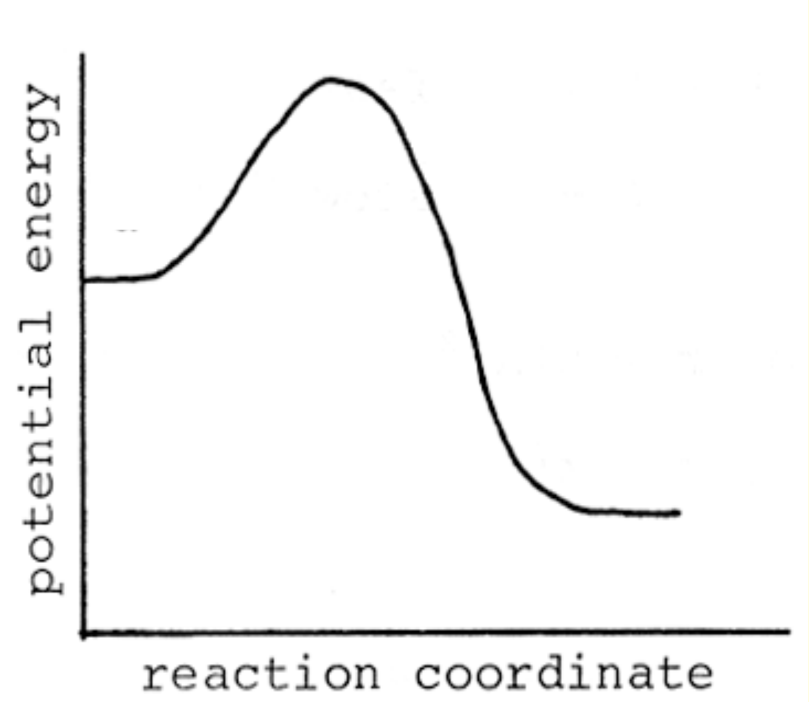
A → B



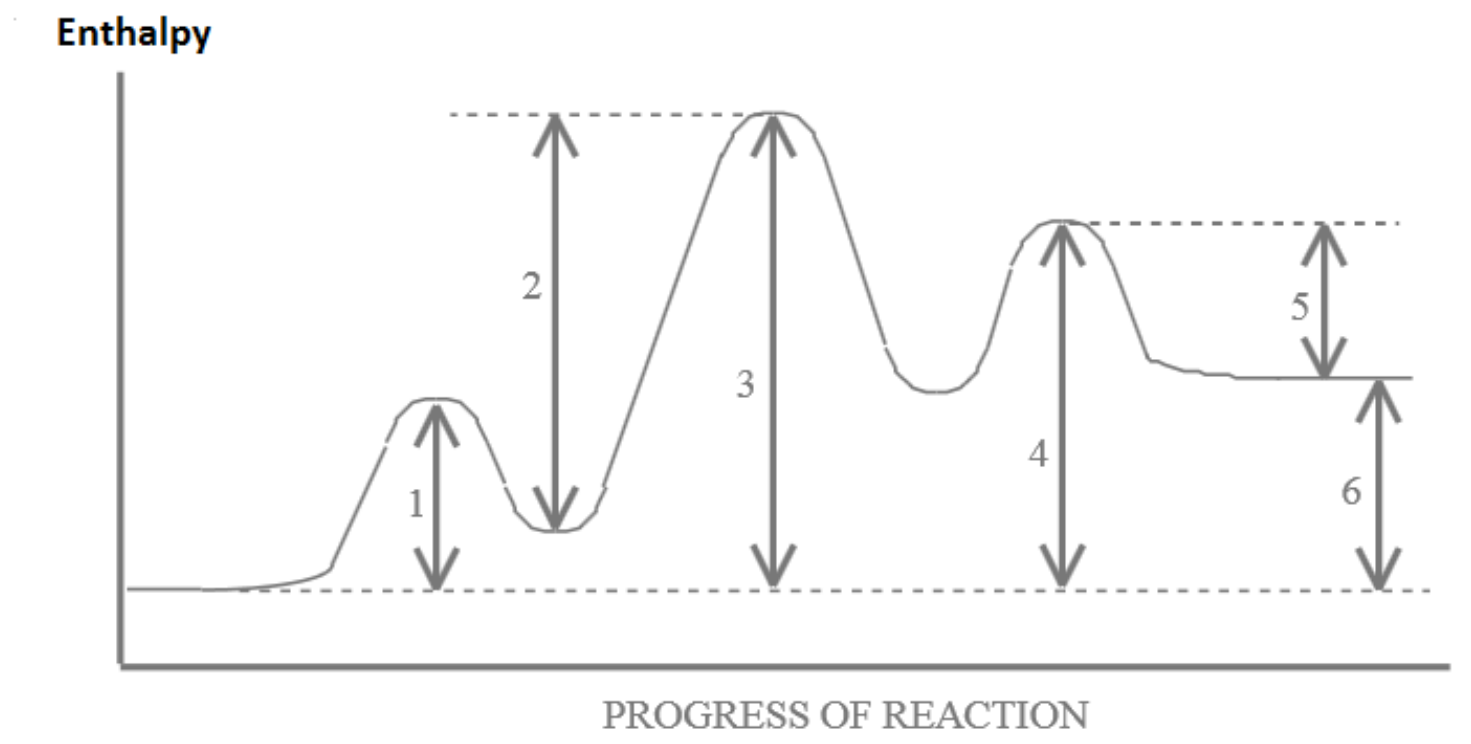
Addition of a catalyst that speeds the forward reaction will also speed the reverse reaction.

