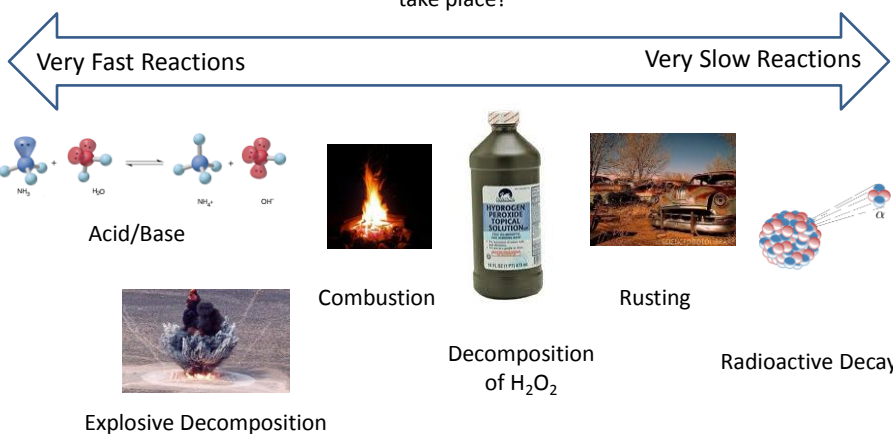


Chapter 14 – Chemical Kinetics

Chemical Kinetics – Rates of Reactions

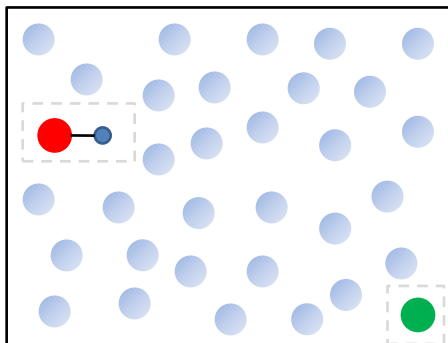
Chemical Kinetics is the study of the rate of reaction. "How fast" does it take place?



Collision Theory

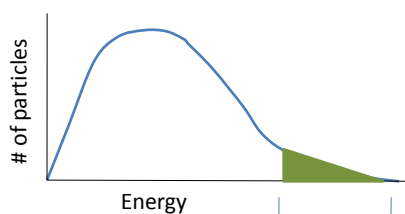
Reaction rates are not constant. They are actually dependant on the conditions under which the reaction takes place. How can we make a reaction go faster? How do we increase the rate of a reaction?

Rule #1: For a reaction to take place, reactants must collide!!



These two reactants cannot react because they are not in contact with one another. They may eventually run into each other, but they need time to diffuse

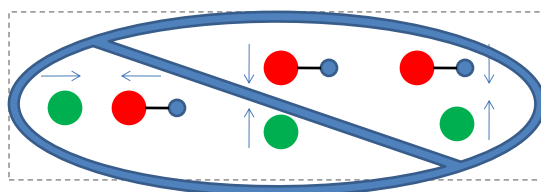
But even if they do collide, it does not guarantee a reaction!!



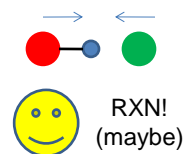
Number of particles that actually react

Collision Theory

Rule #2: When molecules collide, they must be in an optimal orientation.

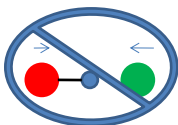


Unfruitful Collisions
(no reactions)



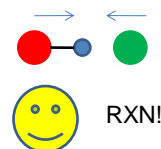
Correct orientation for
a reaction

Rule #3: When molecules collide, they must have a certain minimum amount of energy in order for the reaction to occur.



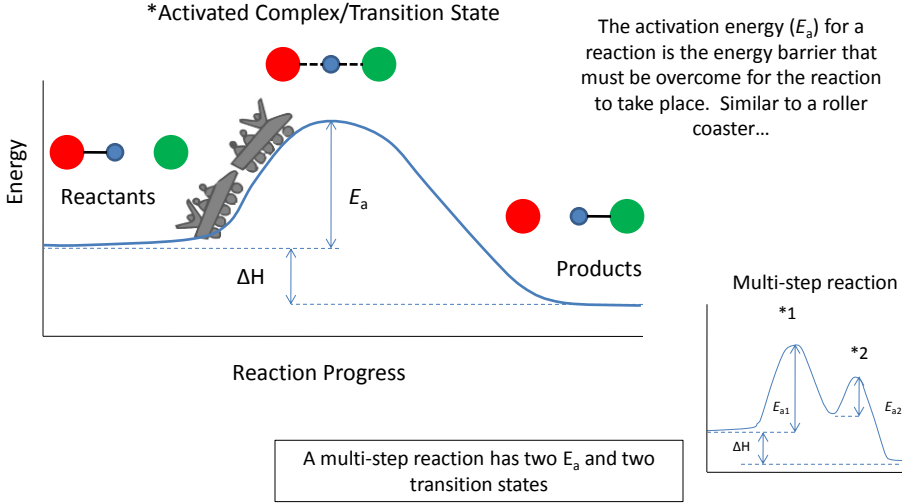
Not enough energy
(no reactions)

Although this collision seems to be in the correct orientation, the reactants do not have enough energy

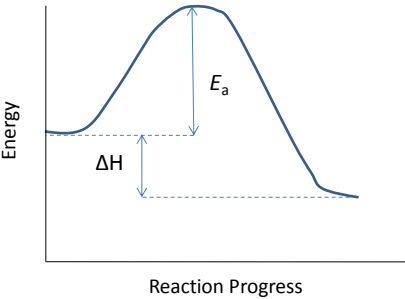


Enough energy for a
reaction

Collision Theory and Activation Energy (E_a)

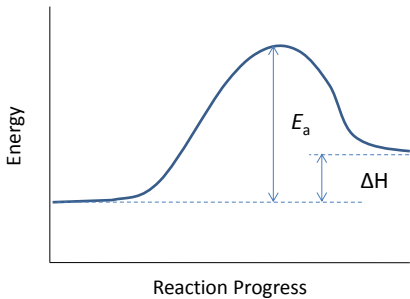


Exothermic vs. Endothermic Reactions



Products have *lower* energy than reactants
Energy released during reaction

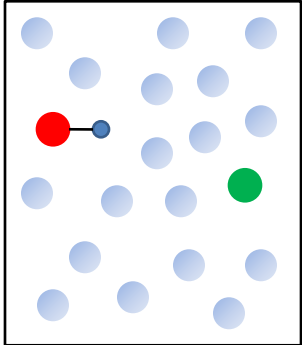
$-\Delta H$
EXOTHERMIC



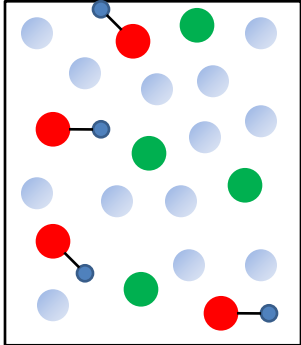
Products have *higher* energy than reactants
Energy absorbed during reaction

