

Chemical Kinetics

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What are Chemical Kinetics?

Chemical Kinetics

We will now study:

• **Kinetics:** the study of how fast chemical reactions occur.

(in contrast to Thermodynamics: which determines if a reaction take place)

Our goal: is to understand chemical reactions at the molecular level.

Speed of a reaction: is measured by the change in concentration with time.

Important factors which affect rates of reactions:

- reactant concentration
- temperature
- action of catalysts
- surface area
- pressure of gaseous reactants or products

Kinetics

- Studies the rate at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).

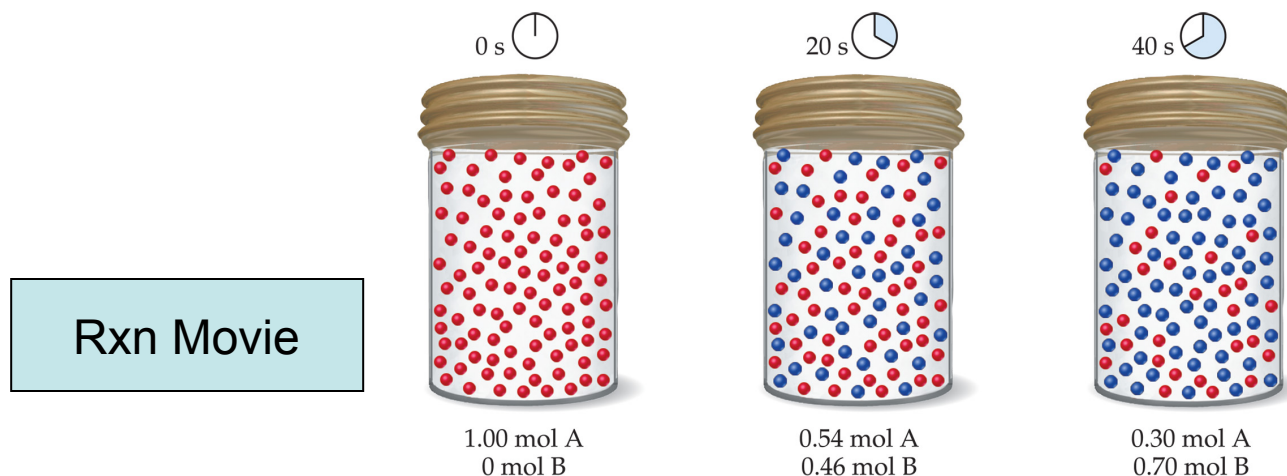
- John D. Bookstaver
- St. Charles Community College

Outline: Kinetics

Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calculate amount left or time to reach a given amount.
Half-life	How long it takes to react 50% of reactants.
Arrhenius Equation	How rate constant changes with temperature.
Mechanisms	Link between rate and molecular scale processes.

Reaction Rates

Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time t .

$[A]$ = concentration of reactant A

Reaction Rate

- For the reaction $A \rightarrow B$ there are two ways of measuring **rate**:
 - (1) the speed at which the reactants disappear
 - (2) the speed at which the products appear
- Reactions are reversible, so as products accumulate they can begin to turn back into reactants.
- Early on the rate will depend on only the amount of reactants present. We want to measure the reactants as soon as they are mixed.
- The most useful (and general) way of measuring the rate of the reaction is in terms of change in concentration per unit time...

$$\text{Rate} = \Delta[A]/\Delta t \text{ limits to } D[A]/Dt$$

Most Common Units... $\text{Rate} = \text{M/s}$

Where Molarity (M) = moles/Liter

Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).



