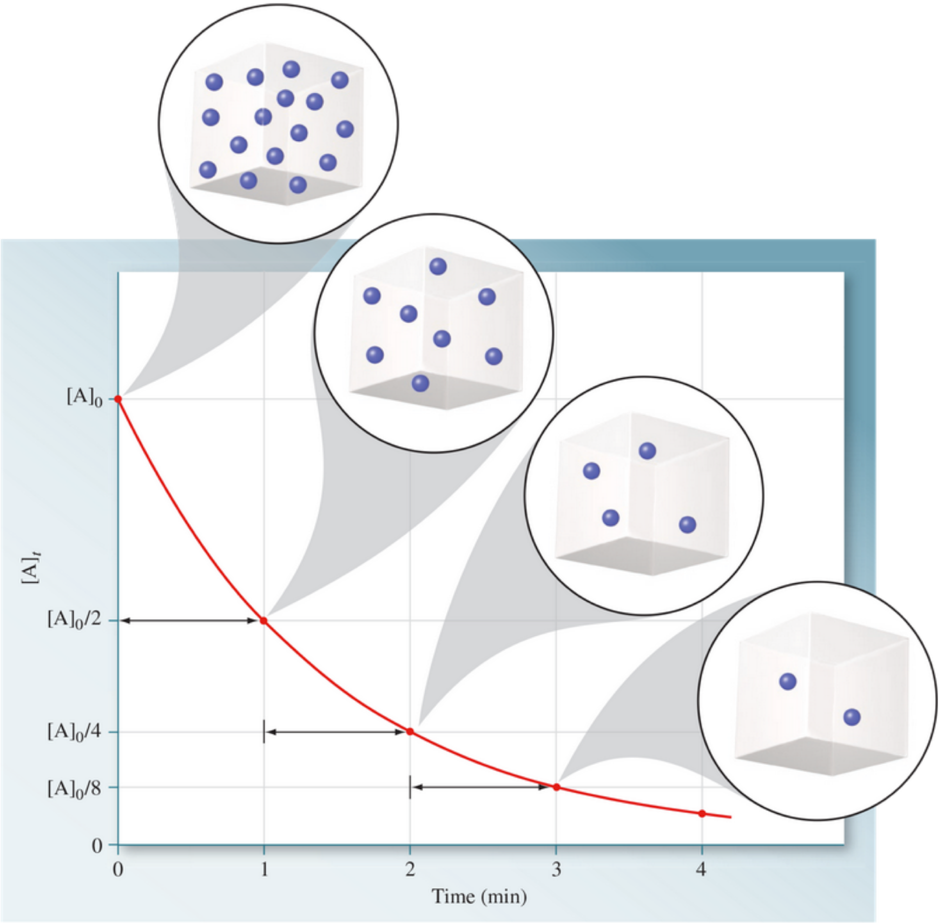
Half-Life ($t_{1/2}$)

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:

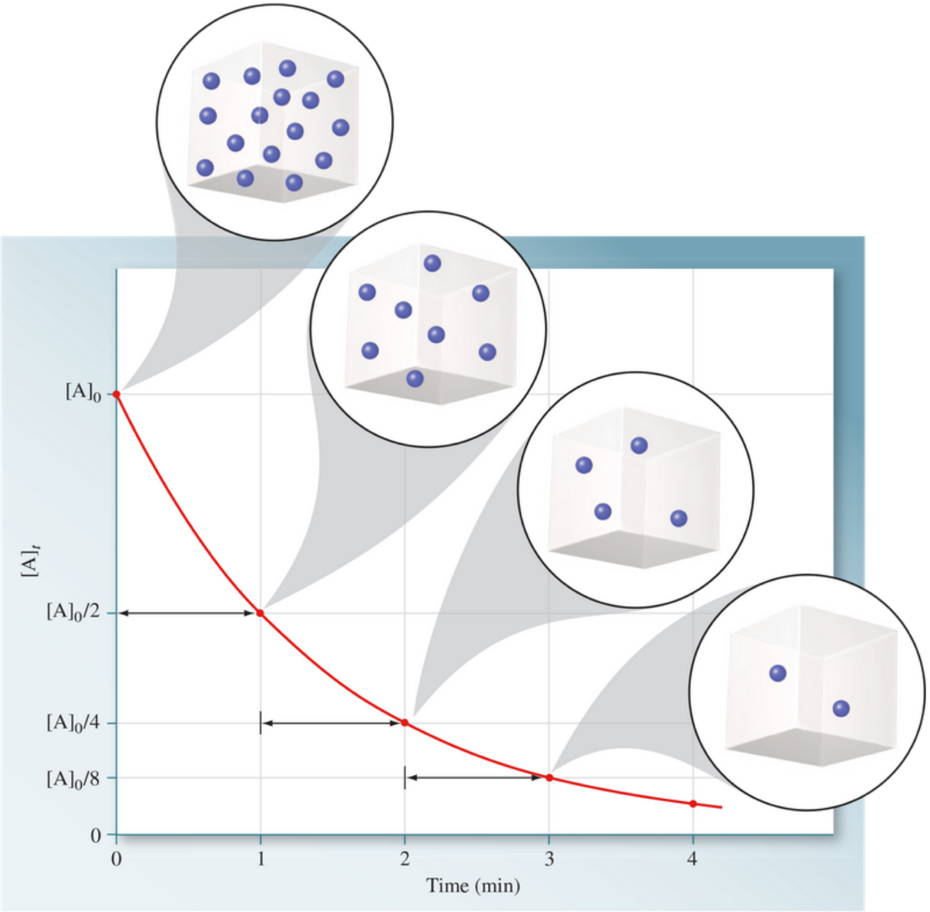
$$\ln \frac{[A]}{[A]_0} = -kt$$

Plug in: $[A]_0 = 1$ & $[A] = \frac{1}{2}$

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

Solve for $t_{1/2}$:

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



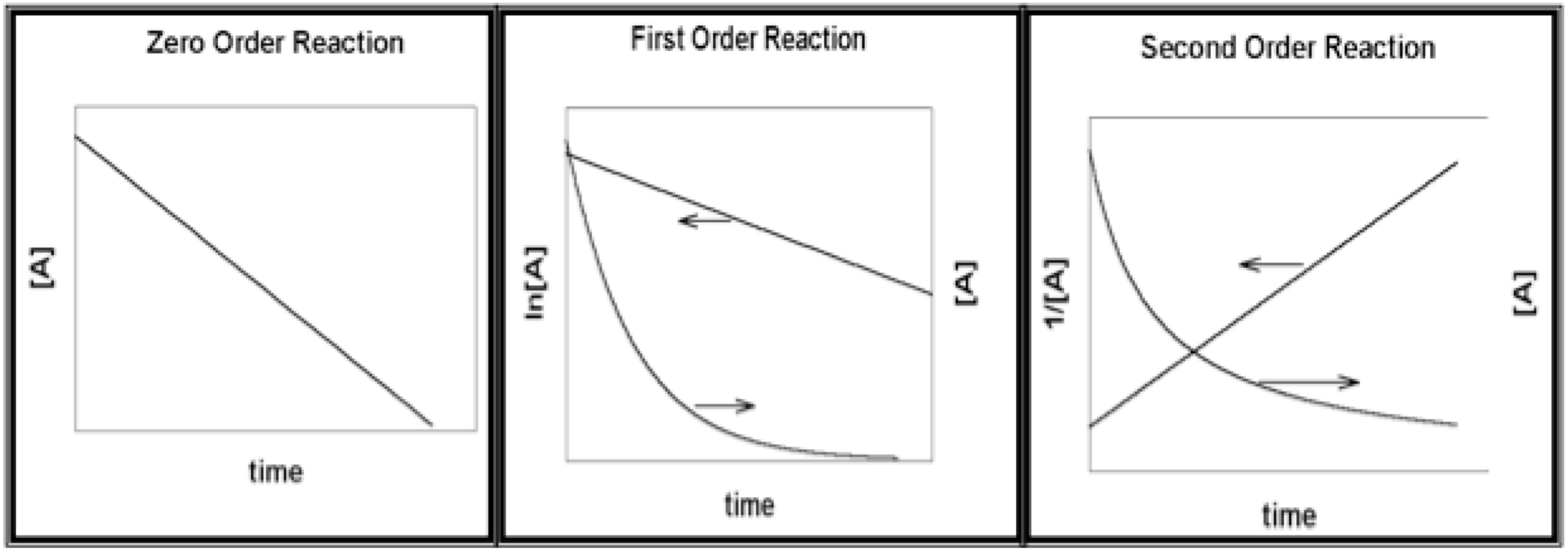
For a First Order Reaction:

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



Half-life Examples

1. For a 1st order reaction, determine the time it will take for only 1/8 of a material to be left if $t_{1/2} = 3.47\times10^2$s

A: 1.04×10^3s

2. The reaction below is first order in $[H_2O_2]$:

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

A solution originally at 0.600M is found to be 0.075M after 54min. Determine the half-life.

A: 18 min

3. The thermal decomposition of phosphine (PH_3) into phosphorus and molecular hydrogen is a first order reaction:

$$4PH_3\,(g) \rightarrow P_4\,(g) + 6\,H_2\,(g)$$

The half-life of the reaction is 35.0s at 680°C. Calculate (a) the first order rate constant for the reaction and (b) the time required for 95% of the phosphine to decompose.

A: (a) $0.0198s^{-1}$ (b) 151s

4. The rate constant for the second-order reaction

$$2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$$

is 0.54 $M^{-1}s^{-1}$ at 300°C.

(a) How long, in seconds, would it take for the concentration of NO_2 to decrease from 0.62M to 0.28M?

A: 3.6s

(b) Calculate the half-lives at these two concentrations.

A: 3.0s, 6.6s

Effect of Temperature on Reaction Rate: Arrhenius Equation

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

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

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 energy units (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

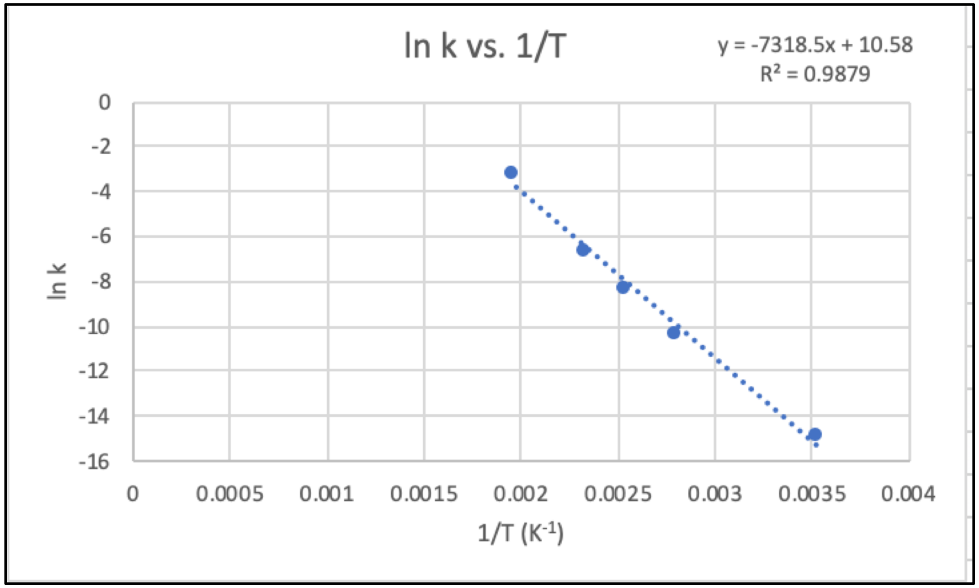
Arrhenius Equation Example

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 (=$-E_a/R$)

Step 4: Multiply slope by $-R$ to get E_a

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: $$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note:
$\ln(k_1/k_2) = \ln k_1 - \ln k_2$

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

Data:
$k_1 = 0.0395\ M^{-1}s^{-1}$
$T_1 = 508\ K$

$k_2 = 0.00116\ M^{-1}s^{-1}$
$T_2 = 427\ K$

$E_a = 78.5$ kJ/mol – note difference from previous slide!

