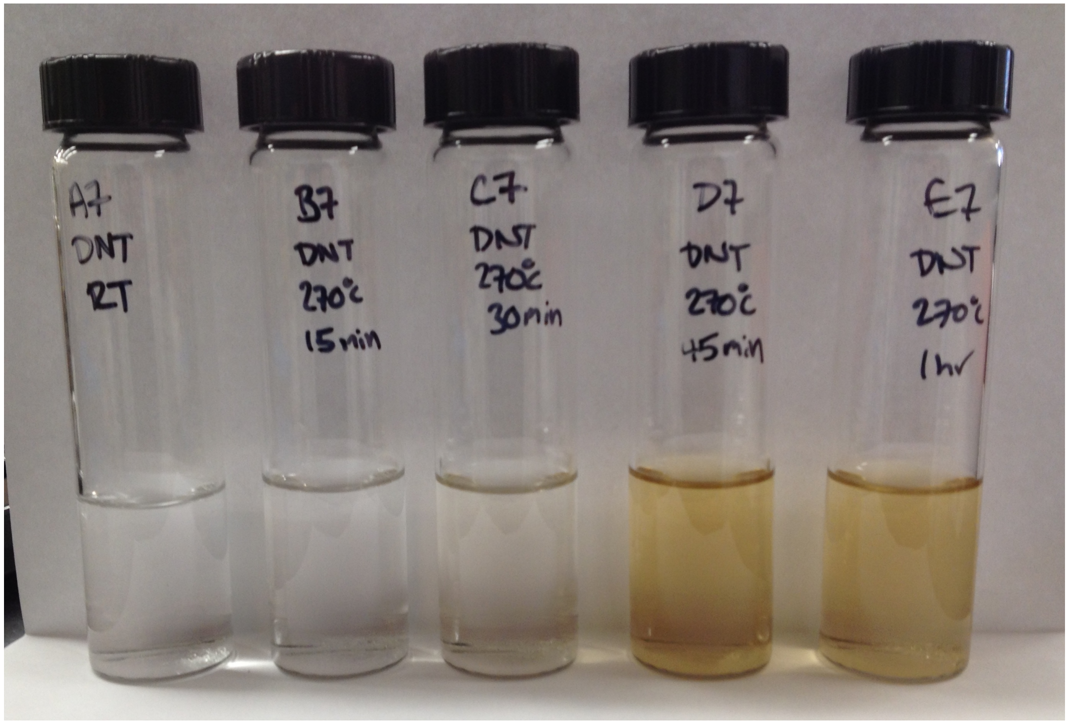
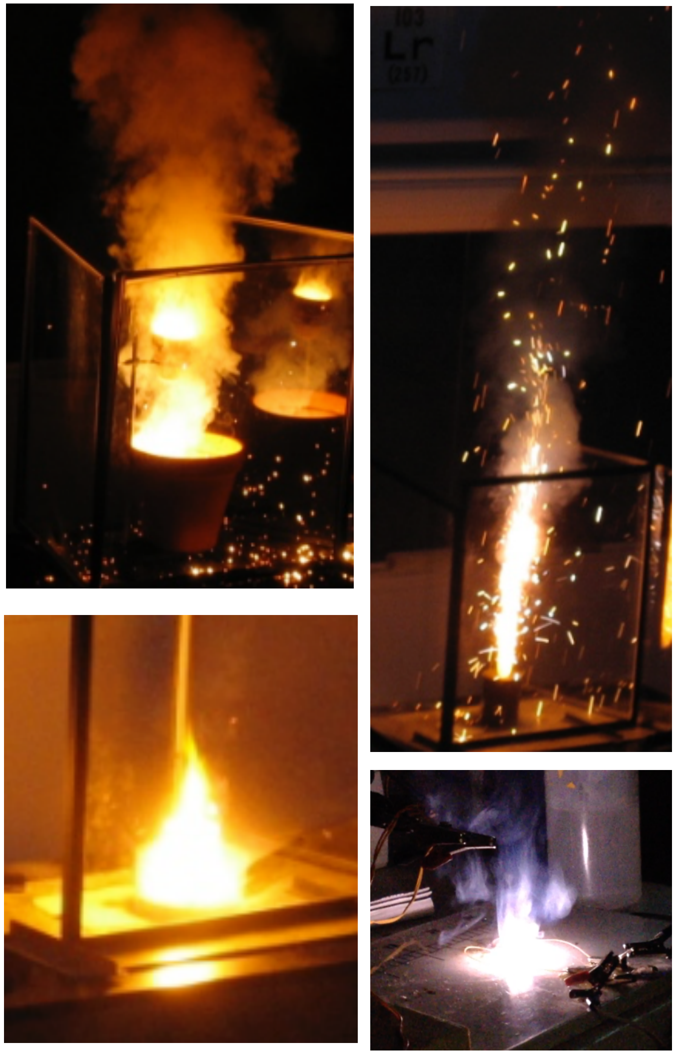
Chapter Fourteen:

Chemical Kinetics



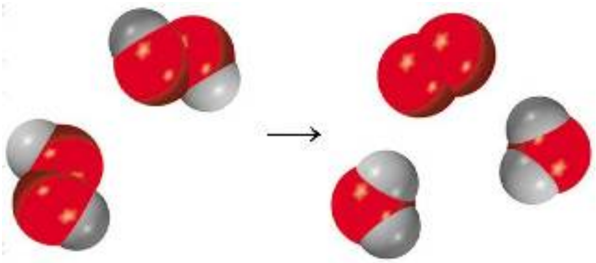
Rate of Reaction = speed



Kinetics & Reaction Rates

Kinetics Topics:

- Study of rates of chemical reactions
- How fast does a reaction proceed?



Reaction Rate:

$$Rate = \frac{\Delta Concentration}{\Delta Time} = \frac{[mol/L]}{\Delta T} = \frac{M}{\sec}$$

$[H_2O_2]$

$[O_2]$

$$2\ H_2O_2\ (l) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$$

Rate of formation of product:

Rate = $+\Delta[O_2]/s$

Rate of disappearance of reactant:

Rate = $-\ \Delta[H_2O_2]/s$

(Use of negative makes rate positive)

When writing rates based on other reactants or products, think about what is happening

Br_2 (aq) + HCOOH (aq) → 2 Br^- (aq) + 2H^+ (aq) + CO_2 (g)

Rate at which Br_2 disappears: X M/s

In terms of Br_2:

What is the rate of formation of Br^- ? 2X M/s

What is the rate of disappearance of HCOOH? X M/s

Rate at which Br^- forms: Z M/s

In terms of Br^-:

What is the rate of disappearance of Br_2? ½ Z M/s

What is the rate of formation of CO_2? ½ Z M/s

This method works for zero order & instantaneous rates, not for more complex rates.

There is much variation in reaction rates

Linearity of Reaction Rates

Reaction rates vary greatly

- Very fast; ex: burning
- Very slow; ex: disintegration of plastic in sunlight

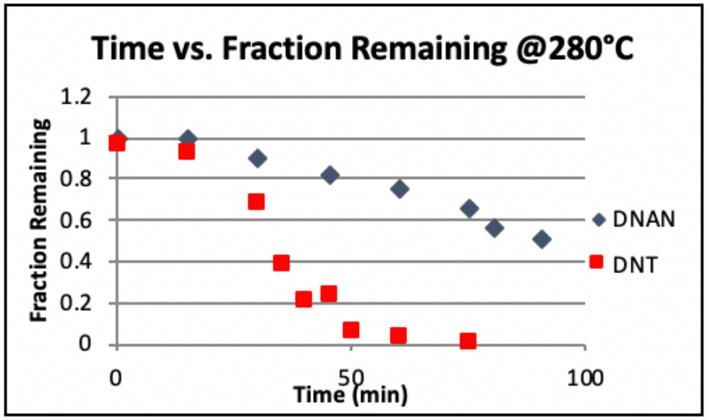
$[H_2O_2]$

$[O_2]$

Often not linear

- Rate is often faster at the beginning
- Rate is slowest at the end
- Some reactant often left over
- Especially pronounced for slow reactions

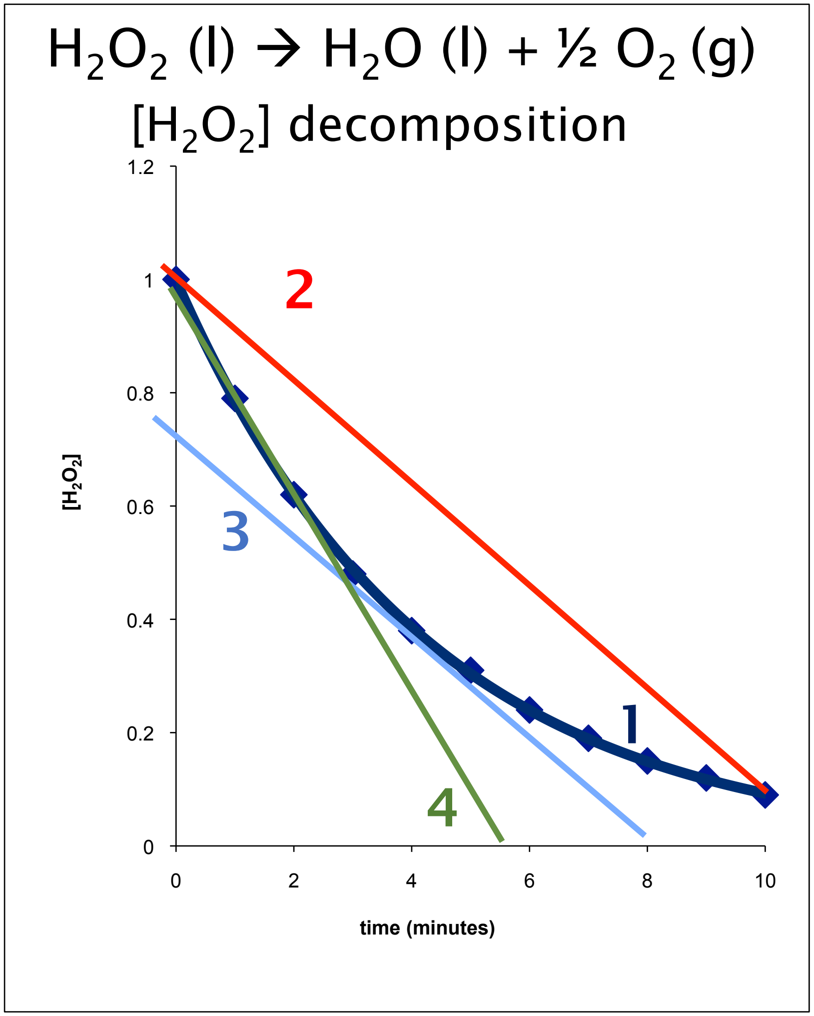
Average Rate of Reaction:



Types of Reaction Rates

Reaction rate = ΔConcentration/Δtime = slope

1. Plot of original data
   - [Conc.] vs time
   - If curved = rate changes
     - Will reach equilibrium
   - If linear = rate is constant
     - Will run out of reactant
2. Average rate of reaction
3. Instantaneous rate
   - Tangent to curve 1
   - Can pick any time
4. Initial rate
   - t=0 to t=given time
   - Generally portion of curve 1 that is linear



H_2O_2 (l) → H_2O (l) + ½ O_2 (g)

$[H_2O_2]$ decomposition

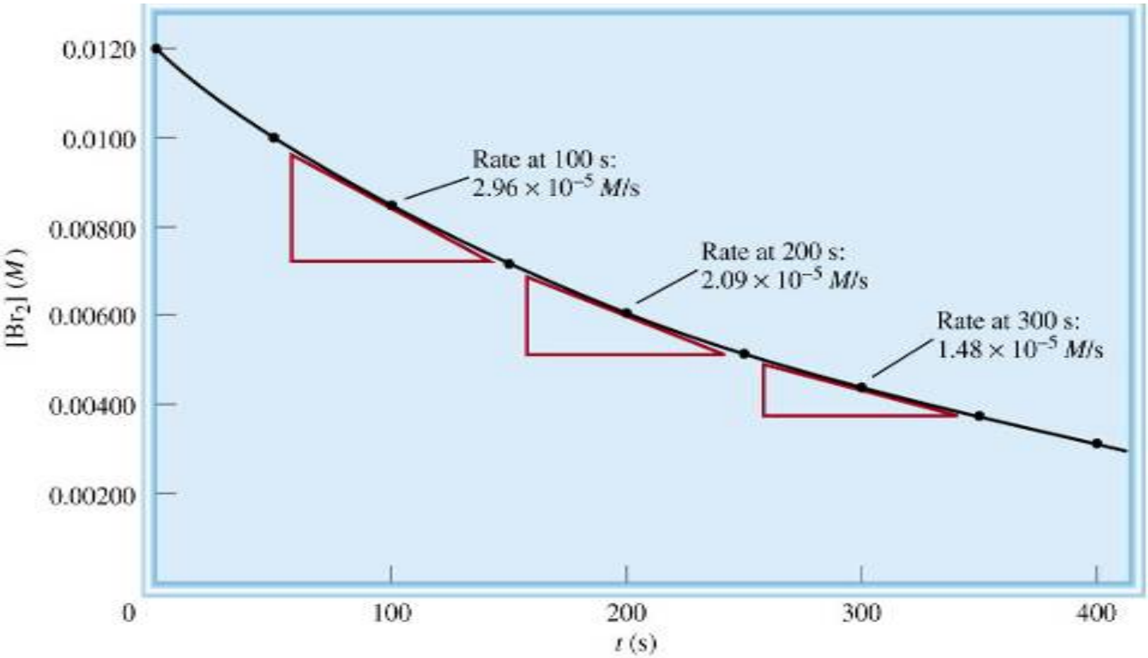
Instantaneous Rate

Br_2 (aq) + HCOOH (aq) → 2 Br^- (aq) + $2H^+$ (aq) + CO_2 (g)

Brown color of Br_2
disappears as
reaction progresses

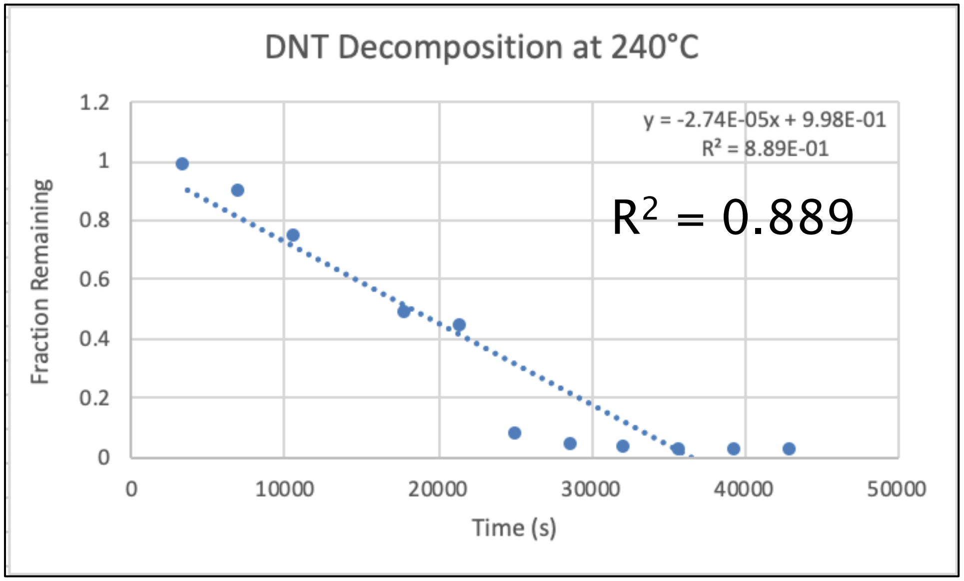
To Find Instantaneous Rate:

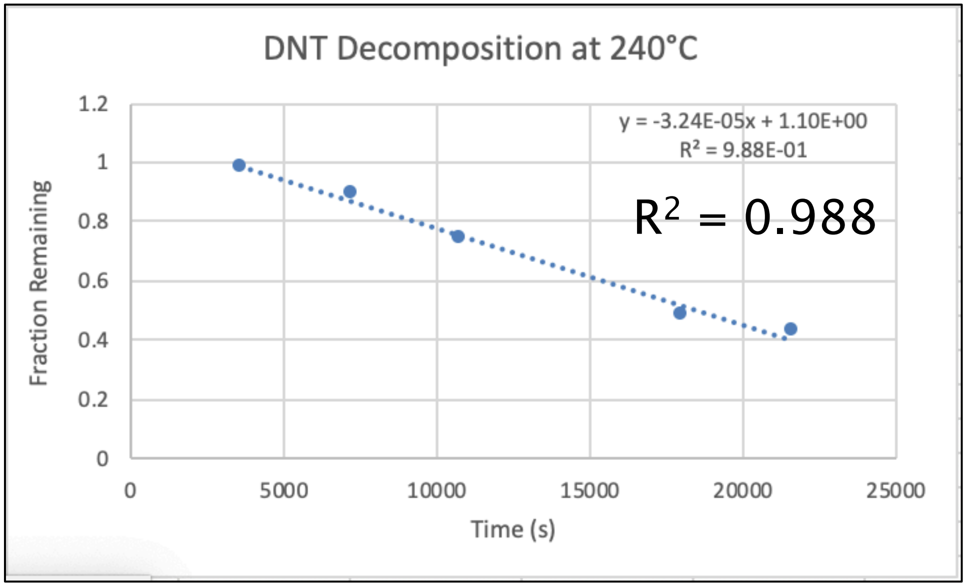
- Select time
- Draw line tangent to curve at that time
- Find slope of the tangent line
- Units of [conc.]/time



Initial Rate

Portion of original data where curve is linear





Rate Laws:

Impact of Reactant Concentration on Rate

Rate Law Format: For the reaction A + B + C .... → Products

Rate Law: Rate = $k[A]^m[B]^n[C]^p$....

Based on initial concentrations and rate

Variables required in Rate Law:
k = rate constant
m = order of reaction in reactant A
n = order of reaction in reactant B
p = order of reaction in reactant C
other letters as needed for additional reactants

Overall Order of Reaction = sum of the orders of reaction for each reactant

Overall Order = m + n + p

Rate Laws account for non-linearity of reactions

Rate Laws con’t

Properties of Rate Laws:

- Orders do not need to be positive integers
  - Ex: if concentration does not impact rate, order is zero
- Orders must be found experimentally
- Catalyst concentrations are included
- Rate Laws hold only for a specific temperature
- Rate Laws do **NOT** come from the balanced equation!

Not squared!

Example:

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ Rate = $k[H_2][NO]^2$

Rate Constant, k

- Depends on reaction, temperature, and catalyst
- Found experimentally

Determining Rate Laws: Isolation Method

Conduct a series of experiments

- Change the concentration of just one reactant each time
- Measure the impact on the rate from each reactant
- Use the ratios of the rates to determine m, n, etc.
- Rearrange the Rate Law & plug in values to solve for k.