$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

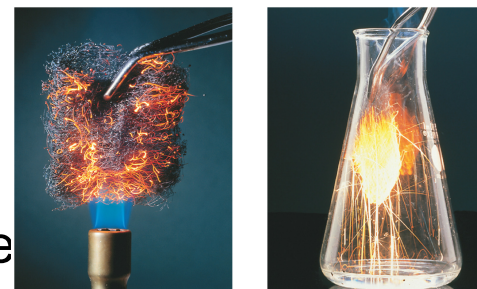
$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

Factors Affecting Reaction Rate Constants

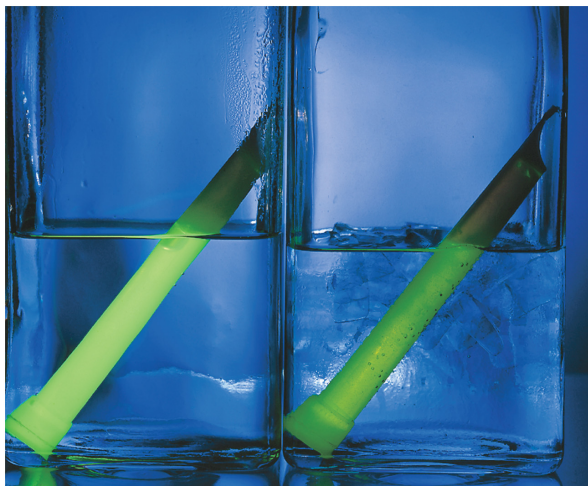
Factors that Affect the Reaction Rate Constant

- 1. Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy
 - **Collision Theory:** When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
 - **Kinetic Theory:** Increasing temperature means the molecules move faster.
- 2. Concentrations of reactants**
 - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide
- 3. Catalysts**
 - Speed up reactions by lowering activation energy
- 4. Surface area of a solid reactant**
 - Bread and Butter theory: more area for reactants to be in contact
- 5. Pressure of gaseous reactants or products**
 - Increased number of collisions

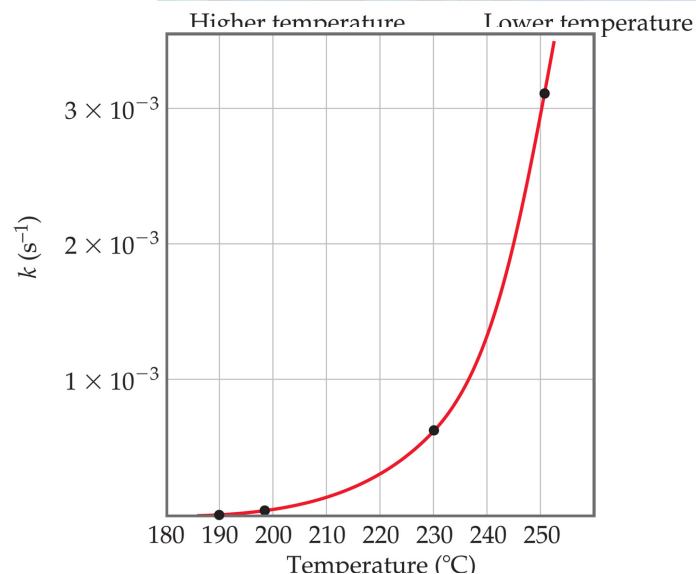


Factors that Affect Reaction Rate Constant

Temperature



- Generally, as temperature increases, so does the reaction rate.
- This is because k is temperature dependent.



Concentration Affects Reaction Rate Constant

- Here's another way of looking at reaction rates...



- Notice that for every 1 mole of O_2 that appears, 4 x as many moles of NO_2 will also appear. In the meantime, twice as many moles of N_2O_5 will be disappearing as moles of O_2 forming.
- Changes in concentrations of the reactants and/or products is inversely proportional to their stoichiometric proportions.
- This means that the rate of the reaction could be written like this...

$$\text{Rate} = -\frac{1}{2} \Delta [\text{N}_2\text{O}_5]/\Delta t = \frac{1}{4} \Delta[\text{NO}_2]/\Delta t = \Delta[\text{O}_2]/\Delta t$$

* (Notice the negative sign on the rate of $[\text{N}_2\text{O}_5]$ reminds us that it is disappearing.)