More uses of the Arrhenius Equation

1. The activation energy of a certain reaction is 31.5 kJ/mol. At 30°C, the rate constant is 0.0190 s^{-1}. At what temperature in degrees Celsius would this reaction go twice as fast?

A: 48°C

2. The gas-phase reaction Cl(g) + HBr(g) → HCl(g) + Br(g) has an overall enthalpy change of −66kJ. The activation energy for the reaction is 7 kJ.

(a) Sketch the energy profile for the reaction, and label E_a and ΔE.

(b) What is the activation energy for the reverse reaction?

A: 73 kJ

3. On the basis of the frequency factors and activation energy values of the following two reactions, determine which one will have the larger rate constant at room temperature (298K). A: second reaction

$$O_3\ (g) + O\ (g) \rightarrow O_2\ (g) + O_2\ (g)$$

$A = 8.0\text{x}10^{-12}$ mL/mol–s $E_a = 17.1$ kJ/mol

$$O_3\ (g) + Cl\ (g) \rightarrow ClO\ (g) + O_2\ (g)$$

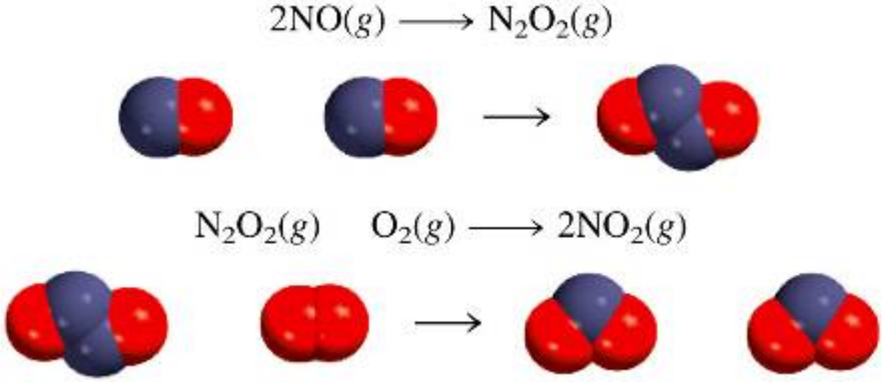
$A = 2.9\text{x}10^{-11}$ mL/mol–s $E_a = 2.16$ kJ/mol

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)