$+\Delta H$
ENDOTHERMIC

Concentration and Rate



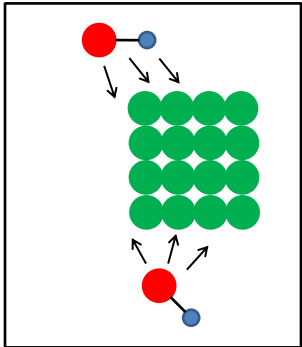
Lower concentration of reactants



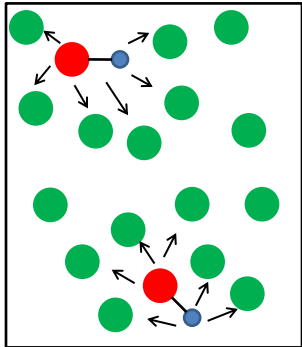
Higher concentration of reactants

Higher concentration of reactants allow more opportunities for collisions.

Surface Area and Rate



Can only collide with particles on the surface of the solid



If the particles are made finer, there are many more opportunities for collisions

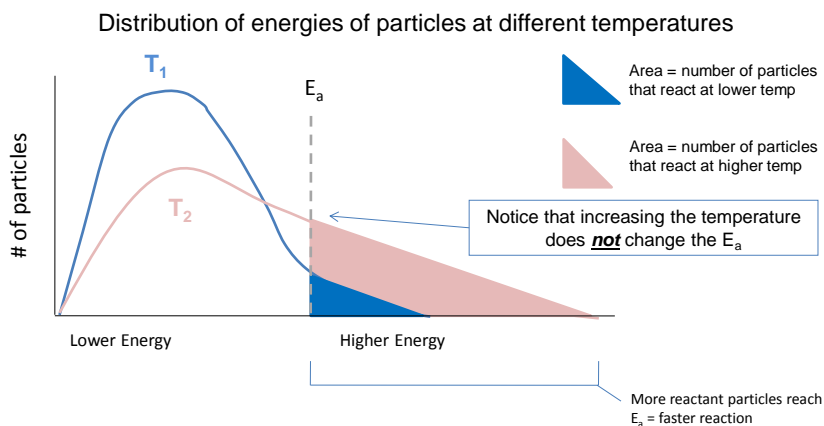
Higher surface area of reactants increase the rate of a reaction

Temperature and Rate

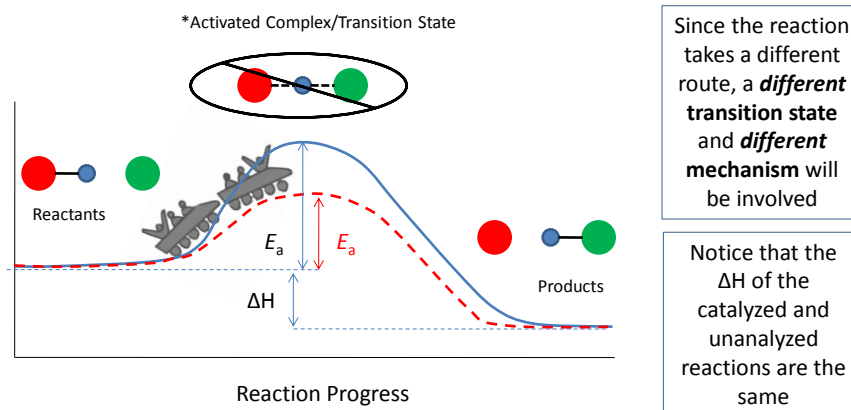
Why does temperature affect rate?

•More collisions: Since particles move faster at higher temperatures there is more opportunity to interact/collide.

•More energy: More particles will have enough energy to overcome E_a



Catalysts and rate

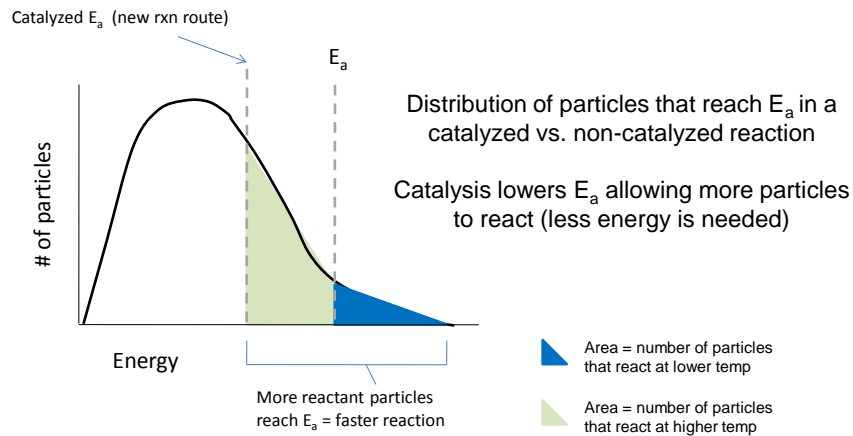


•Catalysts allow a *different path* for the reaction to take place. A path with a lower E_a .

•Catalysts are regenerated in a reaction. That is, they are not consumed

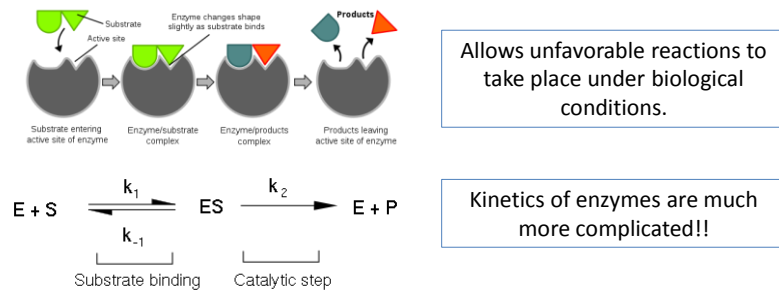
Catalysts

Catalysts allow more particles to react per unit of time



Biological Catalysts / Catalysis

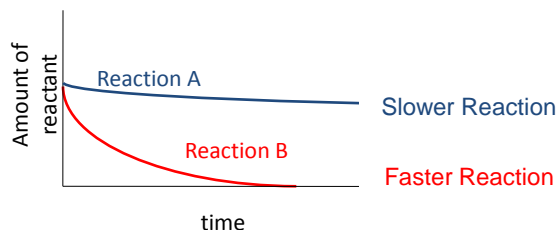
Many reactions in the human body are catalyzed by proteins called enzymes. Enzymes catalyze reactions by binding to reactant particles called substrates.



Chemical Kinetics

What does a graphical representation of different reaction rate look like?

Let's say we have two different decomposition reactions; one faster than the other.