Example: For the reaction $A + B \rightarrow \text{Products}$ $\text{Rate} = k[A]^m[B]^n$

Conduct 3 experiments:
1. Use [A] & [B], measure Rate 1
2. Use $[A]_2$ & [B], measure Rate 2
3. Use [A] & $[B]_2$, measure Rate 3

To determine m, divide
$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{\cancel{k}[A]^m\cancel{[B]^n}}{\cancel{k}[A]_2^m\cancel{[B]^n}} = \frac{[A]^m}{[A]_2^m}$$

To determine n, divide
$$\frac{\text{Rate 1}}{\text{Rate 3}} = \frac{\cancel{k}\cancel{[A]}^m[B]^n}{\cancel{k}\cancel{[A]}^m[B]_2^n} = \frac{[B]^n}{[B]_2^n}$$

To determine k, solve
$$k = \frac{\text{Rate}}{[A]^m[B]^n}$$

When reporting Rate Laws, use the numbers for k, m, & n

Determining Rate Laws: Isolation Method

A set of experiments was run to study the rate of the reaction:

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

The following data was obtained:

Expt #	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Rate (M/s)
1	0.10	0.10	0.10	-1.2×10^{-3}
2	0.20	0.10	0.10	-2.4×10^{-3}
3	0.20	0.30	0.10	-7.4×10^{-3}
4	0.20	0.10	0.15	-5.4×10^{-3}

$$\text{Rate} = k[BrO_3^-]^m[Br^-]^n[H^+]^p$$

Determining Rate Laws: Order of Reactants

Rate=k$[BrO_3^-]^m[Br^-]^n[H^+]^p$

Expt #	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Rate (M/s)
1	0.10	0.10	0.10	-1.2×10^{-3}
2	0.20	0.10	0.10	-2.4×10^{-3}
3	0.20	0.30	0.10	-7.4×10^{-3}
4	0.20	0.10	0.15	-5.4×10^{-3}

Order of reaction in BrO_3^- (m):

Order of reaction in Br^- (n):

Order of reaction in H^+ (p):

Determining Rate Laws: k & Rate Law

Expt #	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Rate (M/s)
1	0.10	0.10	0.10	-1.2×10^{-3}
2	0.20	0.10	0.10	-2.4×10^{-3}
3	0.20	0.30	0.10	-7.4×10^{-3}
4	0.20	0.10	0.15	-5.4×10^{-3}

$\text{Rate}=k[BrO_3^-]^m[Br^-]^n[H^+]^p$

$m = 1$

$n = 1$

$p = 2$

k: Solve using data from each experiment (4X!) & average

$$k = \frac{\text{Rate}}{[BrO_3^-]^1[Br^-]^1[H^+]^2}$$

Rate Law =

Types of Reactions Based on Rate: Zero Order

Change in concentration over time IS linear

Rate Law for A→ Product: rate = k $[A]^0$ = k

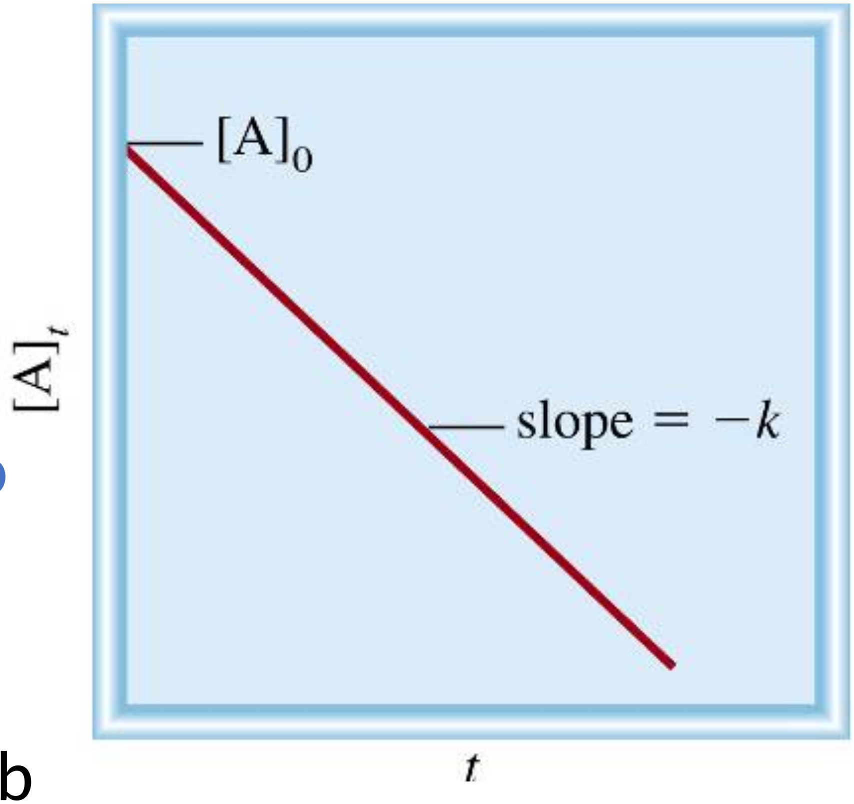
Units of k: k = rate = M/s

Linear Rate Equation:

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

Eventually [A] will go to zero (all reactant will be used up)

Note that this equation is in the form y = mx + b, where b is the y-intercept (i.e. the initial concentration of A).



Types of Reactions Based on Rate: First Order

Change in concentration over time is NOT linear

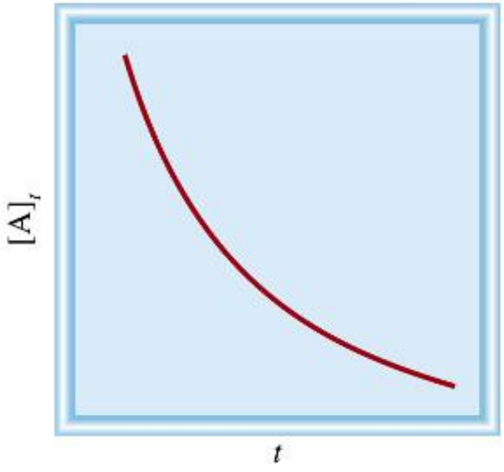
Change in the natural log (ln) of concentration over time IS linear.

Rate Law for A→ Product: $\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$

Units of k: $k = \text{rate}/[A] = (M/s)/M = 1/s = s^{-1}$

[A] vs. time is Nonlinear

$[A] = [A]_0 e^{(-kt)}$

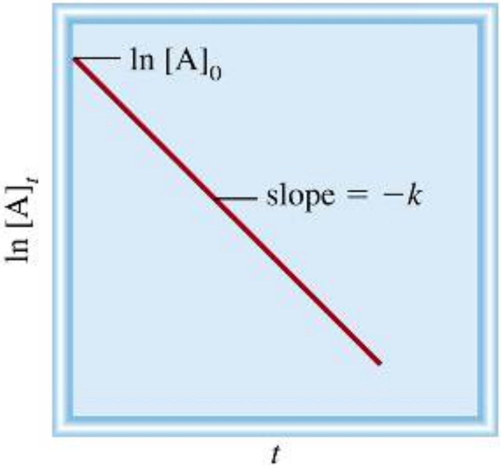


$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$[A]_t$ = [A] at time t
$[A]_0$= [A] at t=0

ln [A] vs time is Linear:

$\ln[A] = -kt + \ln[A]_0$



Types of Reactions Based on Rate: Second Order

Change in concentration over time is NOT linear

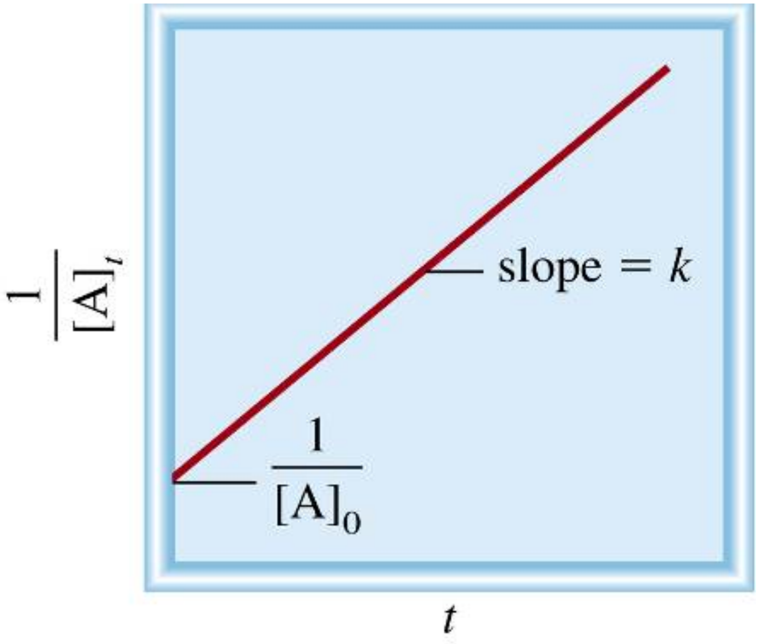
Change in the inverse of concentration (1/[A]) over time IS linear.

Rate Law for A→ Product: $\text{rate} = -\dfrac{\Delta[A]}{\Delta t} = k[A]^2$

Units of k: $k = \text{rate}/[A]^2 = (M/s)/M^2 = 1/Ms = M^{-1}s^{-1}$

The linear equation is:

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



Predicting Reaction Order Graphically

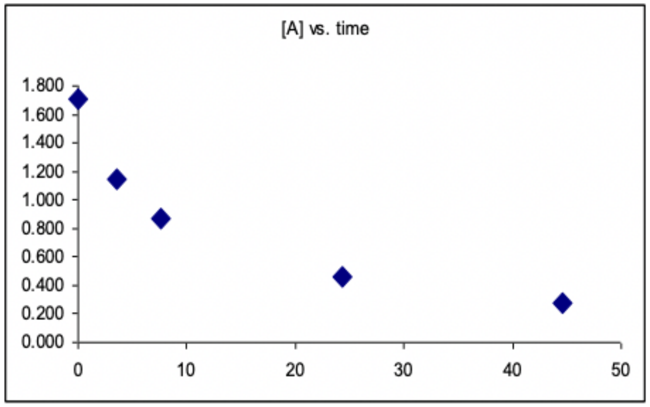
For the reaction A → Products:

1. Calculate ln[A] and 1/[A]
2. Make 3 graphs: [A], ln[A], and 1/[A] vs. time
3. The graph with the best straight line is the reaction order

	Zero	First	Second
time, s	[A] M	ln [A]	1/[A]
0	1.710	0.536	0.585
4	1.150	0.140	0.870
8	0.870	-0.139	1.149
24	0.460	-0.777	2.174
45	0.280	-1.273	3.571