1. True
2. False
3. can not be determined

- Catalysts *generally* provide a completely different mechanism, lowering the overall reaction rate.
- This affects both the forward and the reverse as the highest activation energy will be lowered

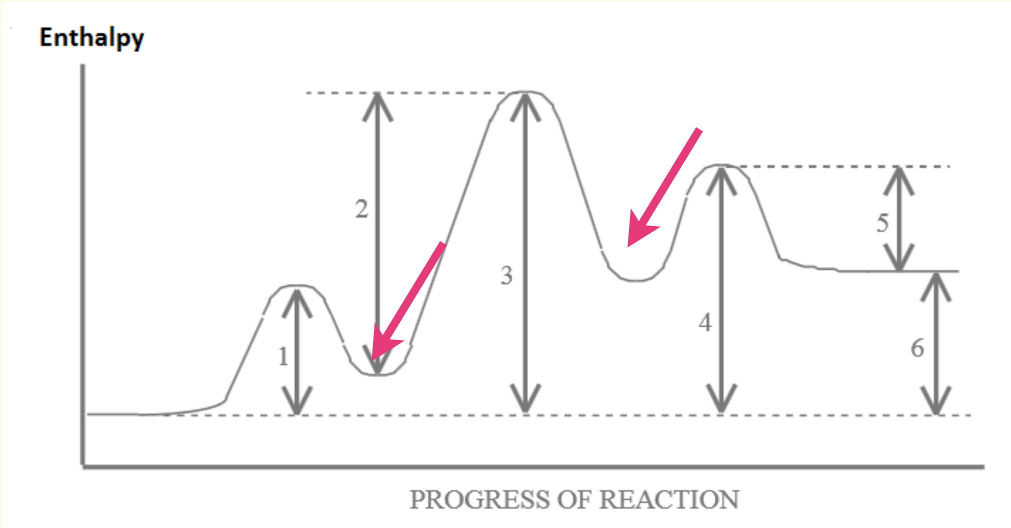


How many reaction intermediates are involved in the reaction indicated in the energy diagram below?