While "fast" and "slow" are good *qualitative* words when comparing rates, how do we *quantitatively* determine this?

$$\text{Rate of reaction} = \frac{-\Delta[\text{reactant}]}{\Delta t} = \frac{\Delta[\text{product}]}{\Delta t}$$

Most often, especially for aqueous solutions, we define "amount" as concentration (M or mol/L) denoted by brackets, [].

Time can be in any units. Very often, we use seconds (s).

How do we determine rate of reaction?

We can measure the concentrations of reactants or products various ways. In some solutions, we can use visible spectroscopy to determine concentration of **reactants** or **products**, usually expressed in M or mol/L. Gases can be expressed in partial pressures (atm).

$$\text{Rate of reaction} = \frac{-\Delta[\text{reactant}]}{\Delta t} = \frac{\Delta[\text{product}]}{\Delta t}$$

$\Delta = \text{final} - \text{initial}$



1.00M
t = 0s



0.50M
t = 25s



0.25M
t = 50s

$$\text{Rate} = \frac{-(0.50\text{M} - 1.00\text{M})}{(25\text{s} - 0\text{s})} = \frac{0.50\text{M}}{25\text{s}} = 0.020 \frac{\text{M}}{\text{s}}$$

$$\text{Rate} = \frac{-(0.25\text{M} - 0.50\text{M})}{(50\text{s} - 25\text{s})} = \frac{0.25\text{M}}{25\text{s}} = 0.010 \frac{\text{M}}{\text{s}}$$

Chemical Kinetics – Rates of Reactions

A → B

$$\text{Rate of reaction} = \frac{-\Delta[\text{reactant(s)}]}{\Delta t} = \frac{\Delta[\text{product(s)}]}{\Delta t} \quad \Delta = \text{final} - \text{initial}$$

Time (min)	[Reactant] (M)
0	5.00
.50	2.50
1.0	1.25
1.5	0.63
2.0	0.31
2.5	0.16
3.0	0.08

$$\text{Avg Rate} = \frac{-(2.50\text{M} - 5.00\text{M})}{(0.50\text{min} - 0.00\text{min})} = \frac{2.50\text{M}}{0.50\text{min}} = 5.0 \frac{\text{M}}{\text{min}}$$

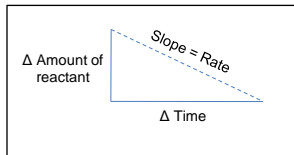
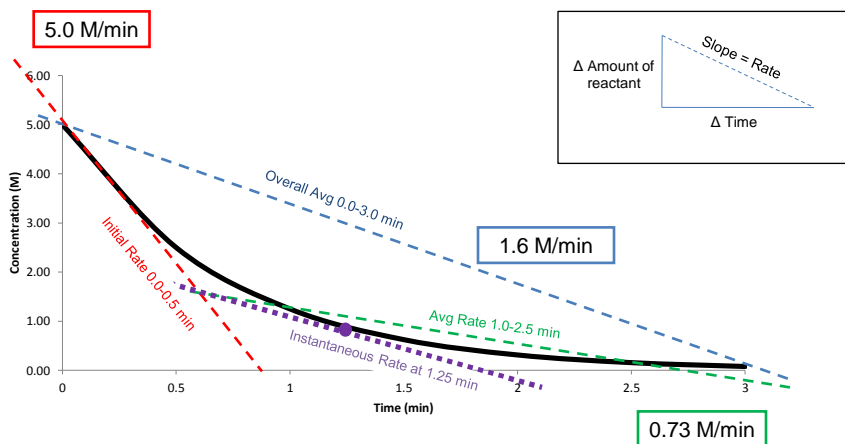
$$\text{Avg Rate} = \frac{-(0.16\text{M} - 0.63\text{M})}{(2.5\text{min} - 1.5\text{min})} = \frac{0.47\text{M}}{1.0\text{min}} = 0.47 \frac{\text{M}}{\text{min}}$$

$$\text{Avg Rate} = \frac{-(0.08\text{M} - 0.16\text{M})}{(3.0\text{min} - 2.5\text{min})} = \frac{0.08\text{M}}{0.5\text{min}} = 0.2 \frac{\text{M}}{\text{min}}$$

We can calculate an "average" rate of the reaction between any two data points during the reaction

$$\text{Overall Avg Rate} = \frac{(5.00\text{M} - 0.08\text{M})}{(0\text{min} - 3.0\text{min})} = \frac{4.92\text{M}}{3.0\text{min}} = 1.6 \frac{\text{M}}{\text{min}}$$

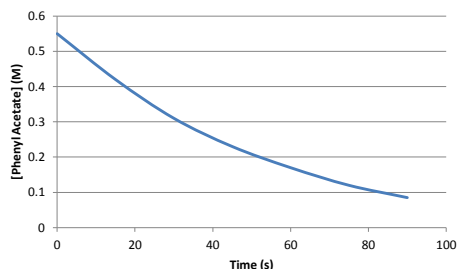
Chemical Kinetics – Rates of Reactions



What about an instantaneous rate?
Let's say at 1.25 minutes?

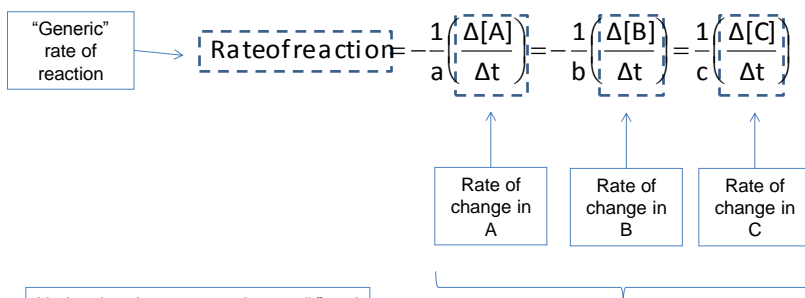
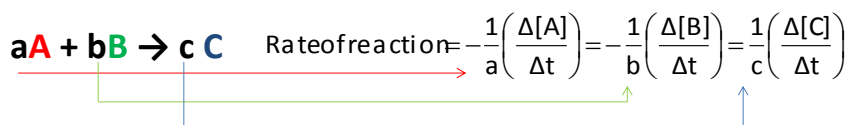
Chemical Kinetics – Rates of Reactions

Time (s)	[Phenyl Acetate] (M)
0.0	0.550
15.0	0.420
30.0	0.310
45.0	0.230
60.0	0.170
75.0	0.120
90.0	0.085



- What is the overall average reaction rate
 $5.17 \times 10^{-3} \text{ M/s}$
 - What is the average rate from $t=0.0\text{s}$ to $t=15.0\text{s}$
 $8.67 \times 10^{-3} \text{ M/s}$
 - Should the average from $t=15.0\text{s}$ to 30.0s be higher or lower than $t=0.0\text{s}$ to $t=15.0\text{s}$???
- The rate from $t=15.0\text{s}$ to 30.0s should be slower

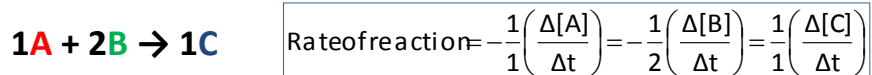
Rate of Disappearance of Reactants and Appearance of Products



Notice that the reactants have a “-” and the products do not.