Predicting Reaction Order Graphically

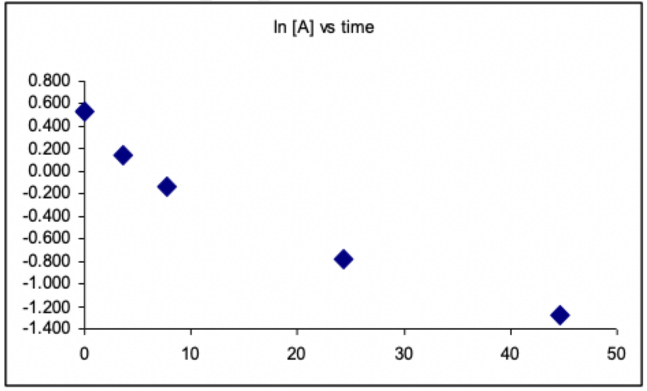
[A] vs. time



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

Not linear, so not Zero Order

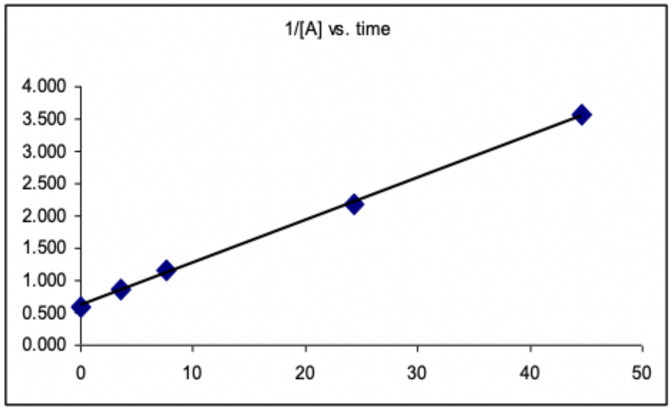
ln[A] vs. time



$\ln[A] = -kt + \ln[A]_0$

Not linear, so not First Order

1/[A] vs. time



$1/[A] = kt + 1/[A]_0$

Linear, so reaction is

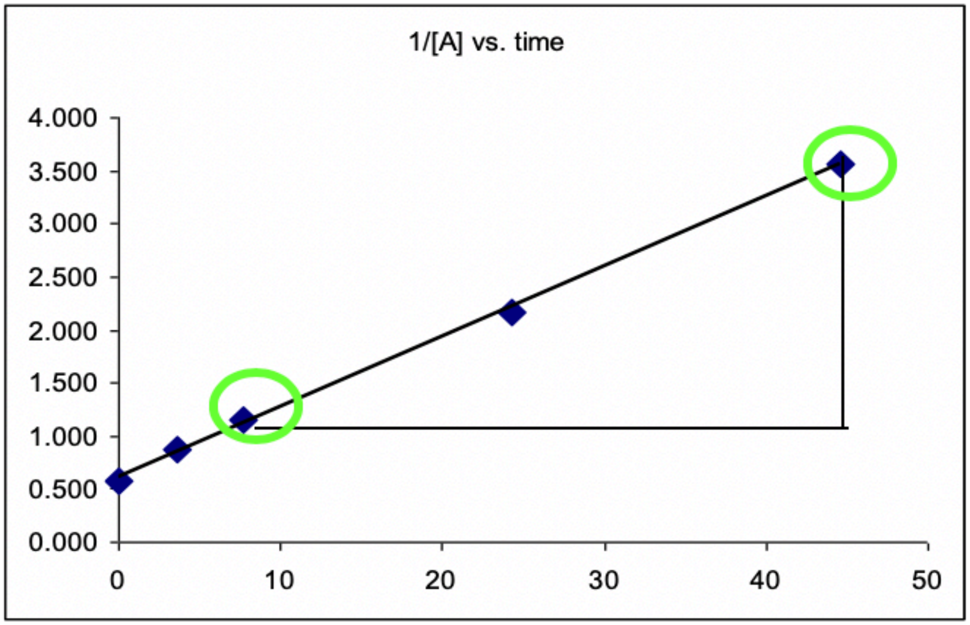
<u>Second Order</u>

Using a Graph to Find Rate Constant, k

Equation of the line is: $y = mx + b$

$1/[A] = kt + 1/[A]_0$

k = m = slope!



$k = m = (y - y_1)/(x - x_1)$

$= (3.57 - 1.15)/(45 - 8)$

$= 0.066\ M^{-1}s^{-1}$

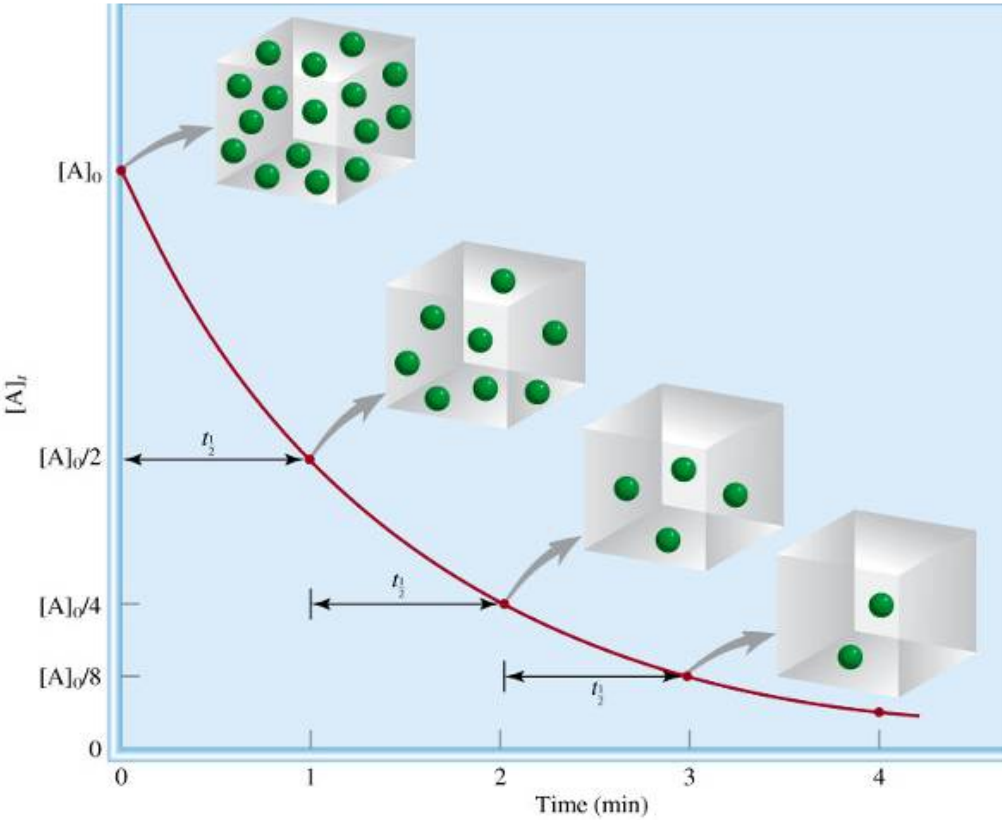
$$\frac{1}{[A]} = 0.066t + \frac{1}{[A]_0}$$

Half-Life ($t_{1/2}$)

The time required for $[A]_0$ to decrease by 50%

- NOT the time for half of the reaction to occur
- Provides another way to get the rate constant

- Symbol is $t_{1/2}$
- $t_{1/2}$ depends on reaction order
- Can solve for $t_{1/2}$ by plugging $[A]_0 = 1$ and $[A] = ½$ into rate equation



Half-Life of a First Order Reaction

Linear Equation:

$$\ln[A] = -kt + \ln[A]_0$$

Rearranged Equation:

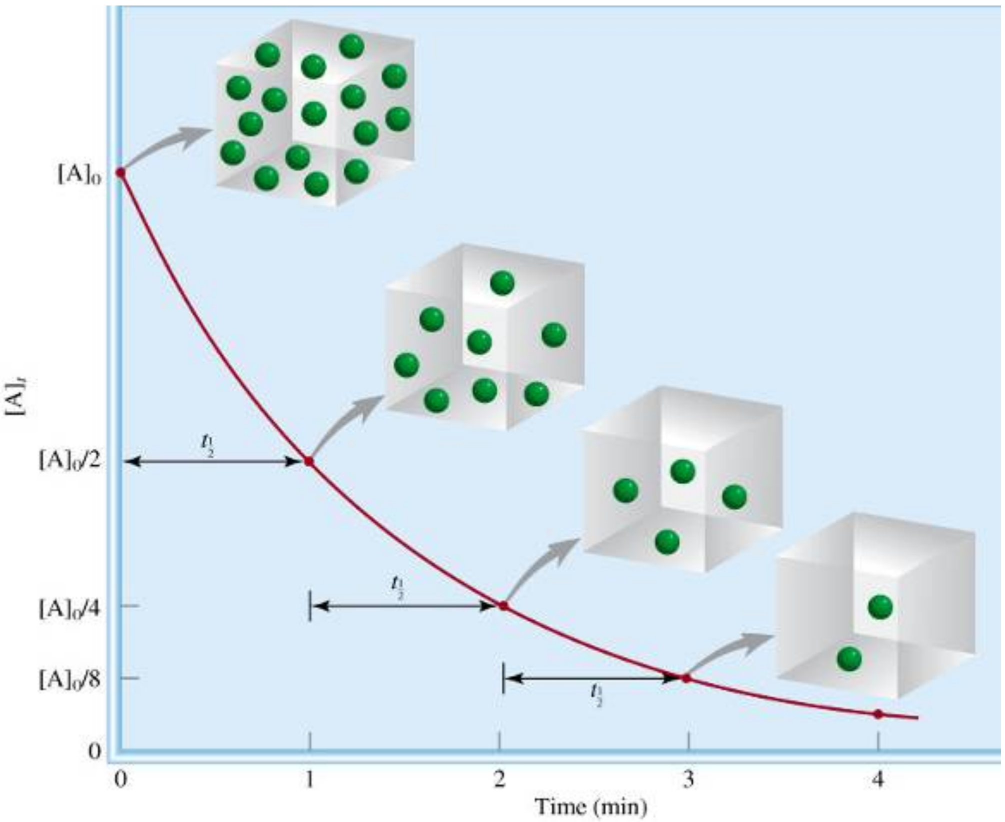
$$\ln\frac{[A]}{[A]_0} = -kt$$

Plug in: $[A]_0 = 1$ & $[A] = ½$

$$\ln(1/2) = -kt_{1/2}$$

Solve for $t_{1/2}$:

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



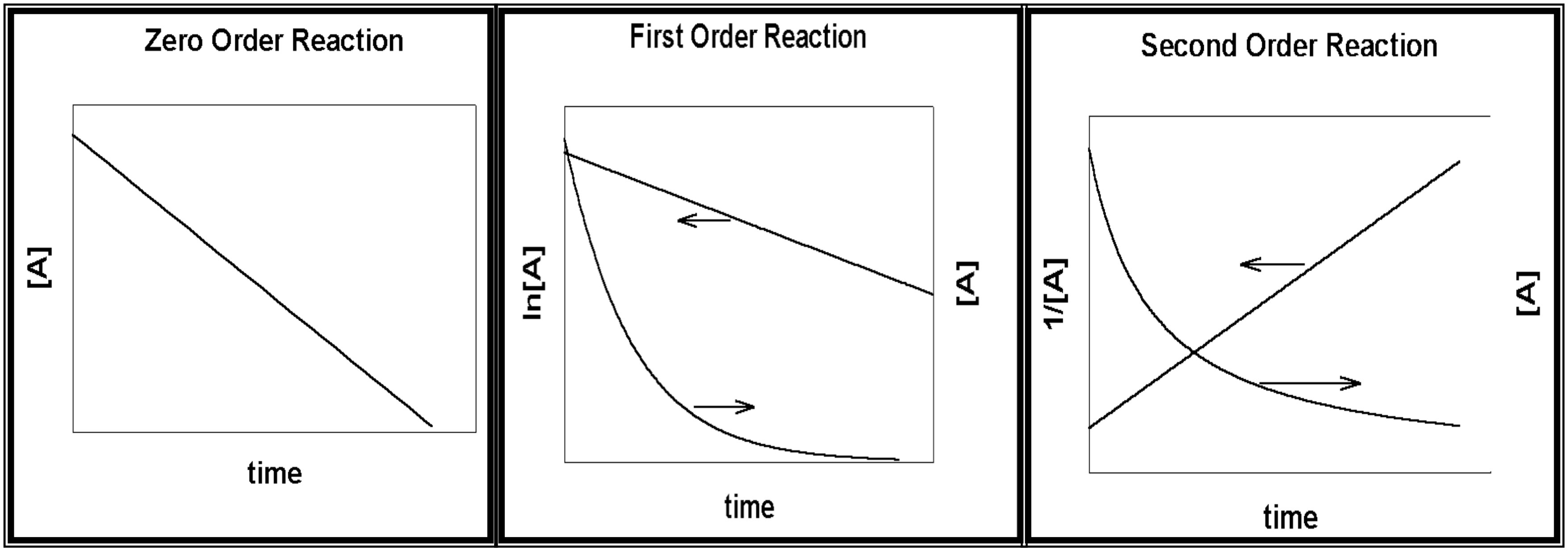
For a First Order Reaction:

$t_{1/2}$ is independent of initial reactant concentration

If you know $t_{1/2}$, you know the rate constant

Summary of Kinetic Data

Order	Rate Law	Integrated Rate Law	Linear Plot	k	Half-life
0	Rate = k	$[A]_t = -kt + [A]_0$	[A] vs. t	-slope	$[A]_0/2k$
1	Rate = k[A]	$\ln[A]_t = -kt + \ln[A]_0$	ln[A] vs. t	-slope	0.693/k
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	1/[A] vs. t	+slope	$1/k[A]_0$



Activation Energy & Temp. Dependence of Rate Constants

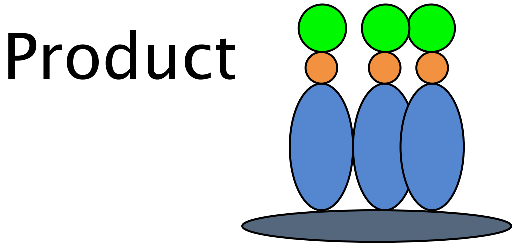
Collision Theory:

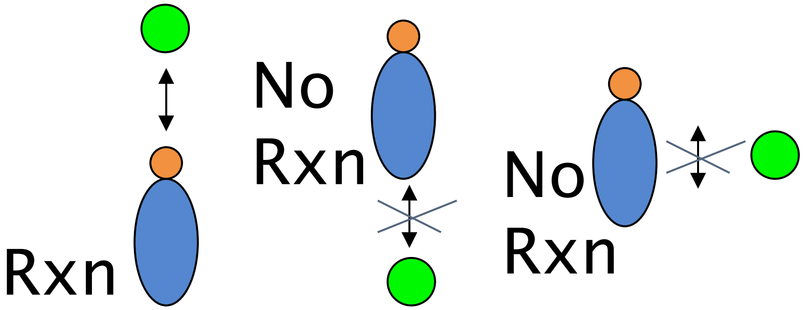
Three things must happen for a reaction to occur:

1. Reacting molecules must collide

   Can increase the number of collisions with
   - increased reactant concentration
   - higher temps (= faster molecules)

2. Molecules must have the correct orientation





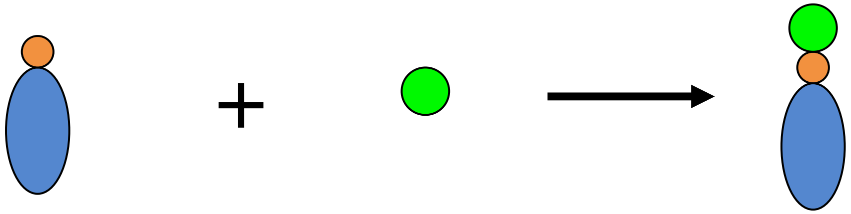
3. Activation Energy (E_a) must be exceeded

E_a = minimum energy required for a reaction to occur

Factors Affecting Reaction Rates

Increasing # collisions increases rate

Reaction:



1. Increase concentration of reactant

more particles in same volume = greater chance of collision

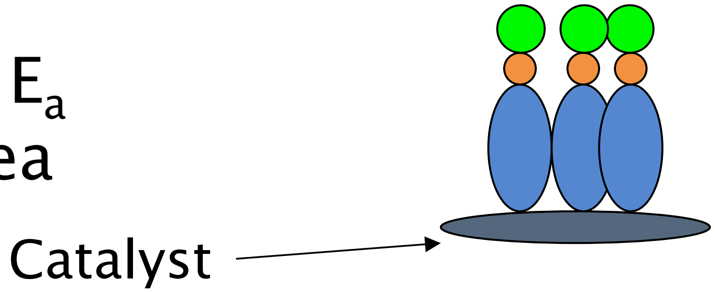
2. Increase temperature

Particles move faster – more likely to collide with enough E_A

3. Add a catalyst

Catalyst: chemical that does not change the amount of overall product or reactants, only the rate of the reaction

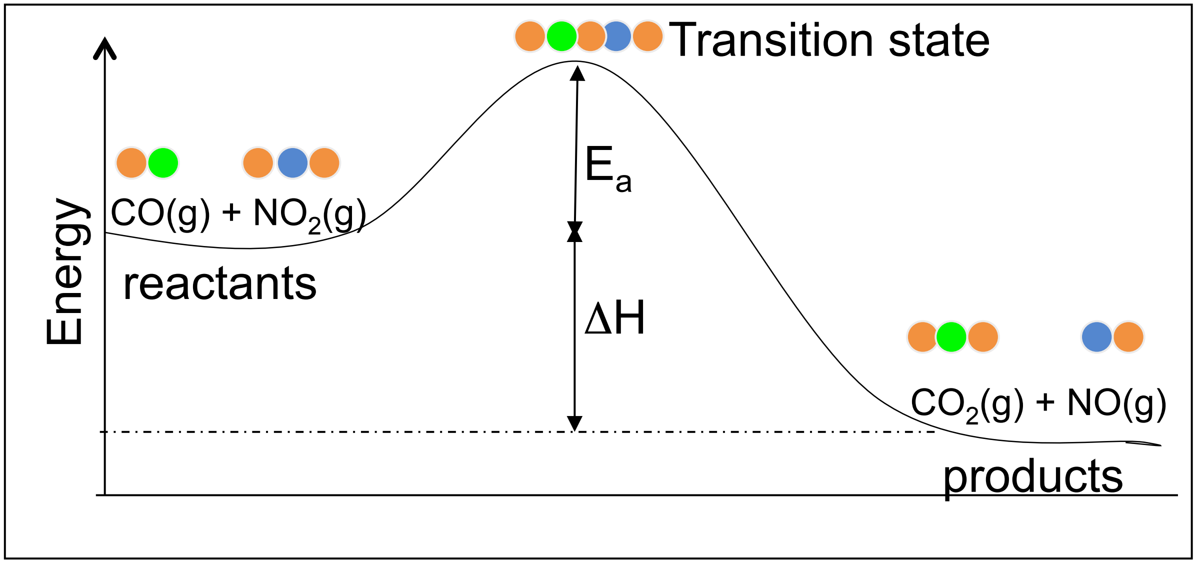
- fix molecular orientation
- alter transition state; lower E_a
- increase desired surface area



Energy Diagrams: Activation Energy & Transition State

Given the following reaction:

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



Reactants: Original components before a reaction

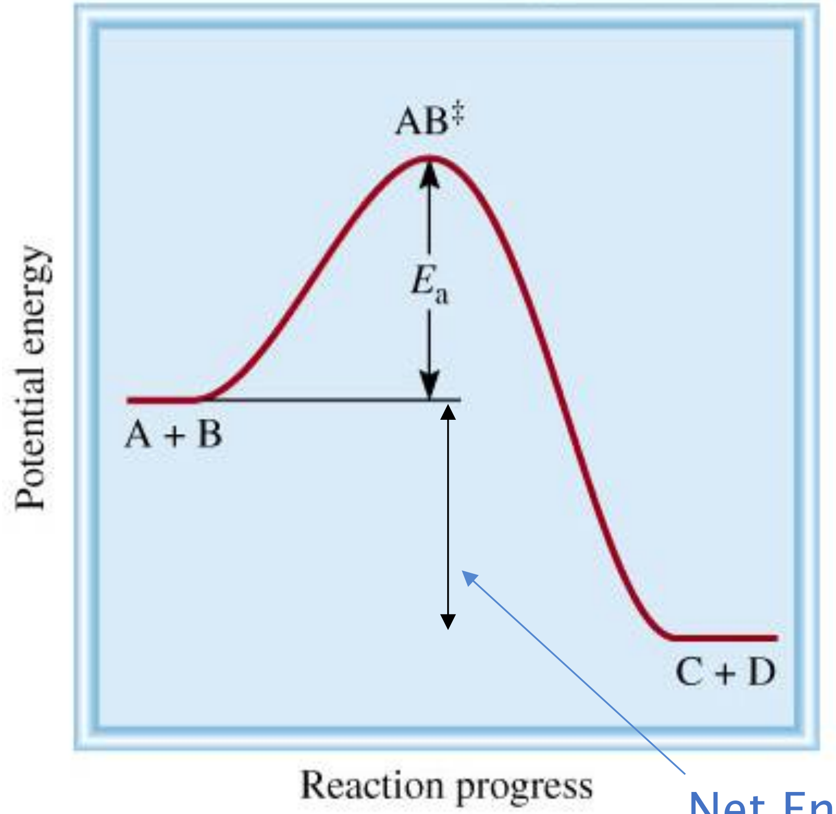
Products: New elements/compounds formed from reaction

Transition State (aka Activated Complex): Temporary & generally unstable combination of atoms formed from molecular collision. Will be transformed into products as the reaction proceeds.

Energy Diagrams: Thermodynamics & Reaction Progress

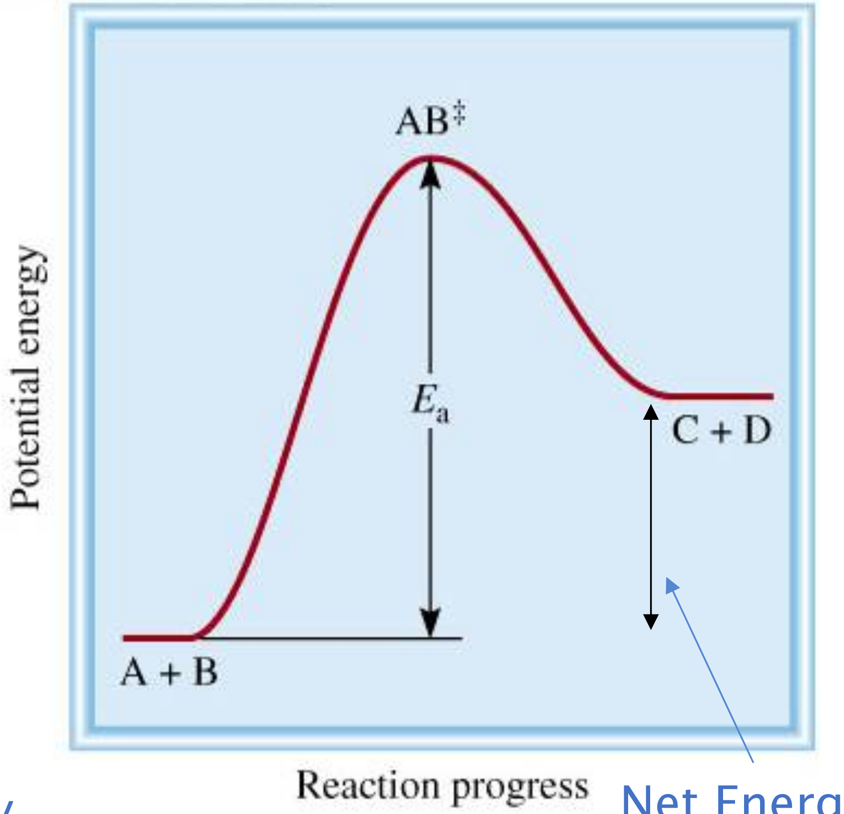
$$A + B \rightarrow AB^{\ddagger} \rightarrow C + D$$

Exothermic Reaction



Net Energy Released

Endothermic Reaction



Net Energy Absorbed

Effect of Temperature on Reaction Rate: Arrhenius Equation

Arrhenius Equation – Shows how temp. affects the rate constant (k)

$$k = Ae^{-E_a/RT} \quad \text{or} \quad \ln k = -E_a/RT + \ln A$$

k = rate constant

A = frequency factor (based on collision frequency & the probability of correct orientation; constant for a given system)

E_a = activation energy

R = gas constant in <u>energy units</u> (8.314 J mol^{-1} K^{-1})

T = temperature in Kelvin

Graphing **ln k vs. 1/T** gives a straight line with **slope = $-E_a/R$**

Provides a method to determine E_a for a reaction

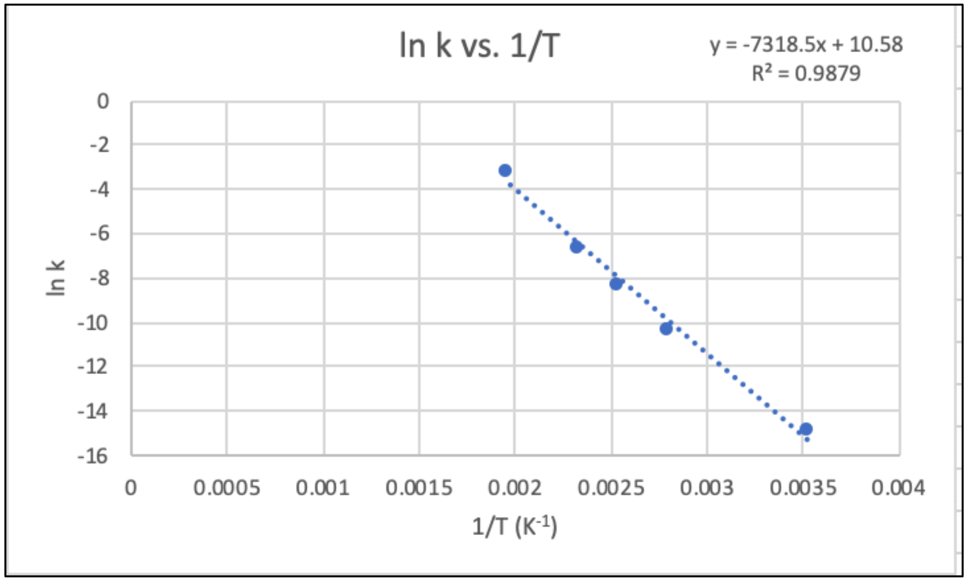
Arrhenius Equation Example

Reaction: $2\,HI(g) \rightarrow H_2(g) + I_2(g)$

Step 1: Find k at several temps.

Temp. (K)	k ($M^{-1}s^{-1}$)
283	3.52×10^{-7}
356	3.02×10^{-5}
393	2.19×10^{-4}
427	1.16×10^{-3}
508	3.95×10^{-2}

Step 2: Graph ln k vs. 1/T



Step 3: Calculate slope (=−E_a/R)

$$\text{slope} = \frac{\Delta Y}{\Delta X} = \frac{(\ln k_2 - \ln k_1)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

slope = −7318.5 K

Step 4: Multiply slope by −R to get E_a

E_a= -7318.5K *-8.314 J/molK

E_a = 60846 J/mol

= 608 kJ/mol

2 –Point Arrhenius Equation Example

Use rate constants at just 2 temps to solve for E_a

- This method is less accurate but only requires 2 k values
- Best to use only if there is limited data
- Equation: $$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Find E_a for the reaction: $2HI(g) \rightarrow H_2(g) + I_2(g)$

Data:

$k_1 = 0.0395\ M^{-1}s^{-1}$

$T_1 = 508\ K$

$k_2 = 0.00116\ M^{-1}s^{-1}$

$T_2 = 427\ K$

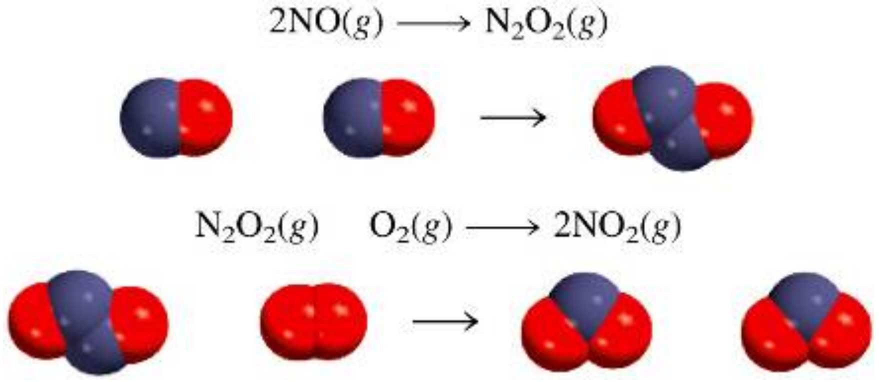
E_a = 27 kJ/mol – note difference from previous slide!

Reaction Mechanism: What (we think) actually happens during a reaction

Series of elementary reactions that lead to an overall rxn

Mechanism info can be used to modify reactions to increase yield, speed, etc.