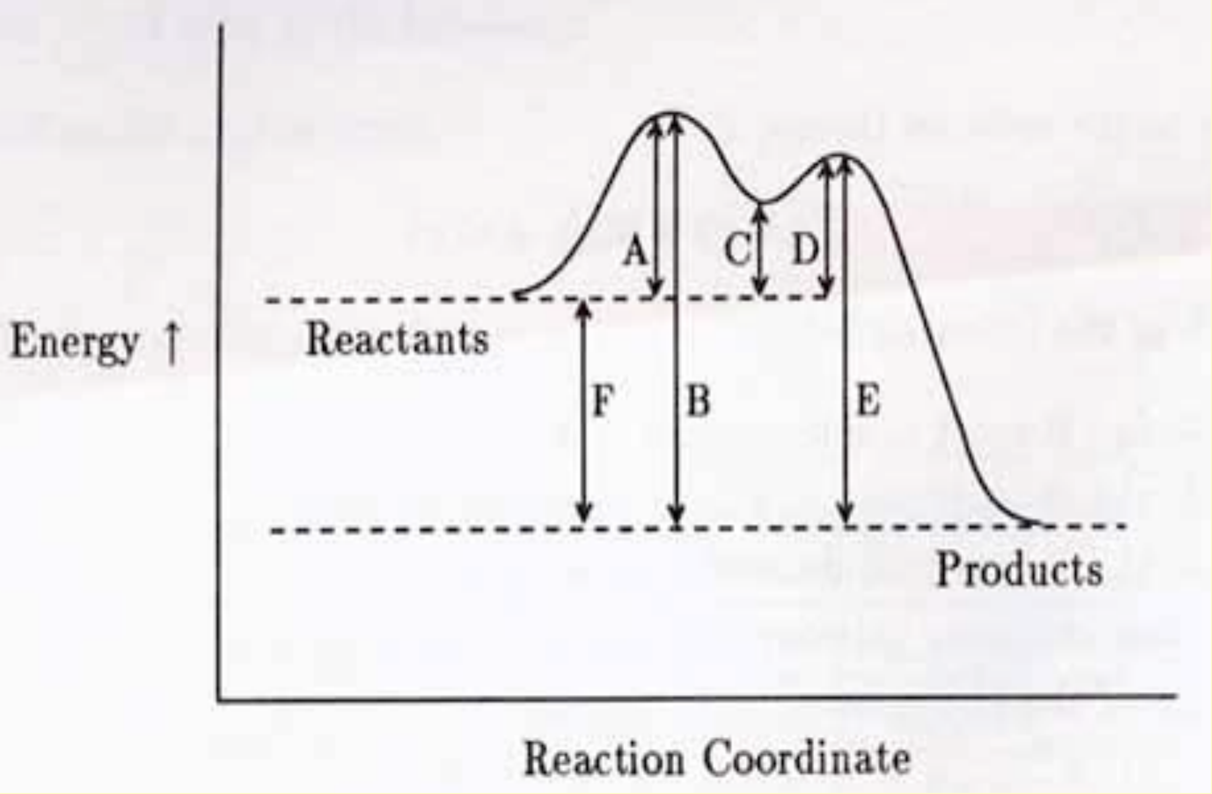
How many reaction intermediates are involved in the reaction indicated in the energy diagram below?

- 2
- The trough in between the three peaks represents the intermediate.



The energy diagram indicates that the second elementary step is the rate determining step.

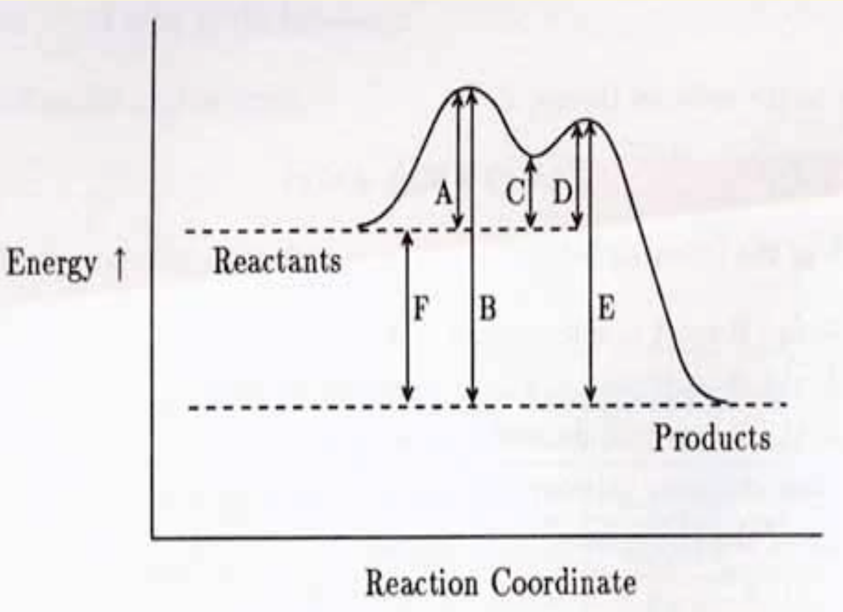
1. True
2. False
3. can not be determined



The energy diagram indicates that the second elementary step is the rate determining step.