If the coefficients are different, the rates will be different

Rate of disappearance of reactants and appearance of products based on coefficients



If C is appearing at 5.0×10^{-5} M/s at what rate is A disappearing?

$$-\frac{1}{1}\left(\frac{\Delta[\mathbf{A}]}{\Delta t}\right) = \frac{1}{1}\left(\frac{\Delta[\mathbf{C}]}{\Delta t}\right) \Rightarrow -\frac{1}{1}\left(\frac{\Delta[\mathbf{A}]}{\Delta t}\right) = \frac{1}{1}(5.0 \times 10^{-5} \text{ M/s}) \Rightarrow \left(\frac{\Delta[\mathbf{A}]}{\Delta t}\right) = -5.0 \times 10^{-5} \text{ M/s}$$

If A is disappearing at -1.0 M/min at what rate is B disappearing?

$$-\frac{1}{1}\left(\frac{\Delta[\mathbf{A}]}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta[\mathbf{B}]}{\Delta t}\right) \Rightarrow -\frac{1}{1}(-1.0 \text{ M/s}) = -\frac{1}{2}\left(\frac{\Delta[\mathbf{B}]}{\Delta t}\right) \Rightarrow -2(-1.0 \text{ M/s}) = -\left(\frac{\Delta[\mathbf{B}]}{\Delta t}\right) \Rightarrow \left(\frac{\Delta[\mathbf{B}]}{\Delta t}\right) = -2.0 \text{ M/s}$$

If B is disappearing at -0.44 M/min at what is the (generic) reaction rate?

$$\text{Rate of reaction} = -\frac{1}{2}\left(\frac{\Delta[\mathbf{B}]}{\Delta t}\right) \Rightarrow \text{Rate of reaction} = -\frac{1}{2}(-0.44 \text{ M/min}) \Rightarrow \text{Rate of reaction} = 0.22 \text{ M/min}$$

Rate of Disappearance of Reactants and Appearance of Products

In the reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ the appearance of NO_2 is 3.12×10^{-1} M/s. What is the rate of disappearance of N_2O_5 ?

$$1.56 \times 10^{-1} \text{ M/s}$$

In the synthesis of Ammonia, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, if the rate of disappearance of H_2 is 4.5×10^{-4} M/s, what is the rate of appearance of ammonia, NH_3 ?

$$3.0 \times 10^{-4} \text{ M/s}$$

Chemical Kinetics and Concentration – Rate Law

Each reaction can be expressed by what is called a “Rate Law”

The rate law describes how each reactant's concentration has an effect on the reaction rate

General Rate Law

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y \dots$$

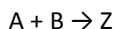
- [A] = concentration (M) of reactant A
- [B] = concentration (M) of reactant B
- k = rate constant (depends on other units)
- Rate = usually in M/s or mol/L·s
- x and y = “order” of each reactant

Only reactants that affect the rate of the reaction are included in the rate law. In other words, not every reactant that appears in the balanced equation will be in the rate law!

Determining Rate Law – Determining the Order of each reactant

While it seems like it should work, we should **never determine the Rate Law based on the balanced equation!!** This is because reactions can have multiple intermediate steps not accounted for in the balanced equation.

We can determine the Rate Law using experimentation data of *initial* rates.



Trial	Initial [A]	Initial [B]	Initial Rate
1	0.100M	0.300M	1.00 M/s
2	0.100M	0.600M	2.00 M/s
3	0.300M	0.300M	9.00 M/s

• First, find two trials where one reactant has the same concentration. This way we can cancel the effect of that reactant has on the rate (For example, trials 1 & 2).

• Plug everything you know into the rate equation.

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y$$

$$\begin{array}{l} \text{Trial 2} \\ \text{Trial 1} \end{array} \left(\frac{2.00 \text{ M/s}}{1.00 \text{ M/s}} \right) = k \left(\frac{0.100 \text{ M}}{0.100 \text{ M}} \right)^x \left(\frac{0.600 \text{ M}}{0.300 \text{ M}} \right)^y \longrightarrow (2) = k(1)^x (2)^y \longrightarrow (2) = (2)^y \longrightarrow \mathbf{y = 1}$$

• Ignore the reactant with the same concentration and ignore k , for now.

• Solve for the exponent

Determining Rate Law – Determining the Order of Each Reactant

So Far...

$$\text{Rate} = k [A]^x [B]$$

We normally do not show the "1" as an exponent

Now, we go through the same process for A:

Trial	Initial [A]	Initial [B]	Initial Rate
1	0.100M	0.300M	1.00 M/s
2	0.100M	0.600M	2.00 M/s
3	0.300M	0.300M	9.00 M/s

$$\begin{matrix} \text{Trial 3} \\ \text{Trial 1} \end{matrix} \left(\frac{9.00 \text{ M/s}}{1.00 \text{ M/s}} \right) = k \left(\frac{0.300\text{M}}{0.100\text{M}} \right)^x \left(\frac{0.300\text{M}}{0.300\text{M}} \right)^y \Rightarrow (9) = k (3)^x (1)^y \Rightarrow (9) = (3)^x \Rightarrow \boxed{x = 2}$$

Therefore, the rate law can be written as:

The reaction is

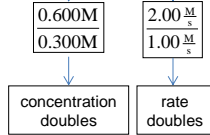
second-order with respect to "A" and
first-order with respect to "B"

$$\text{Rate} = k [A]^2 [B]$$

2 + 1 = 3... This reaction is 3rd order overall

Determining Rate Law – Short Cut

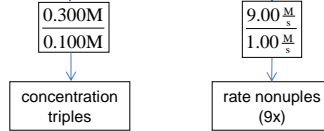
Trial	Initial [A]	Initial [B]	Initial Rate
1	0.100M	0.300M	1.00 M/s
2	0.100M	0.600M	2.00 M/s
3	0.300M	0.300M	9.00 M/s



$$(2)^y = (2)$$

1st order

Trial	Initial [A]	Initial [B]	Initial Rate
1	0.100M	0.300M	1.00 M/s
2	0.100M	0.600M	2.00 M/s
3	0.300M	0.300M	9.00 M/s



$$(3)^x = (9)$$

2nd order

Therefore, the rate law can be written as:

The reaction is

second-order with respect to "A" and
first-order with respect to "B"

$$\text{Rate} = k [A]^2 [B]$$

2 + 1 = 3... This reaction is 3rd order overall

Determining Rate Law – Determining the Rate Law Constant (k)

Since k does not change during the reaction, we can use any trial to calculate the value of k