- In general, for a reaction that looks like this... $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

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

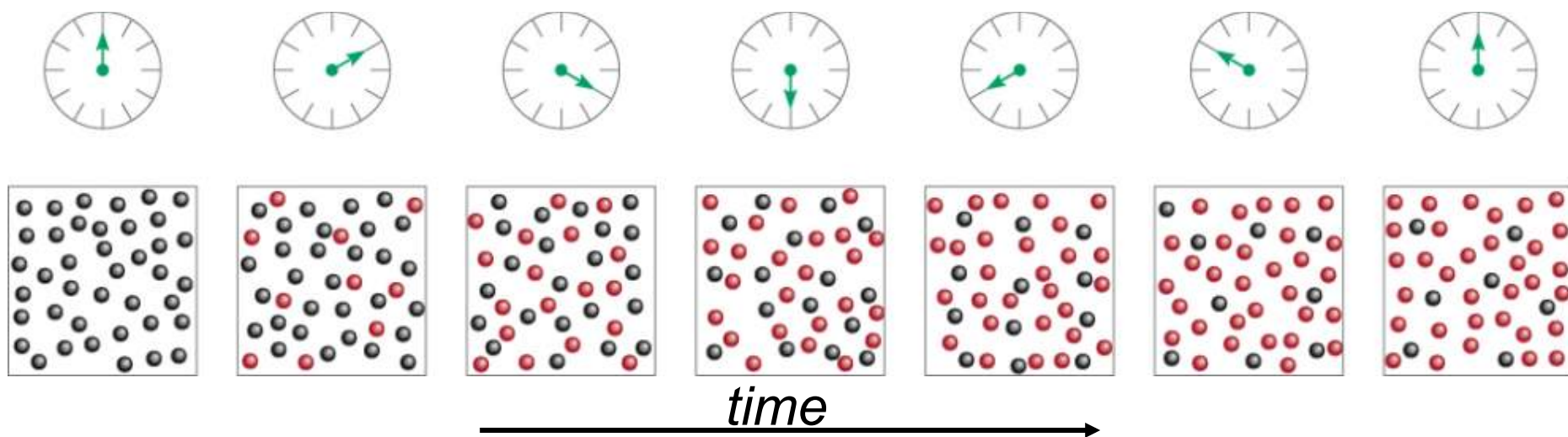
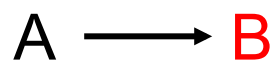
Reaction Rate Laws

Concentration and Rate

Each reaction has its own equation that gives its rate as a function of reactant concentrations.