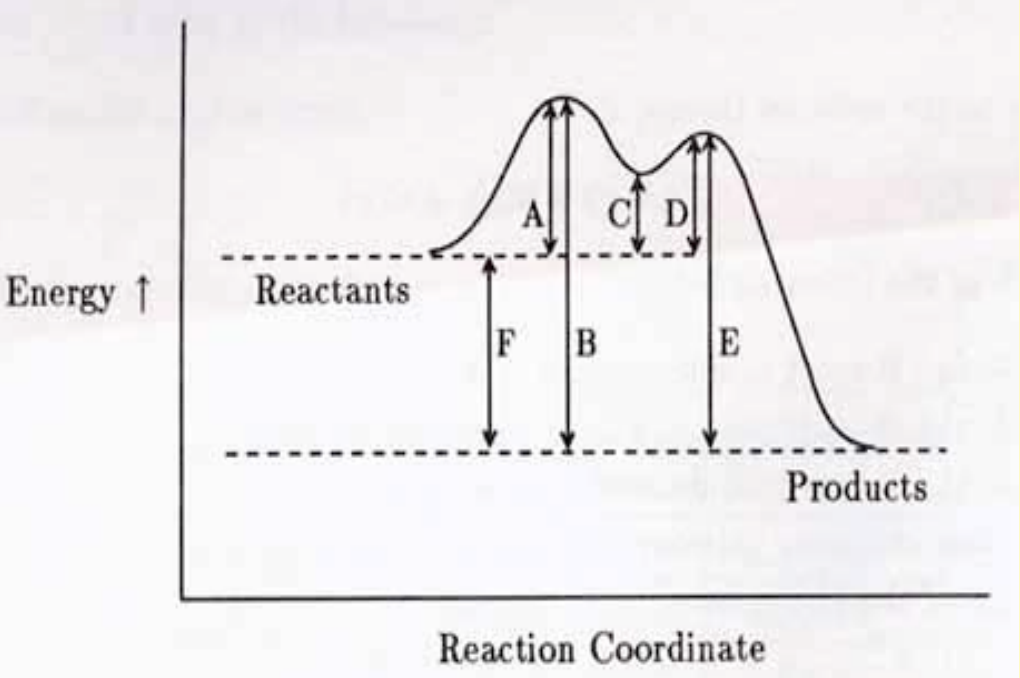
1. True
2. False
3. can not be determined

- The rate determining step would be the step with the highest activation energy which is the first peak.



The energy diagram indicates that the reaction is second order.

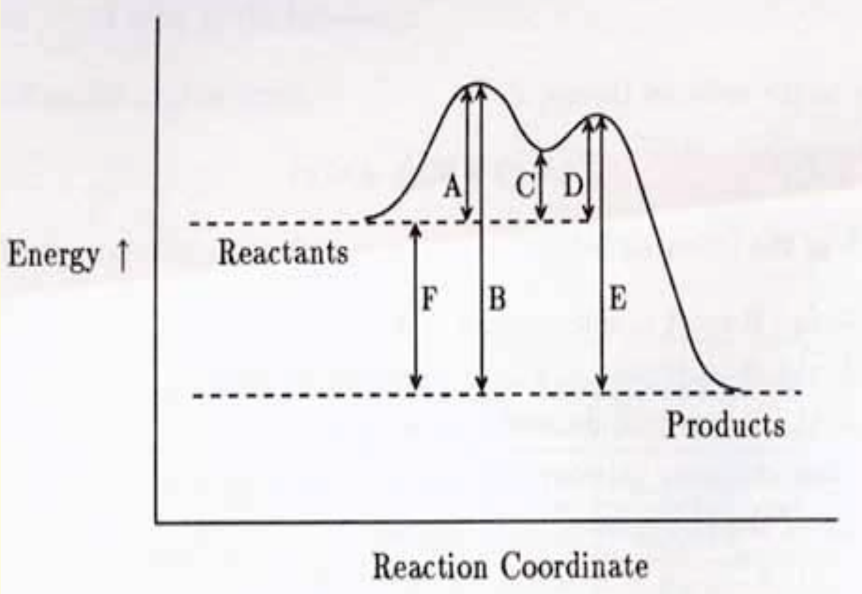
1. True
2. False, some other order
3. False, and the order can not be determined from the information given



The energy diagram indicates that the reaction is second order.

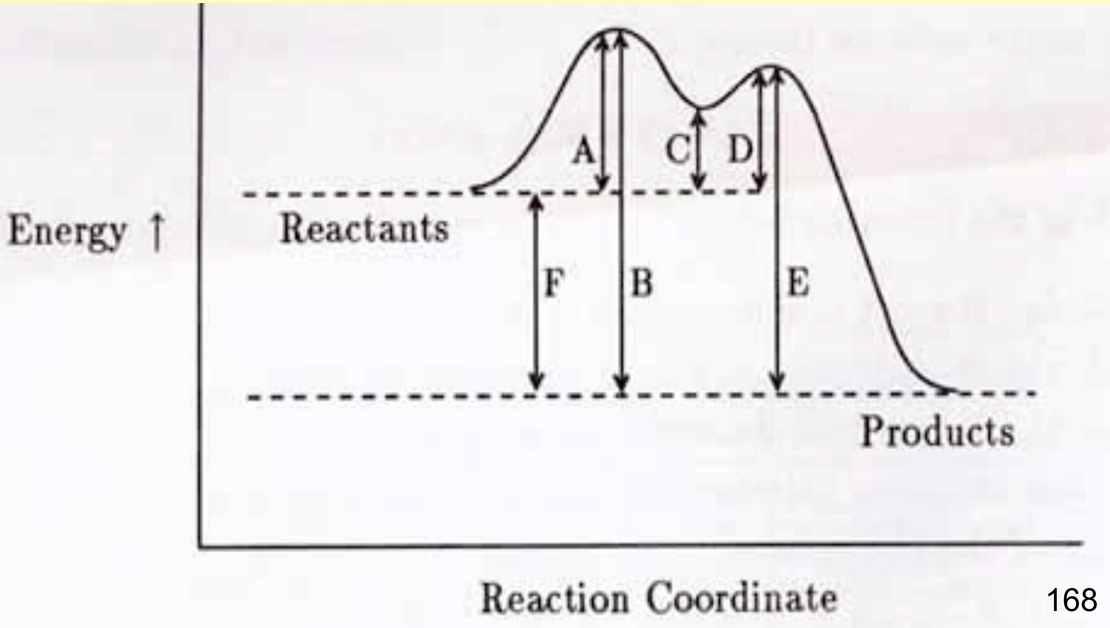
1. True
2. False
3. can not be determined