Trial	Initial [A]	Initial [B]	Initial Rate
1	0.100M	0.300M	1.00 M/s
2	0.100M	0.600M	2.00 M/s
3	0.300M	0.300M	9.00 M/s

Trial 1 Rate = $k[A]^2[B]$ \Rightarrow $1.00 \text{ M/s} = k [0.100]^2 [0.300]$ \Rightarrow $k = \frac{(1.00 \text{ M/s})}{(0.100\text{M})^2(0.300\text{M})}$ Cancel units

$$k = 333 \frac{1}{\text{M}^2\text{s}} \text{ or } \text{M}^{-2}\text{s}^{-1}$$

Trial 2 Rate = $k[A]^2[B]$ \Rightarrow $2.00 \text{ M/s} = k [0.100]^2 [0.600]$ \Rightarrow $k = \frac{(2.00 \text{ M/s})}{(0.100\text{M})^2(0.600\text{M})}$

$$k = 333 \frac{1}{\text{M}^2\text{s}} \text{ or } \text{M}^{-2}\text{s}^{-1}$$

Rate Law
$\text{Rate} = 333 \frac{1}{\text{M}^2\text{s}} [\text{A}]^2 [\text{B}]$

- A = 2nd-order
- B = 1st-order
- Overall reaction = 3rd order
- $k = 333 \text{ 1/M}^2\text{s}$

Determining Rate Law Practice

Use the following data to determine the rate law and the value of k for the reaction between NO and O₂.

Trial	Initial [NO] (M)	Initial [O ₂] (M)	Initial Rate (M/s)
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

Trial	Initial [A] (M)	Initial [B] (M)	Initial [C] (M)	Rate (M/s)
1	0.10	0.10	0.10	1.8×10^{-6}
2	0.30	0.10	0.10	5.4×10^{-6}
3	0.30	3.00	0.10	4.86×10^{-3}
4	0.10	0.10	3.00	1.8×10^{-6}

Determining Rate Law – Tricks Up My Sleeve

Trial	Initial [A] (M)	Initial [B] (M)	Rate (M/s)
1	1.0	1.0	1.67
2	1.0	1.2	2.00
3	1.3	1.0	3.67

Trial	Initial [A] (M)	Initial [B] (M)	Rate (M/s)
1	1.0	1.0	1.67
2	1.0	1.2	2.00
3	1.3	1.0	3.67

Initial [A] (M)	Initial [B] (M)	Rate (M/s)
1.2M	1.0M	2.00 $\frac{M}{s}$
1.0M	1.0M	1.67 $\frac{M}{s}$

concentration changes 1.2x rate changes 1.2x

$(1.2)^y = (1.2)$

1st order

Initial [A] (M)	Initial [B] (M)	Rate (M/s)
1.3M	1.0M	3.67 $\frac{M}{s}$
1.0M	1.0M	1.67 $\frac{M}{s}$

concentration changes 1.3x rate changes 2.2x

$(1.3)^x = (2.2)$

WTF?!

Determining Rate Law – Tricks Up My Sleeve #1

$$\ln(a^x) = x \ln(a)$$

$$(1.3)^x = (2.2)$$

Take natural log of both sides

$$\ln(1.3)^x = \ln(2.2)$$

Rearrange using $\ln(a^x) = x \ln(a)$

$$x \ln(1.3) = \ln(2.2)$$

$$x \ln(1.3) = \ln(2.2)$$

$$x \cdot 0.262 = 0.778$$

solve for "x"

$$x = 2.96 \approx 3$$

Determining Rate Law Group Practice

Trial	Initial P _A (atm)	Initial P _B (atm)	Rate (atm/min)
1	5.97	0.25	1.33
2	0.50	0.25	7.81x10 ⁻⁴
3	0.50	7.62	2.38x10 ⁻²

Trial	Initial [A] (M)	Initial [B] (M)	Rate (M/s)
1	0.10	0.20	2.5x10 ⁻⁴
2	0.10	0.10	1.2x10 ⁻⁴
3	0.30	0.30	1.1x10 ⁻³

*This one may initially look impossible, but it's not.

Hint: Think about what you already know....

Integrated Rate Laws - Rate and Time

With the help of calculus, we can use another form of the rate law that allows us to calculate how concentration of a reactant changes with time. It is called the integrated rate law.

Remember...

1st-order rate law

$$\text{Rate} = k[A] \quad \longrightarrow \quad \ln \frac{[A]_t}{[A]_0} = -kt \quad \text{-or-} \quad \ln[A]_t = -kt + \ln[A]_0$$

2nd-order rate law

$$\text{Rate} = k[A]^2 \quad \longrightarrow \quad \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

What about a reaction where the concentration of the reactants that do not affect the rate. Does it exist? Yup.

0th-order rate law

$$\text{Rate} = k \quad \longrightarrow \quad [A]_t = [A]_0 - kt$$

Integrated Rate Laws – 1st order

•A certain decomposition reaction is 1st order overall. What is the rate constant if the concentration of A goes from an initial concentration of 5.55M to 1.11M in 3.0 minutes?

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$[A]_t = [A]_0 - kt$$

$$\ln \left(\frac{1.11M}{5.55M} \right) = -k(3.0\text{min}) \quad \Rightarrow \quad -1.609 = -k(3.0\text{min}) \quad \Rightarrow \quad k = 0.54\text{min}^{-1}$$

•How long would it take for the concentration to reach 50% of its original concentration?

$$\ln \left(\frac{50\%}{100\%} \right) = -(0.536\text{min}^{-1})t \quad \Rightarrow \quad -0.693 = -(0.536\text{min}^{-1})t \quad \Rightarrow \quad t = 1.3\text{min}$$

Using % directly in the equation will only work with 1st order since k doesn't include a concentration unit. For other orders (2nd and 0th), use actual concentrations in the equations.

Integrated Rate Laws – 1st order More natural log tricks

•What would be the concentration after 13 minutes?

$$\ln \left(\frac{x}{5.55M} \right) = -(0.536\text{min}^{-1})(13\text{min})$$

How do we get rid of natural log (ln)?

$$e^{\ln(x)} = x \quad \Rightarrow \quad e^{\ln \left(\frac{x}{5.55M} \right)} = e^{-(0.536\text{min}^{-1})(13\text{min})} \quad \Rightarrow \quad \frac{x}{5.55M} = 9.42 \times 10^{-4} \quad \Rightarrow \quad x = 0.0052M$$

$$\ln \left(\frac{x}{5.55M} \right) = -(0.536\text{min}^{-1})(13\text{min})$$

$$\ln \left(\frac{x}{y} \right) = \ln x - \ln y$$

CAUTION!

$$\ln \left(\frac{x}{y} \right) \text{ DOES NOT } = \frac{\ln x}{\ln y}$$

$$\ln x - \ln 5.55M = -(0.536\text{min}^{-1})(13\text{min}) \quad \Rightarrow \quad \ln x = -5.254 \quad \Rightarrow \quad x = 0.0052M$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$[A]_t = [A]_0 - kt$$

Integrated Rate Laws – 2nd order

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$[A]_t = [A]_0 - kt$$

- A second-order decomposition has a rate constant of 0.050 M⁻¹min⁻¹. Assuming you start with 3.2M, how long will it take for only 5.0% of the reactant to remain.