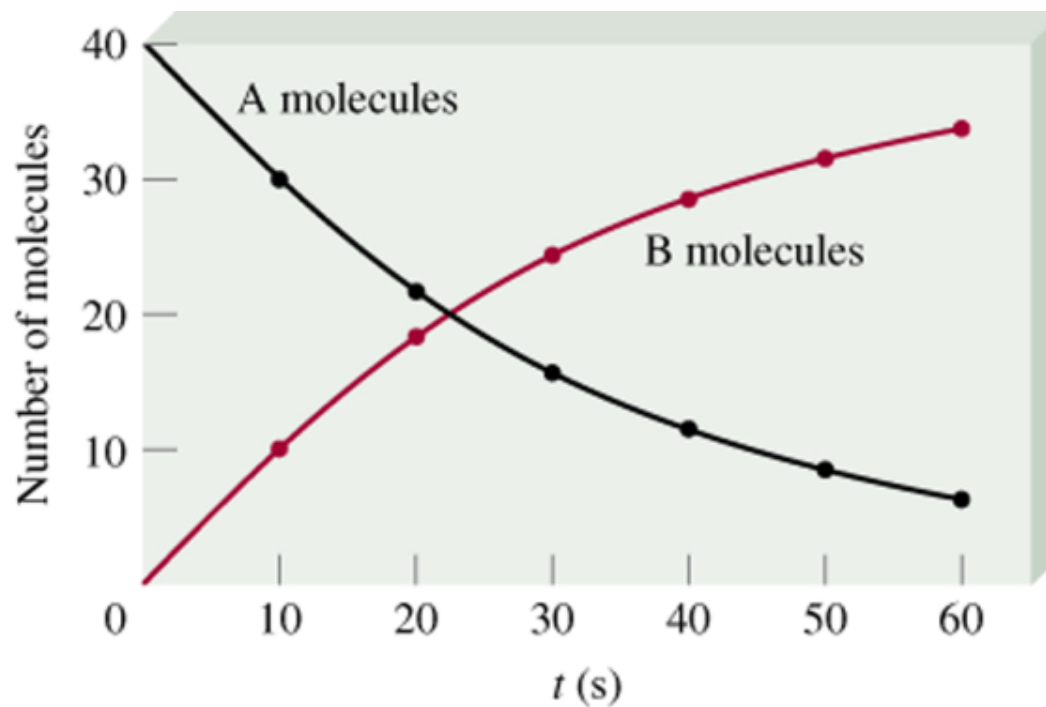
This is called its **Rate Law**

To determine the rate law we measure the rate at different starting concentrations.



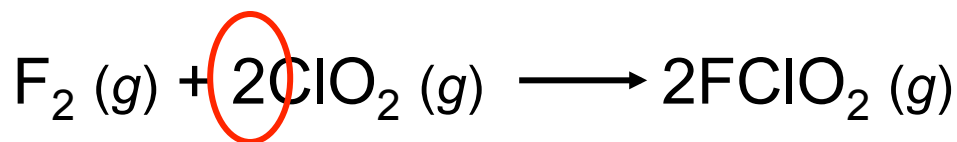
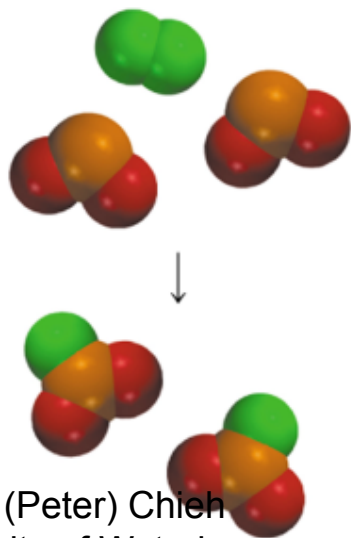
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$\text{rate} = k [\text{F}_2][\text{ClO}_2]^1$$

Rate Law

- In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.
- The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.
- Here's what a general rate law for a reaction will look like...

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

- [A] & [B] represent the reactants.
- The exponents m and n are called “**reaction orders**”.
- The proportionality constant k is called the **rate constant**.
- The **overall reaction order** is the sum of the reaction orders:

$$m + n$$

Reaction Rates and Stoichiometry

- To generalize, for the reaction



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

Reactants (decrease)

Products (increase)

The Rate Law

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.



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



reaction is ***m*th order** in A

reaction is ***n*th order** in B

reaction is **(*m*+*n*)th order overall**

Rate Law Example

- Consider the following reaction:

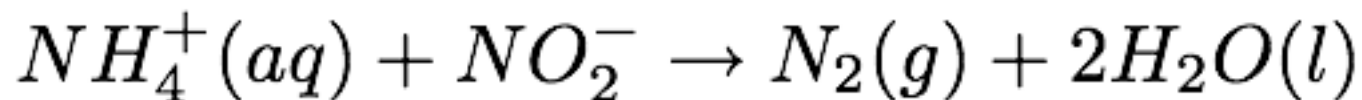


- Let's say that the following observations from several experiments were made...
 - as $[\text{NH}_4^+]$ doubles the rate doubles with $[\text{NO}_2^-]$ constant.
 - as $[\text{NO}_2^-]$ doubles the rate doubles with $[\text{NH}_4^+]$ constant.
- The rate of this reaction would be expressed as....
$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$
- The reaction is said to be “first order” with respect to $[\text{NH}_4^+]$ and “first order” with respect to $[\text{NO}_2^-]$.
- But the overall order of the reaction is said to be “second order.”
- Reaction rates come from experiment data, not stoichiometry!