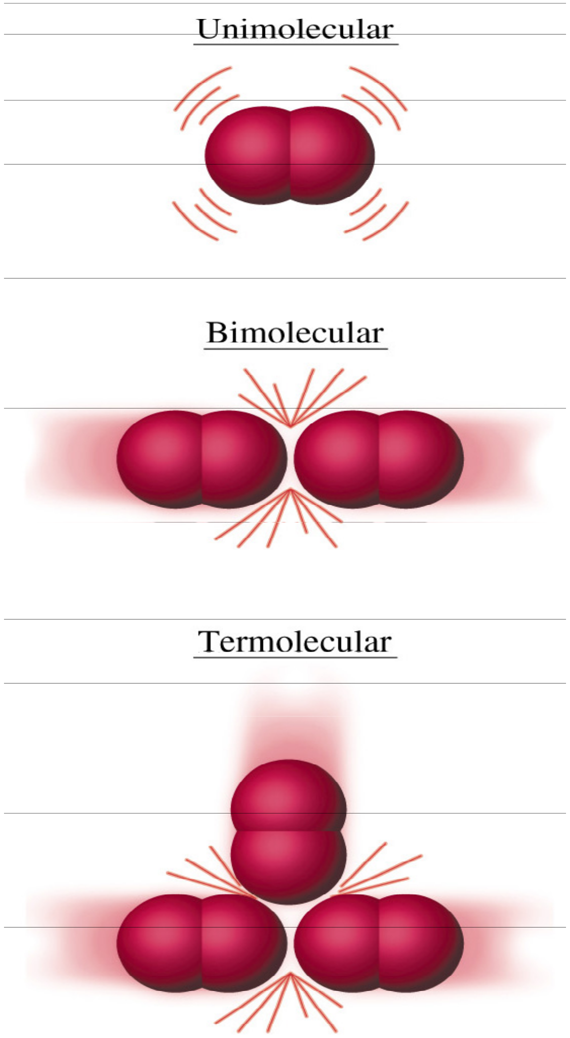


N_2O_2 is detected during the reaction!

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

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 (esp. with correct alignment and energy)

Some More Terminology

Intermediates: **Species that appear in a reaction mechanism but not in the overall reaction**

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

Ex:

N_2O_2 is an intermediate

Elementary Step:	$NO + NO \rightarrow N_2O_2$
+ Elementary Step:	$N_2O_2 + O_2 \rightarrow 2NO_2$
Overall Reaction:	$2NO + O_2 \rightarrow 2NO_2$

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

- Often determined by molecularity

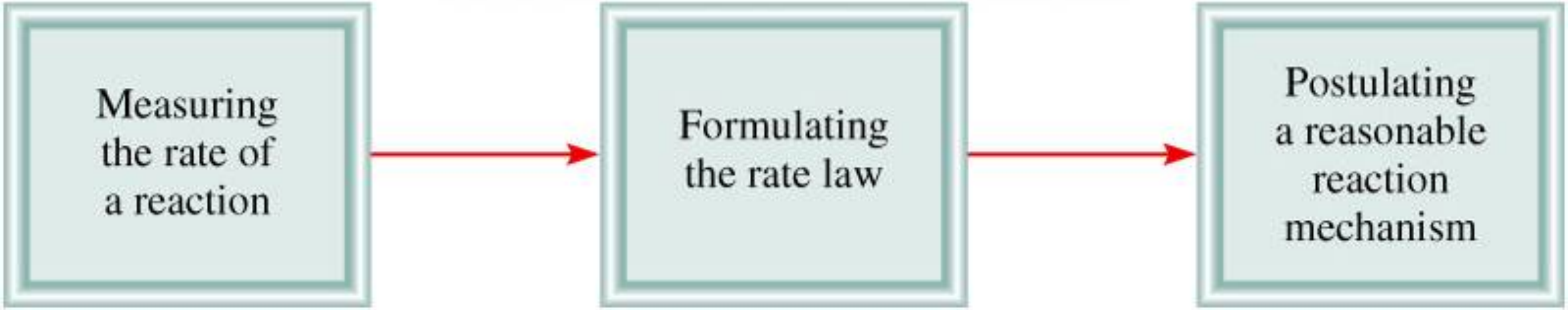
Rate Laws & Intermediate Steps

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



Measuring the rate of a reaction

Formulating the rate law

Postulating a reasonable 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 = $k[NO_3][CO]$

$$\underline{\hphantom{NO_2 + CO \rightarrow NO + CO_2}}$$

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

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

You might also be asked to evaluate possible mechanisms.

Evaluating Mechanisms

Ex: $H_2 + 2ICl \rightarrow 2HCl + I_2$ Rate = $k[H_2][ICl]$

Option #1

Step 1: $ICl + ICl \longrightarrow I_2 + Cl_2$ (slow)

Step 2: $Cl_2 + H_2 \longrightarrow 2HCl$

$$ICl + ICl \longrightarrow I_2 + \cancel{Cl_2} \text{ (slow)}$$

$$\cancel{Cl_2} + H_2 \longrightarrow 2HCl$$

Sum: $H_2 + 2ICl \longrightarrow 2HCl + I_2$ ✓

Rate = $k[ICl]^2$ ✗

Option #2

Step 1: $H_2 + ICl \longrightarrow HI + HCl$ (slow)