Unlike 1st order, you cannot simply use %'s. You must use specific concentrations or amounts for your reactant. $\rightarrow 3.2M \left(\frac{5.0\%}{100.0\%} \right) = 0.16M$

So.. $\frac{1}{0.16M} = (0.050 \text{ M}^{-1}\text{min}^{-1})t + \frac{1}{3.2M} \rightarrow 5.94 = (0.050 \text{ M}^{-1}\text{min}^{-1})t \rightarrow t = 120\text{min}$

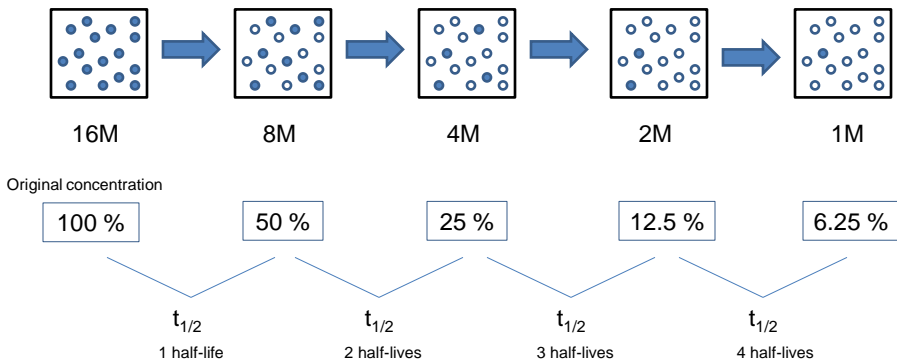
- If the same reaction took 625s to reach 0.222M, what was the original concentration?

Watch for time units. MUST be the same in k and for t $\rightarrow 625s \frac{1\text{min}}{60s} = 10.4 \text{ min}$

$\frac{1}{0.222M} = (0.050 \text{ M}^{-1}\text{min}^{-1})(10.4 \text{ min}) + \frac{1}{[A]_0} \rightarrow 3.98 = \frac{1}{[A]_0} \rightarrow [A]_0 = 0.25M$

Half-lives

The time it takes for a reactant to reach half of its initial amount



General Equation for Half-life

$$[A]_{t_{1/2}} = [A]_0 \left(\frac{1}{2} \right)^x$$

Where "x" = number of half-lives

Half lives

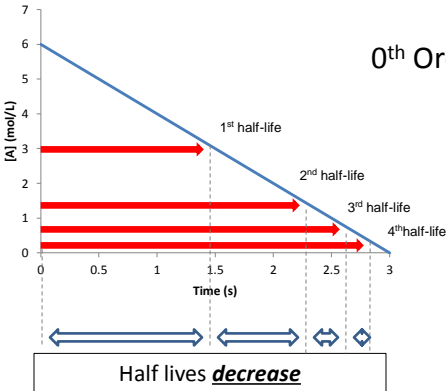


$$t_{1/2} = \frac{\ln(2)}{k}$$



$$t_{1/2} = \frac{1}{k[A]_0}$$

Integrated Rate Laws – Half lives



$$t_{1/2} = \frac{[A]_0}{2k}$$

Half-life equations

General Equation for Half-life

$$[A]_t = [A]_0 \left(\frac{1}{2} \right)^x$$

Where "x" = number of half-lives

Half-lives are related to the rate constant, k , by the following equations

<u>1st Order</u>	$\ln \left(\frac{[A]_0}{2} \right) = -kt$	→	$t_{1/2} = \frac{\ln(2)}{k}$
<u>2nd Order</u>	$\frac{1}{\left(\frac{[A]_0}{2} \right)} = kt + \frac{1}{[A]_0}$	→	$t_{1/2} = \frac{1}{k[A]_0}$
<u>0th Order</u>	$\left(\frac{[A]_0}{2} \right) = [A]_0 - kt$	→	$t_{1/2} = \frac{[A]_0}{2k}$

Half-Life Examples

$$t_{1/2} = \frac{\ln(2)}{k}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

A certain reaction has a rate constant of 1.25 hr^{-1} . What is the half life of this reaction in *hours*? *Minutes*?

0.555hr

How many half lives will it take for the same reaction above to go from 6.0M to 0.020M?

8.2 half-lives

If a *2nd order* reaction has a half life of 3.1 days, how many hours will it take for 10.0% of the reactant to disappear if the concentration starts at 1.0M?

Graphing Integrated Rate Laws

Equation of a straight line	slope	y-intercept	
$y = m x + b$			
1 st -order rate law	$\ln[A]_t = -k t + \ln[A]_0$	$\ln[A]_0$	$\ln[A]_t$ vs. t
2 nd -order rate law	$\frac{1}{[A]_t} = k t + \frac{1}{[A]_0}$	$\frac{1}{[A]_0}$	$\frac{1}{[A]_t}$ vs. t
0 th -order rate law	$[A]_t = -k t + [A]_0$	$[A]_0$	$[A]_t$ vs. t

Determining order by graphing

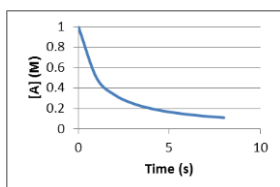
To determine the "order" of the reactant, you must graph the data three different ways: Time vs. Conc.; Time vs. ln(Conc.); and Time vs. 1/Conc.

Time (s)	[A] (M)
0	1
1	0.5
2	0.3333333
3	0.25
4	0.2
5	0.1666667
6	0.142857
7	0.125
8	0.111111

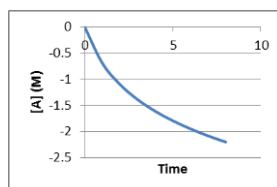
Time (s)	ln[A]
0	0
1	-0.69315
2	-1.09861
3	-1.38629
4	-1.60944
5	-1.79176
6	-1.94591
7	-2.07944
8	-2.19722

Time (s)	1/[A] (1/M)
0	1
1	2
2	3
3	4
4	5
5	6
6	7
7	8
8	9

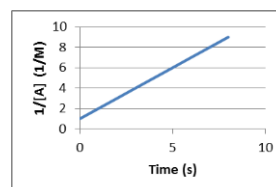
Time vs. Conc.



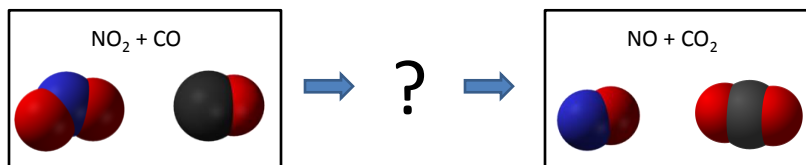
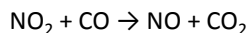
Time vs. ln(Conc.)