Examples of Reaction Rate Laws

Example Reaction: Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

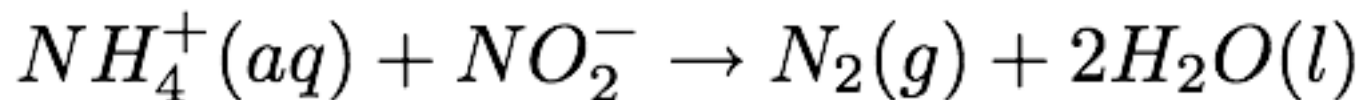


Compare Experiments 1 and 2:

when $[\text{NH}_4^+]$ **doubles**, the initial rate **doubles**.

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
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6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}



Likewise, compare Experiments 5 and 6:
when $[\text{NO}_2^-]$ doubles, the initial rate doubles.

Concentration and Rate

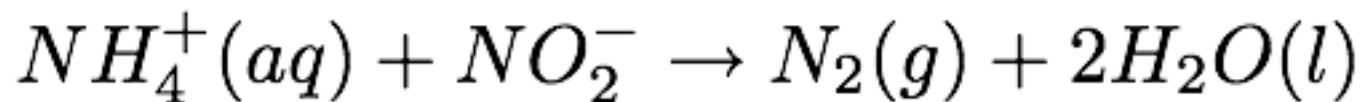
$$\text{rate} \propto [\text{NH}_4^+]$$

$$\text{rate} \propto [\text{NO}_2^-]$$

$$\text{rate} \propto [\text{NH}_4^+] [\text{NO}_2^-]$$

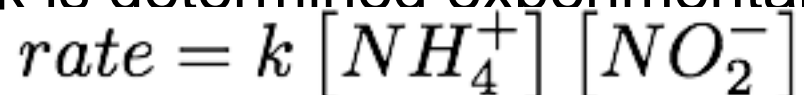
$$\text{rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

This equation is called the rate law,
and k is the rate constant.



Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
 - For gas-phase reactants use P_A instead of $[A]$.
- The rate constant k is a constant that has a specific value for each reaction.
- The value of k is determined experimentally. For example



“Constant” is relative here:

k is unique for each reaction

k changes with Temperature

Rate Laws

- Exponents tell the **order** of the reaction with respect to each reactant.
- This reaction is
 - First-order* in $[\text{NH}_4^+]$
 - First-order* in $[\text{NO}_2^-]$
- The **overall reaction order** can be found by adding the exponents on the reactants in the rate law.
- This reaction is *second-order overall*.

$$\text{rate} = k [\text{NH}_4^+]^1 [\text{NO}_2^-]^1$$

Integrated Reaction Rate Laws

Integrated Rate Laws

Consider a simple 1st order reaction:



$$rate = k [A]$$

Differential form:

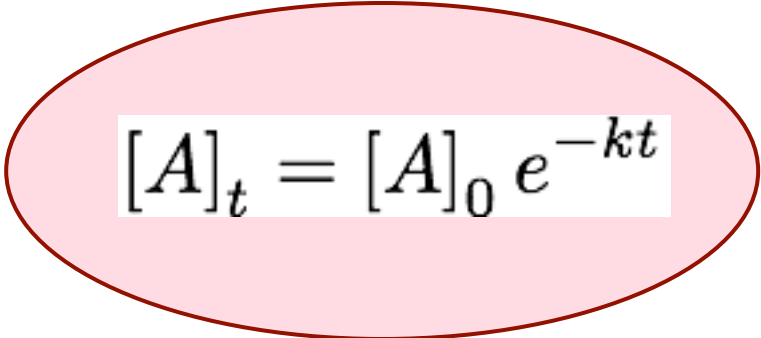
$$-\frac{d[A]}{dt} = k [A]$$

How much A is left after time t ? Integrate:

$$-d[A] = k [A] dt$$

$$\frac{d[A]}{[A]} = -k dt$$

$$\int \frac{d[A]}{[A]} = - \int k dt$$


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

Integrated Rate Laws

The integrated form of first order rate law:

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

Can be rearranged to give:

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

$[A]_0$ is the initial concentration of A ($t=0$).