Step 2: $ICl + HCl \longrightarrow HI + Cl_2$

$$H_2 + ICl \longrightarrow HI + \cancel{HCl} \text{ (slow)}$$

$$ICl + \cancel{HCl} \longrightarrow HI + Cl_2$$

Sum: $H_2 + 2ICl \longrightarrow 2HI + Cl_2$ ✗

Rate = $k[H_2][ICl]$ ✓

Option #3

Step 1: $H_2 \longrightarrow 2H$ (slow)

Step 2: $ICl + H \longrightarrow HCl + I$

Step 3: $H + I \longrightarrow HI$

$$H_2 \longrightarrow 2\cancel{H} \text{ (slow)}$$

$$ICl + \cancel{H} \longrightarrow HCl + \cancel{I}$$

$$\cancel{H} + \cancel{I} \longrightarrow HI$$

✗

Sum: $H_2 + ICl \longrightarrow HCl + HI$ Rate = $k[H_2]$ ✗

Option #4

Step 1: $H_2 + ICl \longrightarrow HCl + HI$ (slow)

Step 2: $HI + ICl \longrightarrow HCl + I_2$

$$H_2 + ICl \longrightarrow HCl + \cancel{HI} \text{ (slow)}$$

$$\cancel{HI} + ICl \longrightarrow HCl + I_2$$

Sum: $H_2 + 2ICl \longrightarrow 2HCl + I_2$ ✓

Rate = $k[H_2][ICl]$ ✓

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**

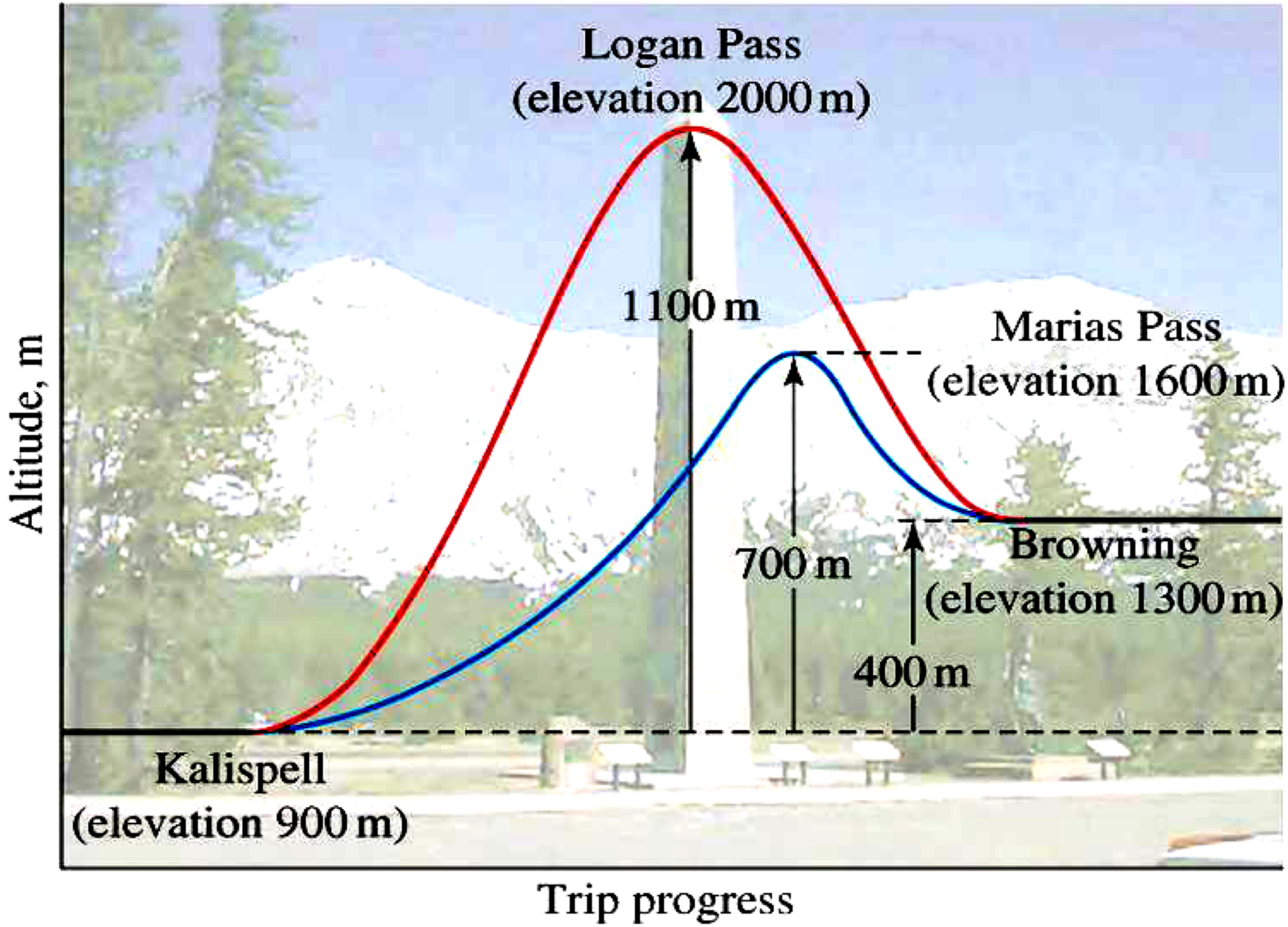
Heterogeneous catalysts

- 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

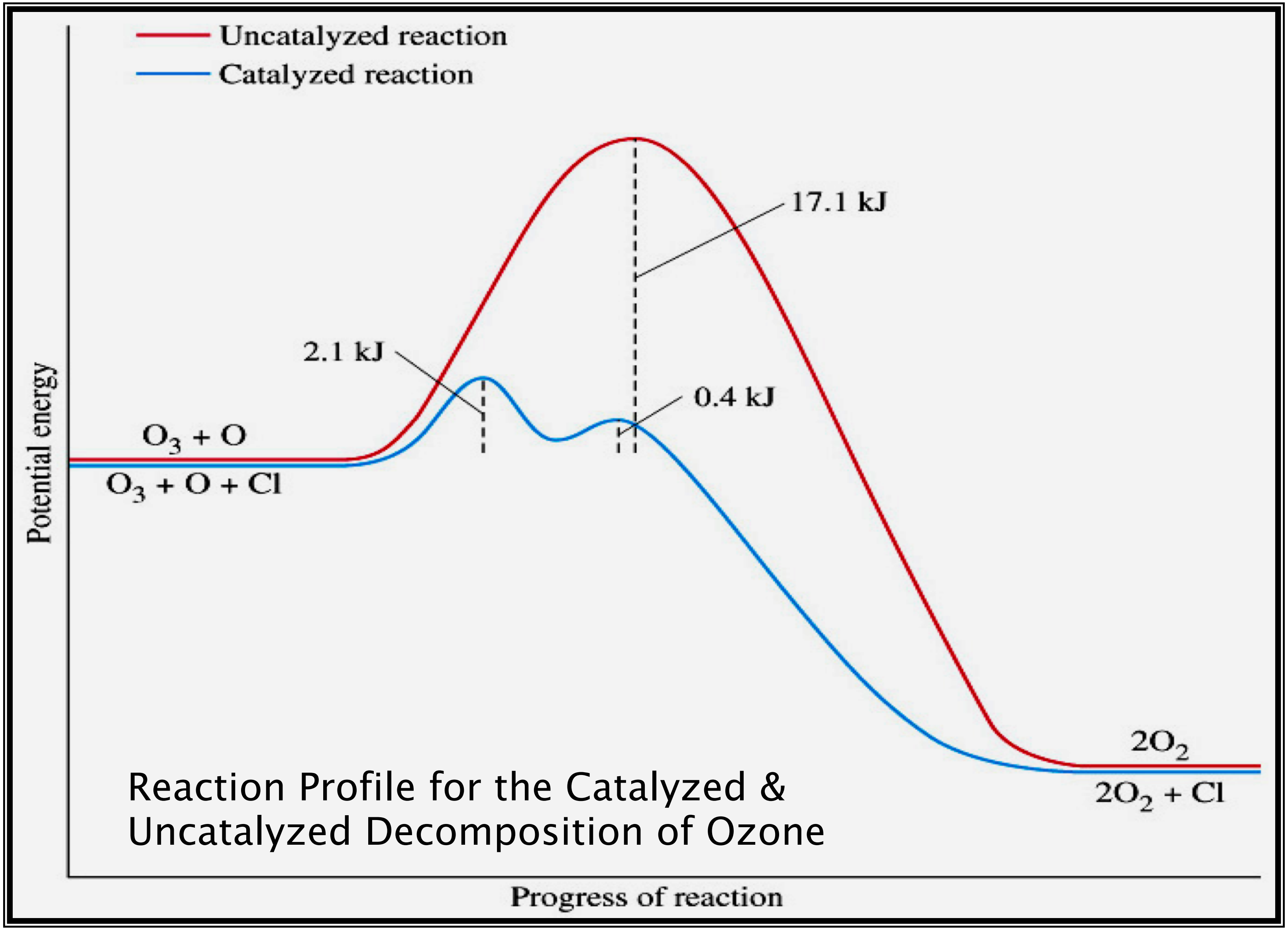
Homogeneous catalysts