Time vs. 1/(Conc.)



Multistep Reactions – Reaction Mechanisms

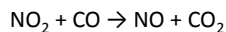
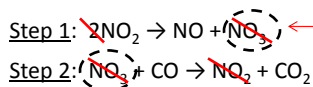


This reaction happens in multiple steps. But what are they? And how can we figure it out?

First we need to learn about these steps.

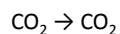
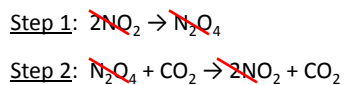
Multistep Reactions – Reaction Mechanisms

Reactions that have multiple steps are made of individual steps called elementary steps.
Elementary steps are single (concerted) steps.



Elementary steps **must** add up to the overall reaction equation.

Intermediates are chemical species that are created during the reaction, but *not* a part of the overall reaction equation. Intermediates are created in an elementary step and consumed in another



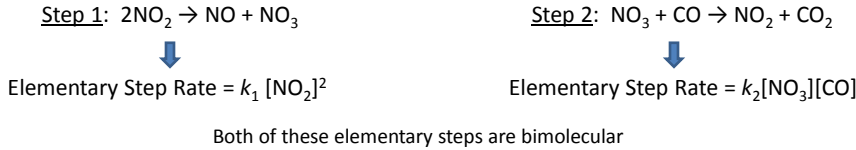
These are not plausible steps because the steps add up to a different overall reaction

Molecularity and Rate Laws of Elementary steps

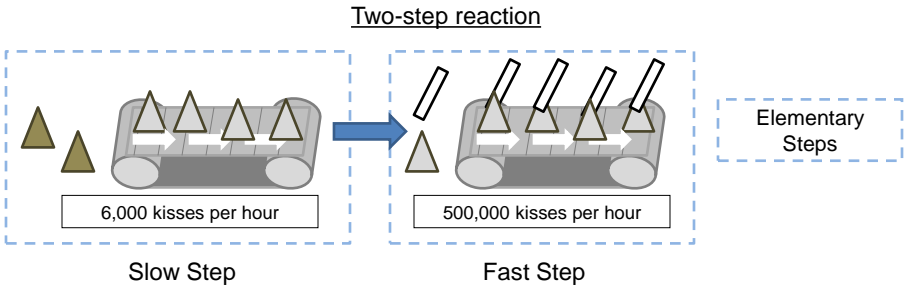
Rate laws for elementary steps can be determined directly from the balanced equation The molecularity of an elementary step is based on the rate law for that step

Molecularity	Equation	Rate Law
Unimolecular	$A \rightarrow \text{Product(s)}$	$\text{Rate} = k[A]$
Bimolecular	$A + A \rightarrow \text{Product(s)}$	$\text{Rate} = k[A]^2$
	$A + B \rightarrow \text{Product(s)}$	$\text{Rate} = k[A][B]$
Termolecular	$A + A + A \rightarrow \text{Product(s)}$	$\text{Rate} = k[A]^3$
	$A + B + B \rightarrow \text{Product(s)}$	$\text{Rate} = k[A][B]^2$
	$A + B + C \rightarrow \text{Product(s)}$	$\text{Rate} = k[A][B][C]$

Since elementary steps are single steps, rate laws for each step can be determined from the balanced chemical equation



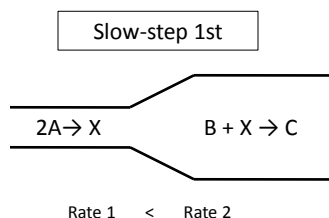
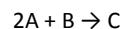
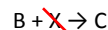
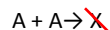
Overall reaction rates of multi-step reactions



How many kisses can be processed per hour overall???

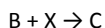
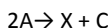
The overall reaction can go no faster than the slow step. This step is called the rate-determining or rate-limiting step.

Just remember that reaction rates are not static; reaction rates are variable based on concentration.

Multiple-step Reactions – Elementary Steps – Rate-limiting Step 1stOverall Chemical Formula

The elementary-step formulas must add up to the overall chemical formula

Rate laws for elementary steps can be determined directly from the balanced equation

Step 1 Rate Law

Rate = $k_1 [A]^2$

~~Step 2 Rate Law~~

~~Rate = $k_2 [B][X]$~~

If the slow, rate-determining, step is first, the overall rate law is the same as the slow step

Step 1 Rate Law

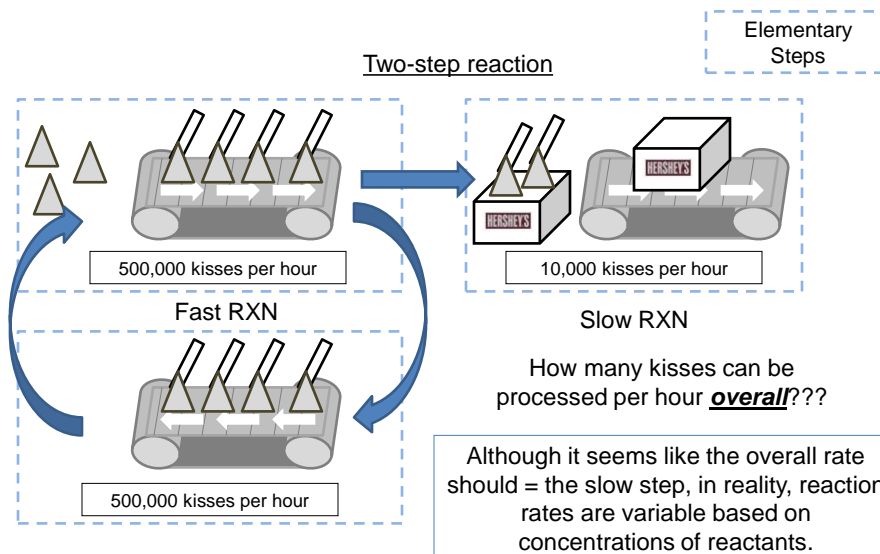
Rate = $k_1 [A]^2$

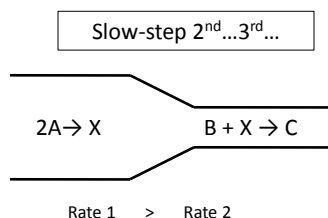
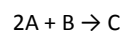
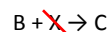
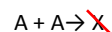
Overall Rate Law

Rate = $k [A]^2$

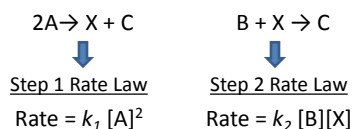
Notice that the concentration of "B" does not affect the rate of reaction