$[A]_t$ is the concentration of A at some time, t , during the course of the reaction.

Integrated Rate Laws

Manipulating this equation produces...

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

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

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

...which is in the form

$$y = ax + b$$

Example Reaction Rate Laws

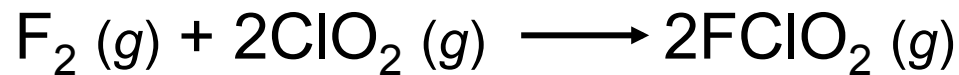


Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

	$[\text{F}_2](M)$	$[\text{ClO}_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k [\text{F}_2]^x [\text{ClO}_2]^y$$

Double $[\text{F}_2]$ with $[\text{ClO}_2]$ constant

Rate doubles

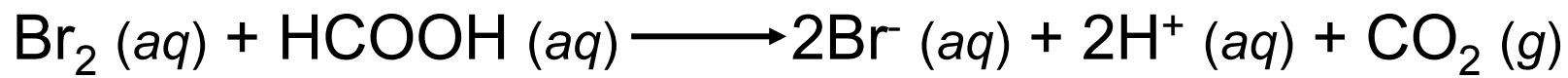
$$x = 1$$

Quadruple $[\text{ClO}_2]$ with $[\text{F}_2]$ constant

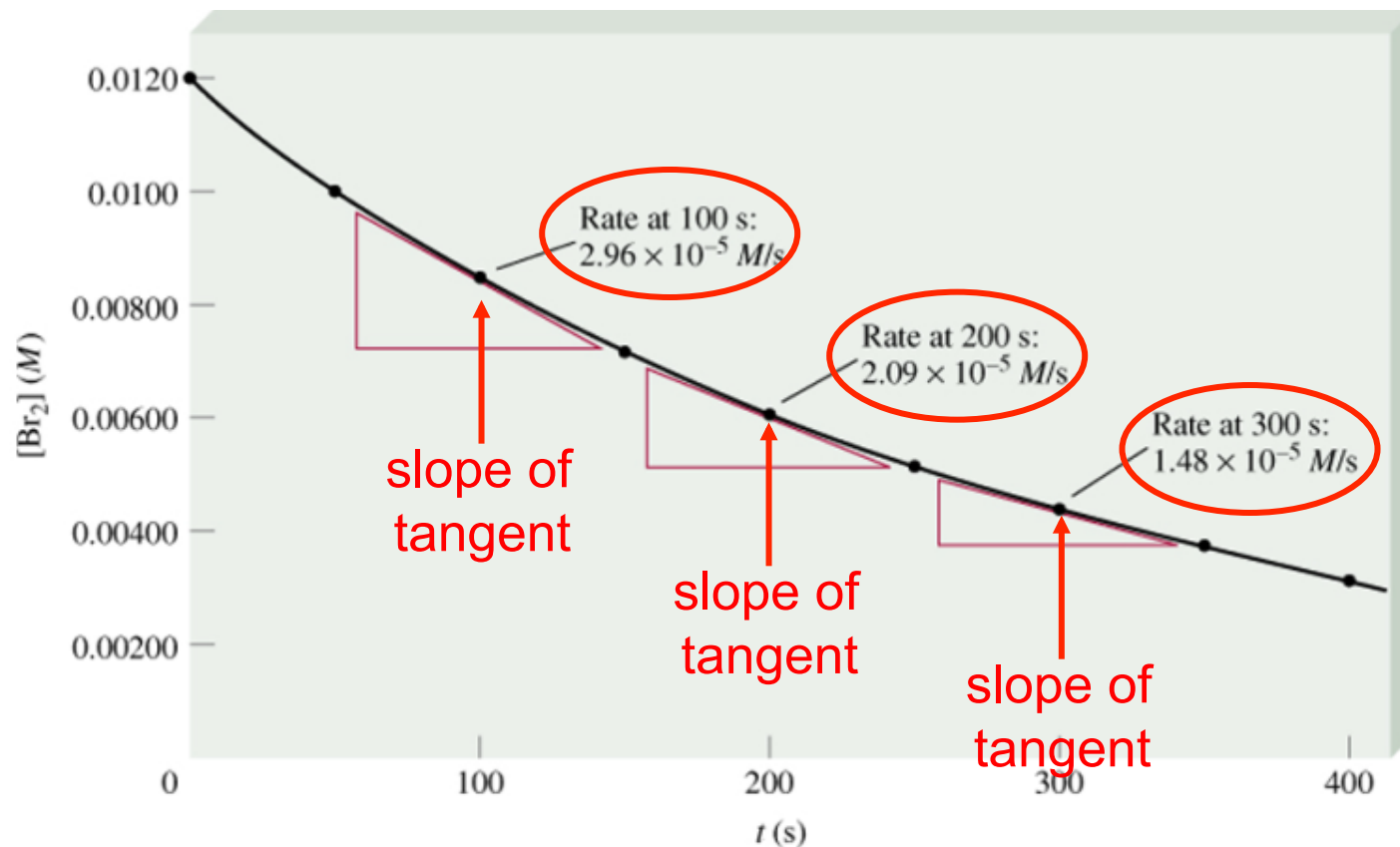
Rate quadruples

$$y = 1$$

$$\text{rate} = k [\text{F}_2][\text{ClO}_2]$$



Time (s)	[Br ₂] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



$$\text{average rate} = - \frac{\Delta[\text{Br}_2]}{\Delta t} = - \frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

instantaneous rate = rate for specific instance in time

TABLE 13.1

Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

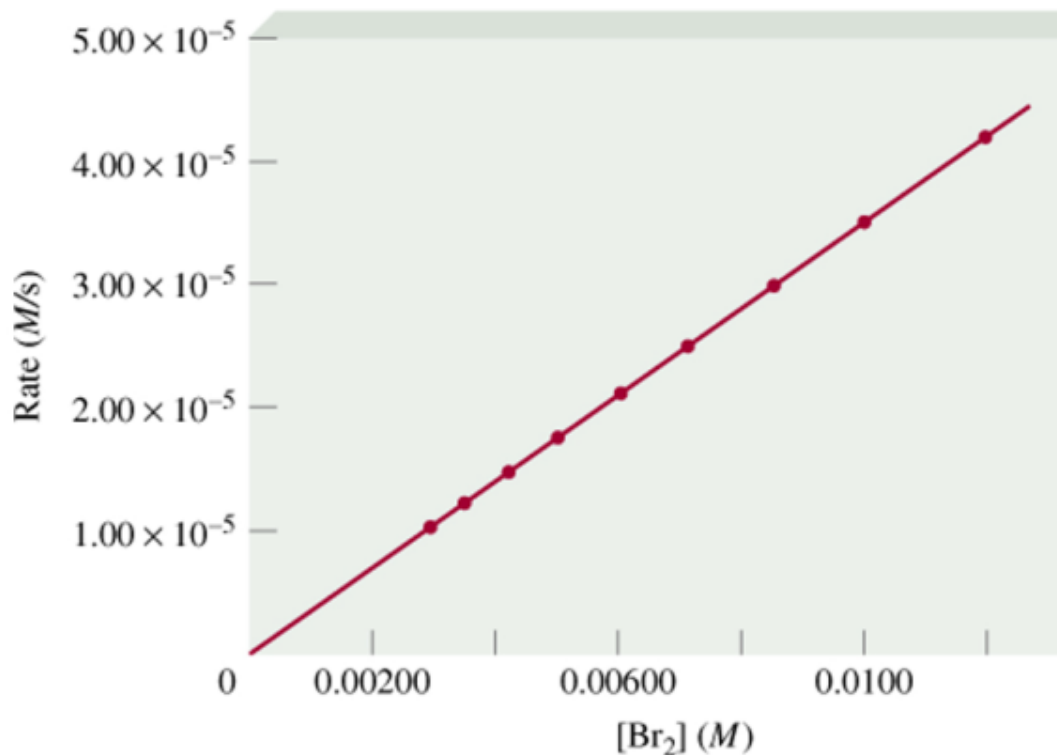
Time (s)	[Br ₂] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s}^{-1}\text{)}$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