- 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

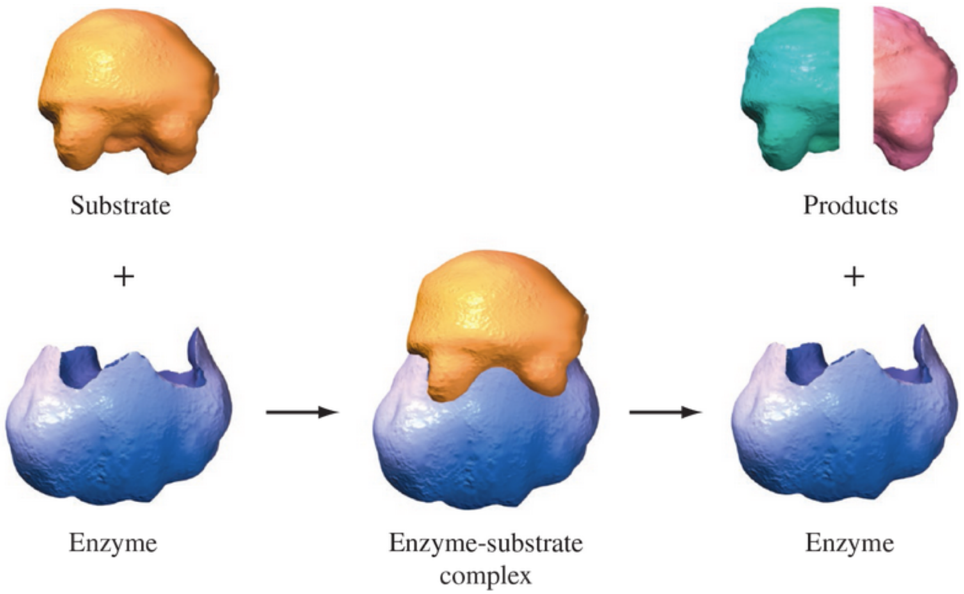


Reaction Profile for the Catalyzed & Uncatalyzed Decomposition of Ozone

Enzymes

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**



Catalysts & Reaction Mechanisms

When considering mechanisms:

- Catalysts control the rate of the reaction.
- The rate of the elementary step that involves the catalyst will control the observed rate.
- Rate constant is different from the rate constant without the catalyst – called the catalytic rate constant.