Overall reaction rates of multi-step reactions



Multiple-step Reactions – Elementary Steps – Rate-limiting Step 2ndOverall Chemical Formula

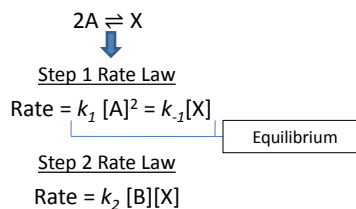
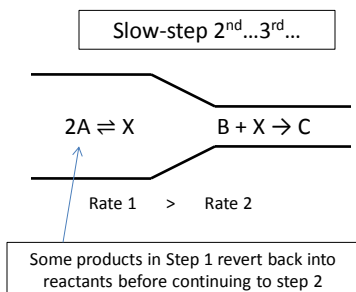
The elementary-step formulas will add up to the overall chemical formula



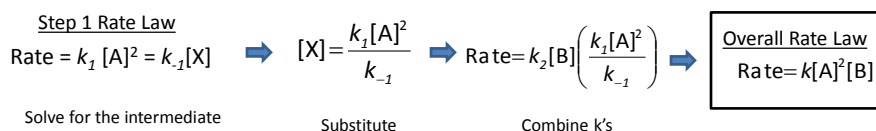
However, unlike the rate-limiting step being first, If the slow, rate-determining, step is second...it's much more complicated.....

Multiple-step Reactions – Elementary Steps – Rate-limiting Step 2nd

If the slow step is second, the bottleneck creates an equilibrium in the first step.

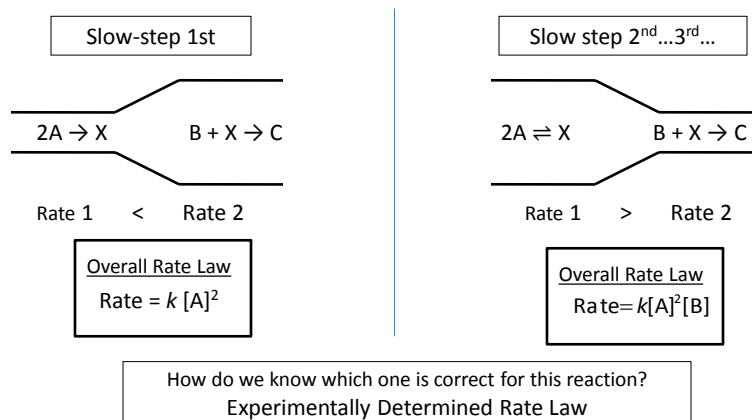
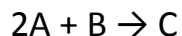


Intermediates *cannot* be in the overall rate law. The overall rate law cannot be based solely on the Step 2 rate law. We must combine both rate laws.



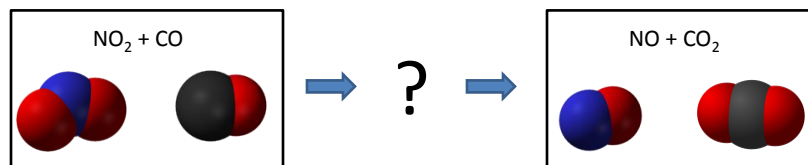
Multiple-step Reactions – Elementary Steps – Rate-limiting Step

Notice that the same reaction with the same elementary steps can give us different overall rate laws because of the location of the slow step.

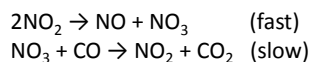
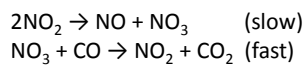
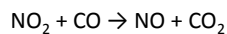


Multiple-step Reactions – Elementary Steps

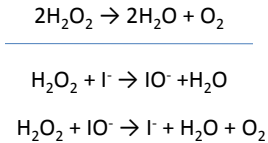
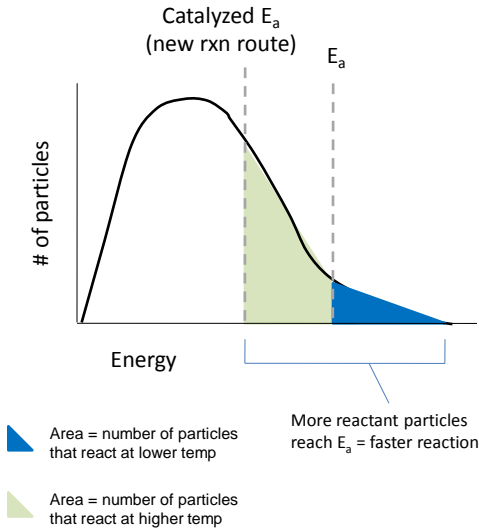
$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ has an experimentally determined rate law of $\text{Rate} = k[\text{NO}_2]^2$



Which of the following is most likely to represent the mechanism for the reaction?



Catalysts #2 – Mechanisms



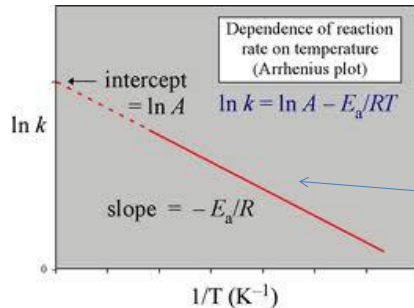
Notice that the *catalyst*, I⁻, is regenerated in the end. There is no net change in catalyst in the reaction.

The *intermediate*, IO⁻, is completely used in the reaction (as it should be).

Arrhenius Equation

Svante Arrhenius determined that activation energy (E_a) of a reaction is related to the reaction constant.

That is...at any temperature the lower the activation energy, the faster a reaction will proceed.



$$k = Ae^{\frac{-E_a}{RT}}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

y = m x + b

Arrhenius Equation

We can also do calculations without graphing, but combining two equations into one.

$$\begin{aligned} \ln k_1 &= \ln A - \frac{E_a}{RT_1} \\ \ln k_2 &= \ln A - \frac{E_a}{RT_2} \end{aligned} \quad \Rightarrow \quad \boxed{\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

If we know both k_1 and k_2 , along with T_1 and T_2 we calculate the energy of activation

$$R = 8.314 \frac{\text{J}}{\text{molK}}$$

In a certain equation, the rate constant at 701K was measured as $2.57\text{M}^{-1}\text{s}^{-1}$ and that at 895 K was measured as $556\text{M}^{-1}\text{s}^{-1}$. Find the activation energy of the reaction.

$$\ln \frac{556 \frac{1}{\text{Ms}}}{2.57 \frac{1}{\text{Ms}}} = \frac{E_a}{8.314 \frac{\text{J}}{\text{molK}}} \left(\frac{1}{701\text{K}} - \frac{1}{895\text{K}} \right) \Rightarrow 5.38 = \frac{E_a}{8.314 \frac{\text{J}}{\text{molK}}} \left(3.09 \times 10^{-4} \frac{1}{\text{K}} \right) \Rightarrow 1.45 \times 10^5 \text{ J/mol}$$