- The order of the reaction can not be determined from the potential energy diagram.



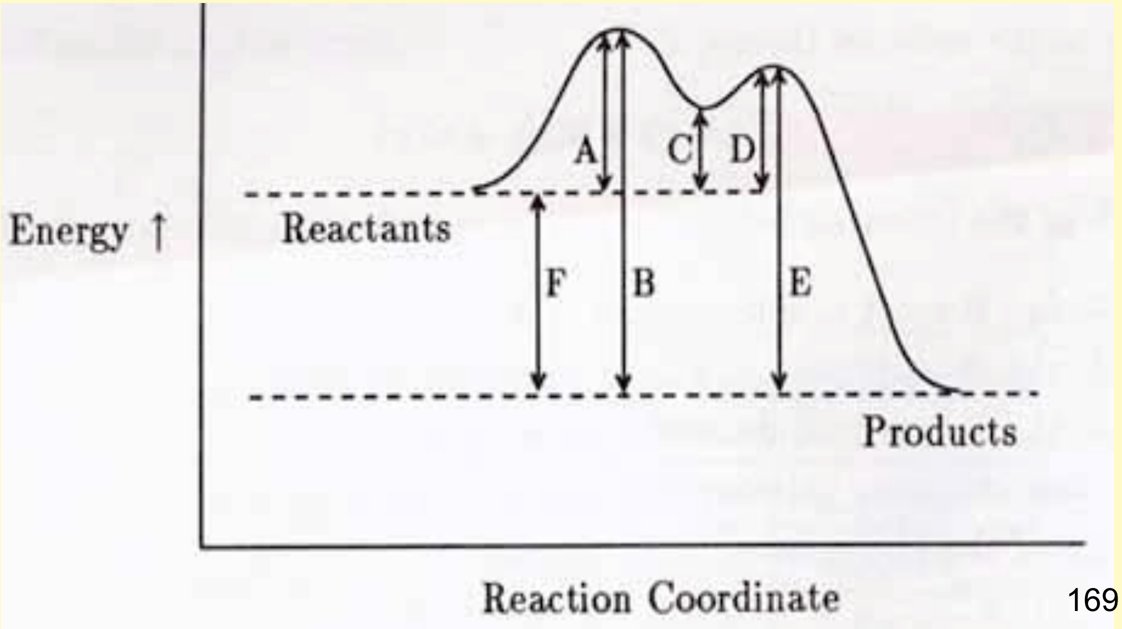
The overall reaction is

1. exothermic, Δ E released = E
2. exothermic, Δ E released = B
3. exothermic, Δ E released = F
4. endothermic, Δ E absorbed = A
5. endothermic, Δ E absorbed = B
6. endothermic, Δ E absorbed = F
7. some other energy value not listed above
8. can not be determined



The overall reaction is

1. exothermic, Δ E released = E
2. exothermic, Δ E released = B
3. exothermic, Δ E released = F
4. endothermic, Δ E absorbed = A
5. endothermic, Δ E absorbed = B
6. endothermic, Δ E absorbed = F
7. some other energy value not listed above
8. can not be determined