Ex: 2 NO(g) + O_2(g) → 2NO_2(g)

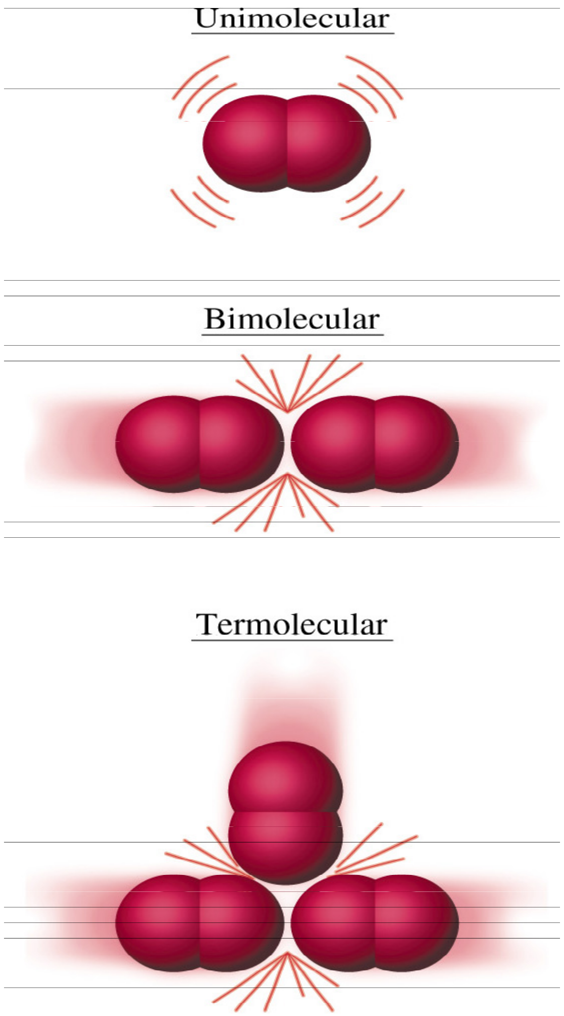


N_2O_2 is detected during the reaction!

$$\begin{array}{ll} \text{Elementary Step:} & NO + NO \cancel{\rightarrow N_2O_2} \\ + \text{ Elementary Step:} & \cancel{N_2O_2} + O_2 \rightarrow 2NO_2 \\ \hline \text{Overall Reaction:} & 2NO + O_2 \rightarrow 2NO_2 \end{array}$$

Some Terminology: **Molecularity**

Number of molecules reacting in an elementary step



Unimolecular - one

- Fastest
- Molecule simply breaks apart
- No molecular alignment needed

Bimolecular – two

- Most common
- May require correct alignment

Termolecular – three

- Usually rate limiting (slow!)
- Low probability that all 3 particles will collide simultaneously

Some More Terminology

Intermediates: **Species that appear in a reaction mechanism but <u>not in the overall reaction</u>**

- Formed in an early elementary step
- Consumed in a later elementary step

Ex:

N_2O_2 is an intermediate

$$\begin{array}{ll} \text{Elementary Step:} & NO + NO \rightarrow N_2O_2 \\ \text{+ Elementary Step:} & N_2O_2 + O_2 \rightarrow 2NO_2 \\ \hline \text{Overall Reaction:} & 2NO + O_2 \rightarrow 2NO_2 \end{array}$$

Rate Determining Step: **Slowest step in the sequence of steps leading to the overall reaction**

- Often determined by molecularity

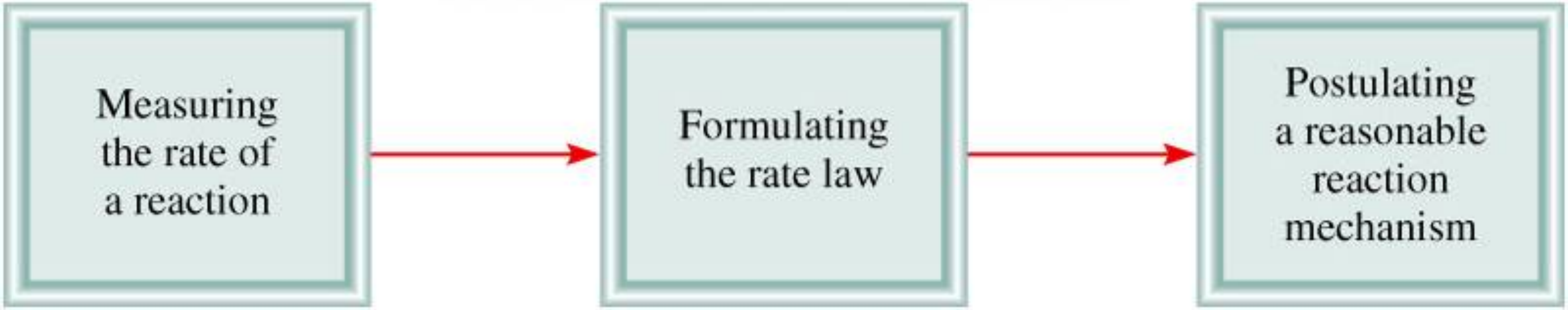
Rate Laws & Intermediate Steps

Unimolecular reaction:	$A \rightarrow \text{Products}$	$\text{rate} = k[A]$
Bimolecular reaction:	$A + B \rightarrow \text{Products}$	$\text{rate} = k[A][B]$
Bimolecular reaction:	$A + A \rightarrow \text{Products}$	$\text{rate} = k[A]^2$

Writing reaction mechanisms:

- The sum of the elementary reactions **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally
- The rate law for each step is found from the coefficients of the reactants. This is **ONLY** true for **ELEMENTARY** reactions!

Developing a Reaction Mechanism



Measure the rate of the reaction:

- Run a set of isolation method experiments
  - Run 1 experiment for each reactant + a control
  - Measure [A] vs. time

Formulate the rate law

- Determine the order of each reactant based on data
- Use the results to calculate an average value for k
- Determine the overall rate of the reaction

Suggest a reaction mechanism

- Elementary steps must match stoichiometry of overall rxn
- Use molecularity to determine rate determining step
- Order of rate-determining step must match overall rxn order

Ex: Developing a Reaction Mechanism for $NO_2 + CO \rightarrow NO + CO_2$

Based on the results of a set of isolation method experiments, the overall rate was found to be:

$$\text{Rate} = k[NO_2]^2$$

Suggested reaction mechanism:

- Need to account for rate being 2nd order in NO_2
- Need to account for rate being zero order in CO

Step1: $NO_2 + \cancel{NO_2} \rightarrow NO + \cancel{NO_3}$ rate = $k[NO_2]^2$

Step2: $\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$ rate = $k[NO_3][CO]$

$$\underline{}$$

$$NO_2 + CO \rightarrow NO + CO_2$$

Step 1 would be the rate-determining step, because the rate matches the overall reaction rate.

Catalysis

Catalysts alter the rate of a chemical reaction

- Not part of the overall reaction (not a reactant or product)
- Often work by lowering activation energy
  - Since less energy is needed, rate increases
- Materials that slow reaction rates are called **inhibitors**

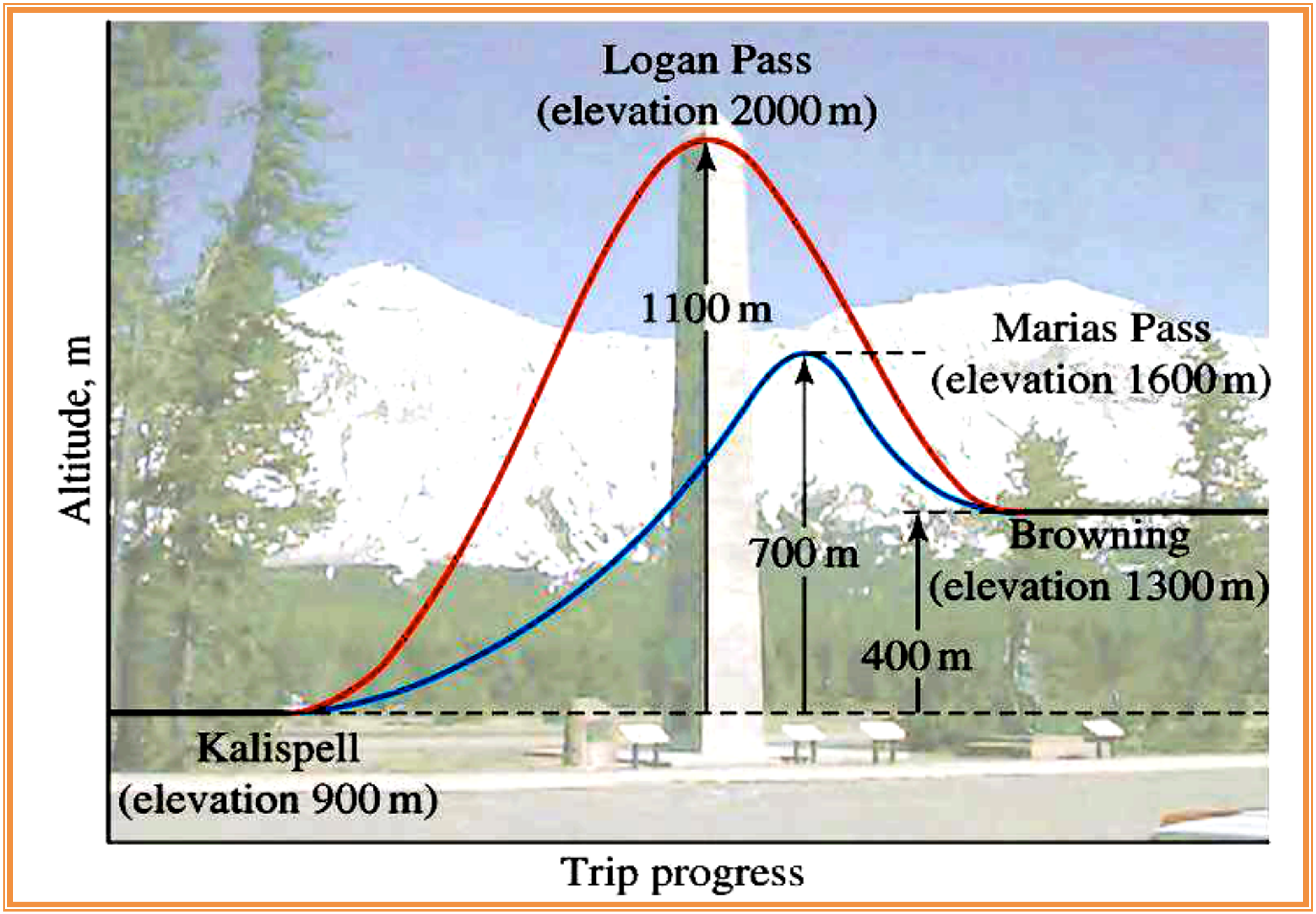
Heterogeneous catalysts

- In a different phase than the reacting medium
- Solids often used to catalyze reactants in solution
- Often used as a surface to align molecules correctly
- Benefit – often easy to remove & re-use