Activation Energy

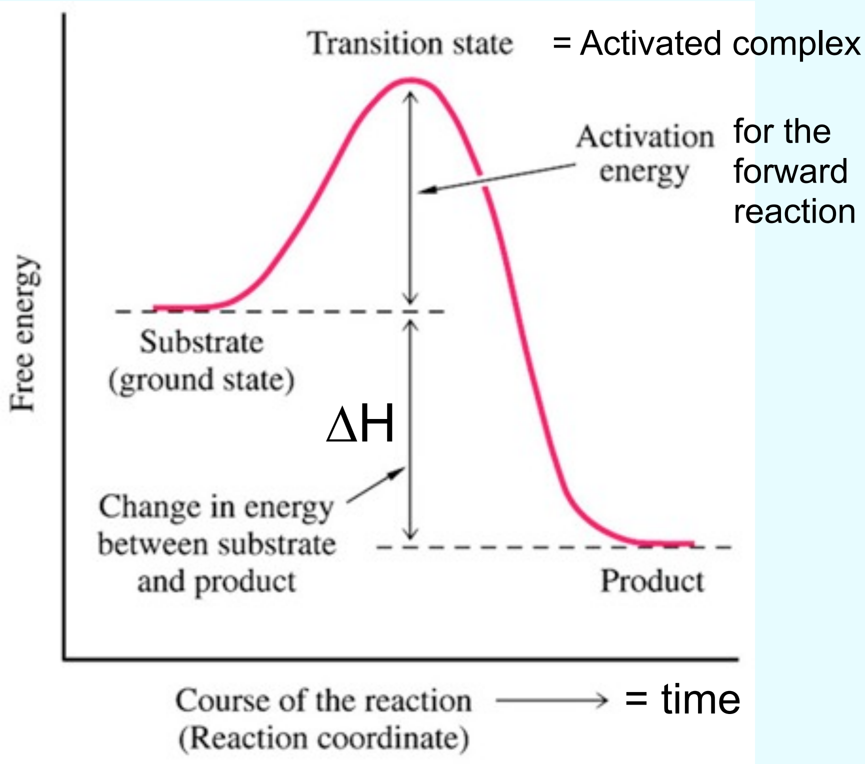
Arrhenius Equation
Climbing up over the energy hump.
This is no longer part of the AP Curriculum

Activation Energy

- As you know, for reactions to occur, the reactants must collide with enough force and appropriate orientation.
- The minimum energy needed to initiate a reaction is called the activation energy E_a
- As molecules collide, the “smooshed” together “thing” is called the *activated complex* or *transition state*.
- It is the “thing” that exists at the top of the hump on an energy profile graph (aka energy diagram).

Energy Profile Graphs

- As the reactants crash and turn into products, the molecules pass through an activated complex at the top of the graph.
- E_a represents the activation energy.



- ΔH represents the net energy released.
- The fraction (f) of molecules that have an energy equal to or greater than E_a can be represented by
  - ✓ $f = e^{-Ea/RT}$
- In 1888, Arrhenius determined that the increase in rate with increase in temp is nonlinear. He turned the previous equation into
  - ✓ $k = Ae^{-Ea/RT}$

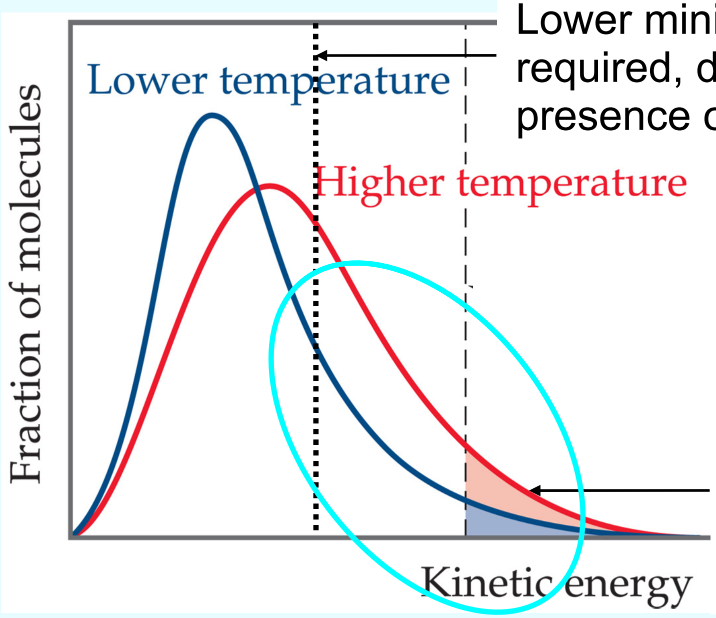
more info on next slide

Arrhenius Equation

- $k = Ae^{-Ea/RT}$
  - ✓ k is the rate constant
  - ✓ A is the frequency factor which is nearly constant even at different temperatures.
  - ✓ E_a is the activation energy
  - ✓ R is the gas constant, 8.31 J/mole K
  - ✓ T is temperature in Kelvin
- As the magnitude of E_a increases, the value of k, and therefore reaction rate, decreases because the number of collisions that achieve the larger E_a energy decreases.

Temperature and Activation Energy

- Temp is a measure of the Kinetic Energy of particles.
- The graph below represents the distribution of kinetic energies of molecules at different temperatures.
- For every reaction there is a minimum activation energy needed to make the reaction happen.



Lower minimum energy required, due to the presence of a catalyst.

more area under curve at higher temps

- Note that the curve flattens out at higher temps.
- Thus more molecules will have the minimum KE that is equal to or greater than E_a
- If you added a catalyst, the minimum energy ($E_{a)}$ needed to initiate the reaction is lowered

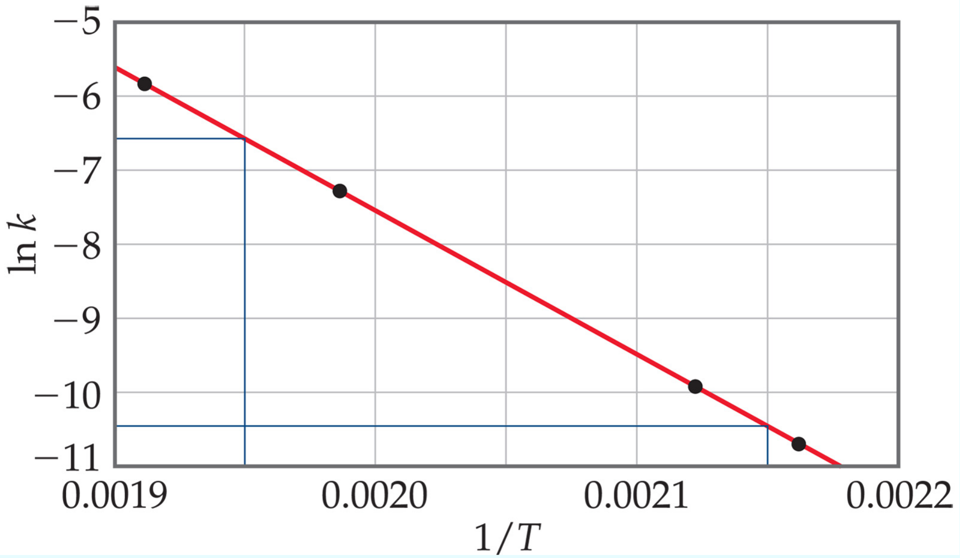
A greater number of molecules meet the energy requirement.

- This of course is what causes catalyst to speed up reactions.

Graphically Determining E_a

- k = A$e^{-Ea/RT}$
- Take the natural log of both sides… log rules
- $\ln k_1 = \frac{-E_a}{R}\left(\frac{1}{T_1}\right) + \ln A$ on the blue sheets
- This is now: y = mx + b
- Thus graphing $\ln k_1 vs \frac{1}{T_1}$
- will give a straight line.
  - ✓ Slope = $\frac{-E_a}{R}$
  - ✓ y intercept = ln A
- This allows for the determination of the activation energy.

Gathering experimental data at various temperatures, *k* can be determined for different temps, which can be graphed.



LAD E.1 Decomposition of H_2O_2 Collecting concentration and rate data

- Note, for all of these trials, we did not collect data that's so neatly packaged as the data on Practice E.1. *Graphing* will be the easiest way to determine the order of the reaction with respect to each substance.
- Let's see take a look at how graphing will help us write the rate law for the reaction.
  - ✓ $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

Algebra 2 Public Announcement Reminder

Handy Log Rules

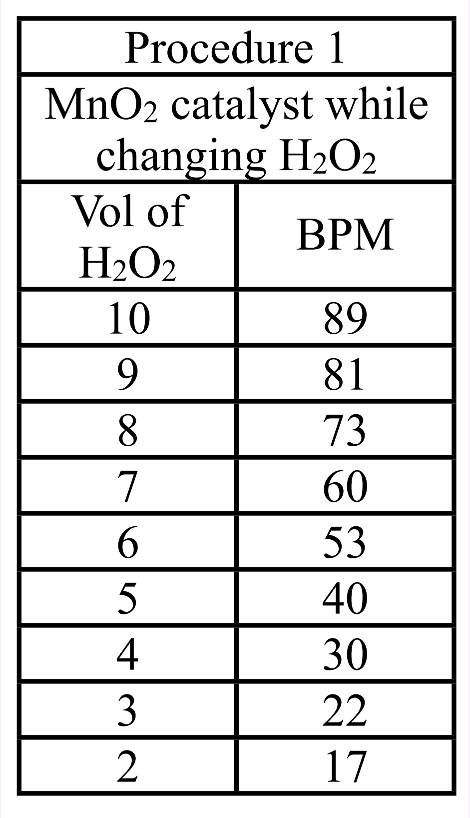
- log[A][B] =
  - ✓ log[A][B] = log[A] + log[B]
- $\log[A]^m$ =
  - ✓ $\log[A]^m = m\log[A]$
- By logging both sides of the rate law, we and get at the “mystery” exponent (order)