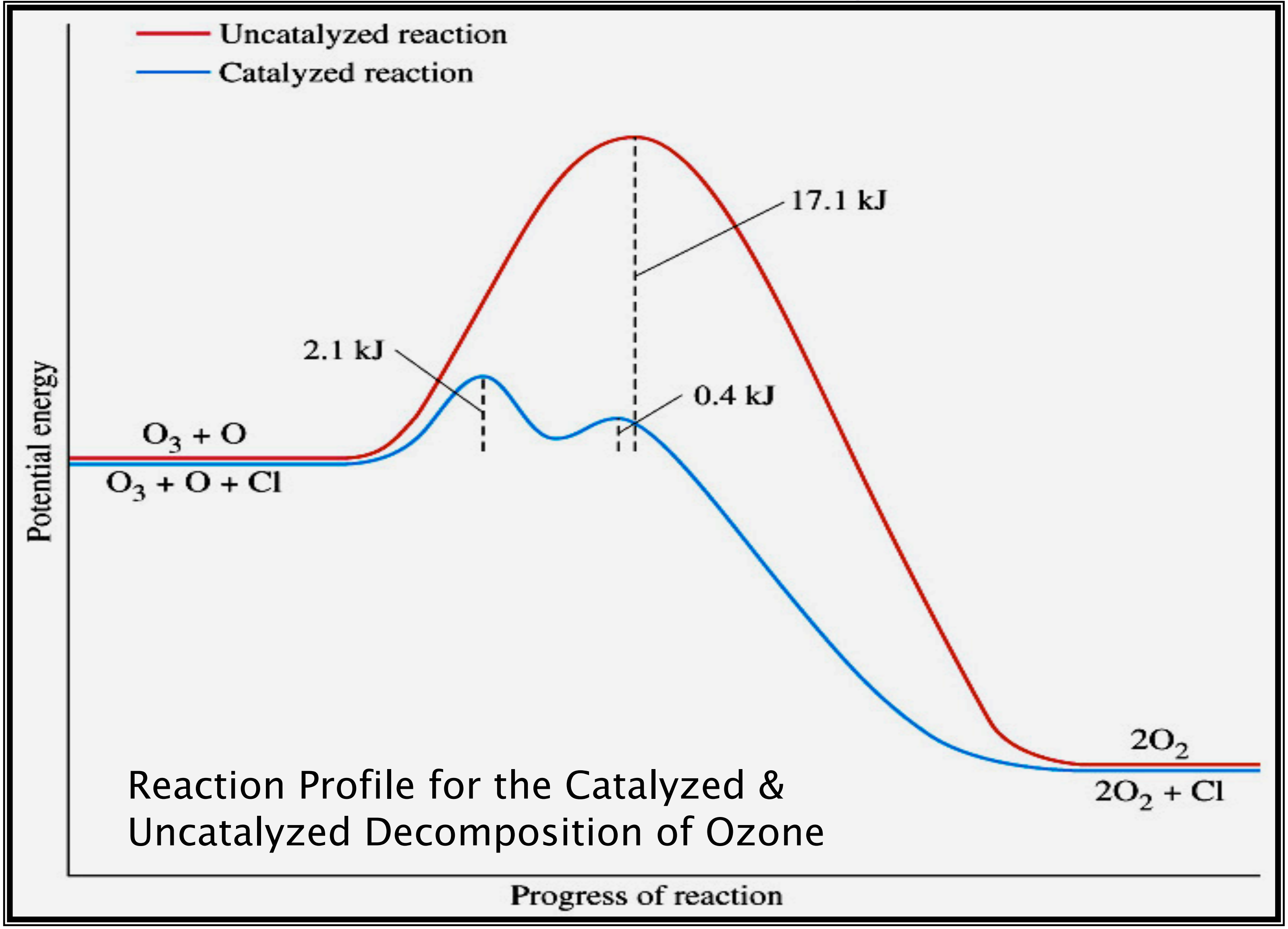
Homogeneous catalysts

- In the same phase as the reacting medium
- May have larger impact on rate (may be able to create a lower energy activated complex than heterogeneous)

Effect of a Catalyst on Reaction Profile & Activation Energy



Effect of a Catalyst on Reaction Profile & Activation Energy



Reaction Profile for the Catalyzed & Uncatalyzed Decomposition of Ozone

Catalysis

Enzymes

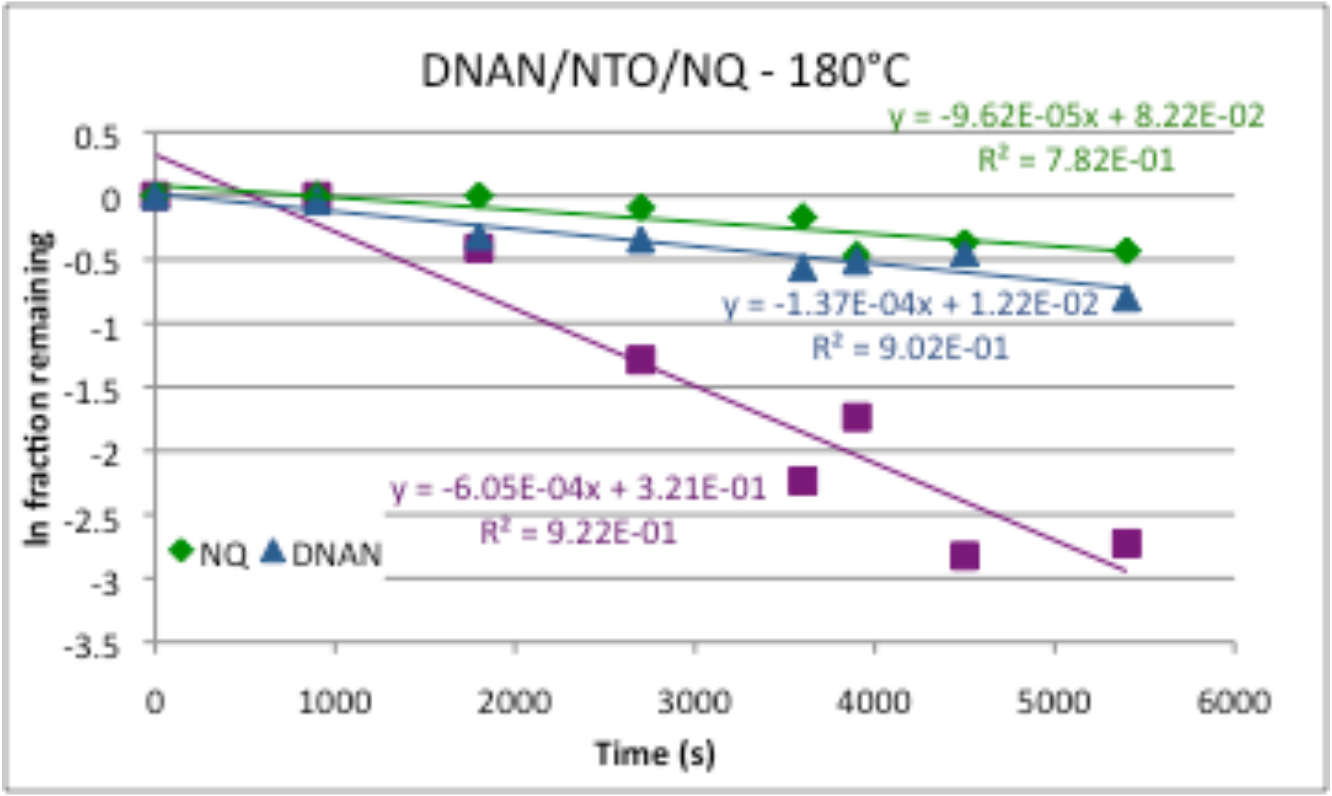
- Control the rate of biological reactions
- Very specific
    - Only act on specific molecules called **substrates**
- Often proteins – shape determines functionality
    - Partially due to hydrogen bonding (CHM101!)
- Some enzymes also act as **inhibitors**

When considering mechanisms:

- The rate constant of the elementary reaction that has a catalyst will be part of observed rate constant
- Catalysts in general (not just enzymes)

Summary

- Reaction rates are based on the rate of disappearance of a reactant or formation of a product.
- The order of a reaction determines the linear relationship between concentration & time.
- The half-life of a reaction is the time in which one-half of the reactant initially present is consumed.
- Chemical reactions occur when sufficiently energetic molecules collide in the proper orientation.
- Reaction mechanisms provide a plausible explanation of how a reaction proceeds.
- Reactions generally go faster at higher temperatures or in the presence of a catalyst. They slow down with an inhibitor.
- You do need to know more detail than this summary.


DNAN/NTO/NQ - 180°C
y = -9.62E-05x + 8.22E-02
R² = 7.82E-01
y = -1.37E-04x + 1.22E-02
R² = 9.02E-01
y = -6.05E-04x + 3.21E-01
R² = 9.22E-01
◆ NQ
▲ DNAN
ln fraction remaining
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0
1000
2000
3000
4000
5000
6000
Time (s)