Graphing rate data to determine order and rate constant

Note, for LAD E1, we did not collect data that's as neatly packaged as the data on P E.1, so *graphing* will be the easiest way to determine the order of the reaction with respect to each substance.

- rate = k$[A]^{m}$
- log(rate) = $m$log[A] + log(k)
- y = mx + b
- we can graph the volume data to determine the slope which will be order of the reaction.
- We can unlog the y intercept to determine the rate constant, k.

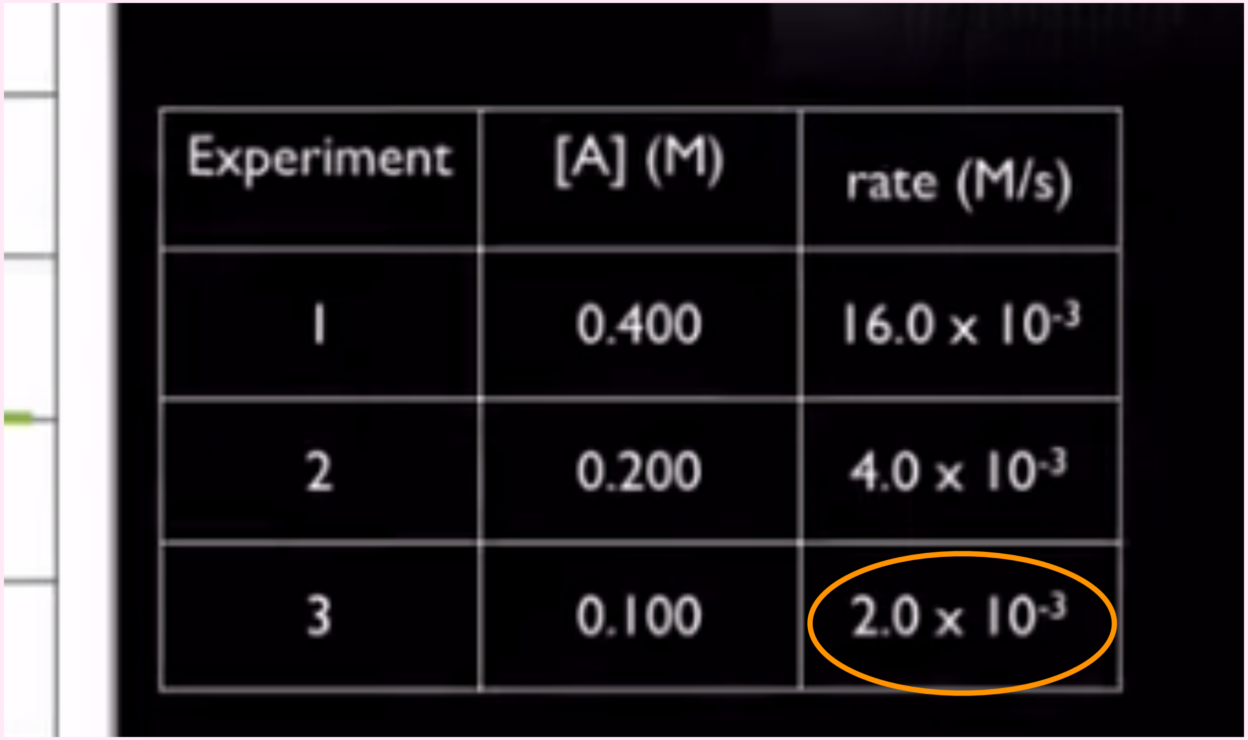
LAD E1



Procedure 1 MnO_2 catalyst while changing H_2O_2	
Vol of H_2O_2	BPM
10	89
9	81
8	73
7	60
6	53
5	40
4	30
3	22
2	17

Beware the Bozeman Video #36 at 5 min

- Trial 3 data should have been a rate of 1.0 x 10^{-3}
- I have sent an email, but have not heard back yet.



Experiment	[A] (M)	rate (M/s)
1	0.400	16.0 x 10^{-3}
2	0.200	4.0 x 10^{-3}
3	0.100	2.0 x 10^{-3}