$$\text{rate} \propto [\text{Br}_2]$$

$$\text{rate} = k [\text{Br}_2]$$

$$k = \frac{\text{rate}}{[\text{Br}_2]} = \text{rate constant}$$

$$= 3.50 \times 10^{-3} \text{ s}^{-1}$$



Another Example of Reaction Kinetics

Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ 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

In this reaction, the concentration of butyl chloride, $\text{C}_4\text{H}_9\text{Cl}$, was measured at various times, t .

Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (M)	Average Rate, M/s
0.0	0.1000	
50.0	0.0905	1.9×10^{-4}
100.0	0.0820	1.7×10^{-4}
150.0	0.0741	1.6×10^{-4}
200.0	0.0671	1.4×10^{-4}
300.0	0.0549	1.22×10^{-4}
400.0	0.0448	1.01×10^{-4}
500.0	0.0368	0.80×10^{-4}
800.0	0.0200	0.560×10^{-4}
10,000	0	

The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{average rate} = \frac{\Delta [\text{C}_4\text{H}_9]}{\Delta t}$$

$$\text{average rate} = \frac{\Delta [\text{C}_4\text{H}_9]}{\Delta t} = \frac{0.1000 - 0.0905 \text{ M}}{50.0 - 0.0 \text{ s}}$$

Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (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	

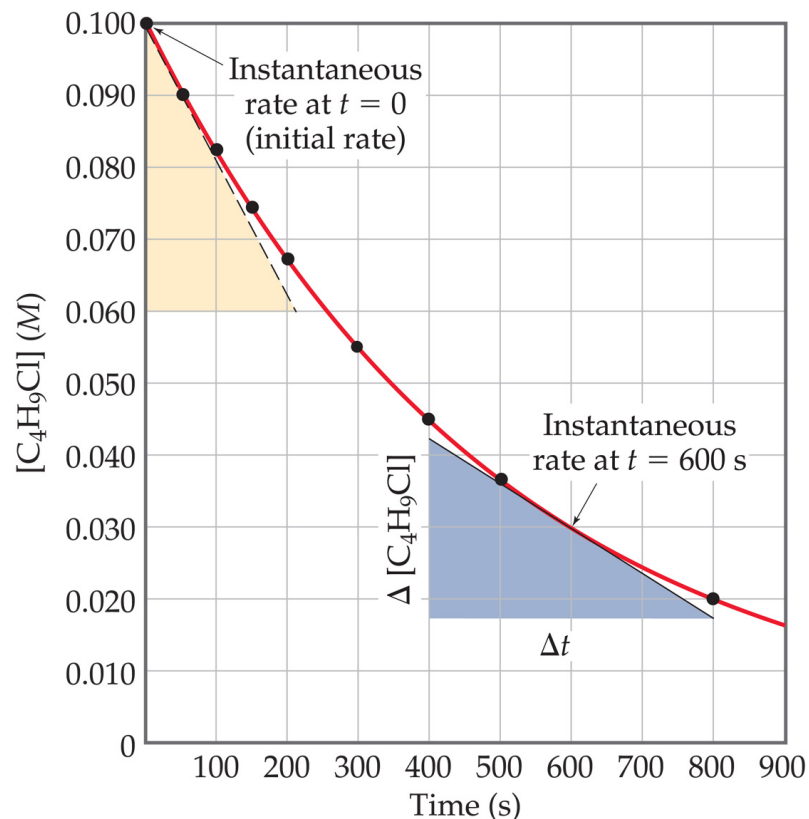
- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Reaction Rates



- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.

$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

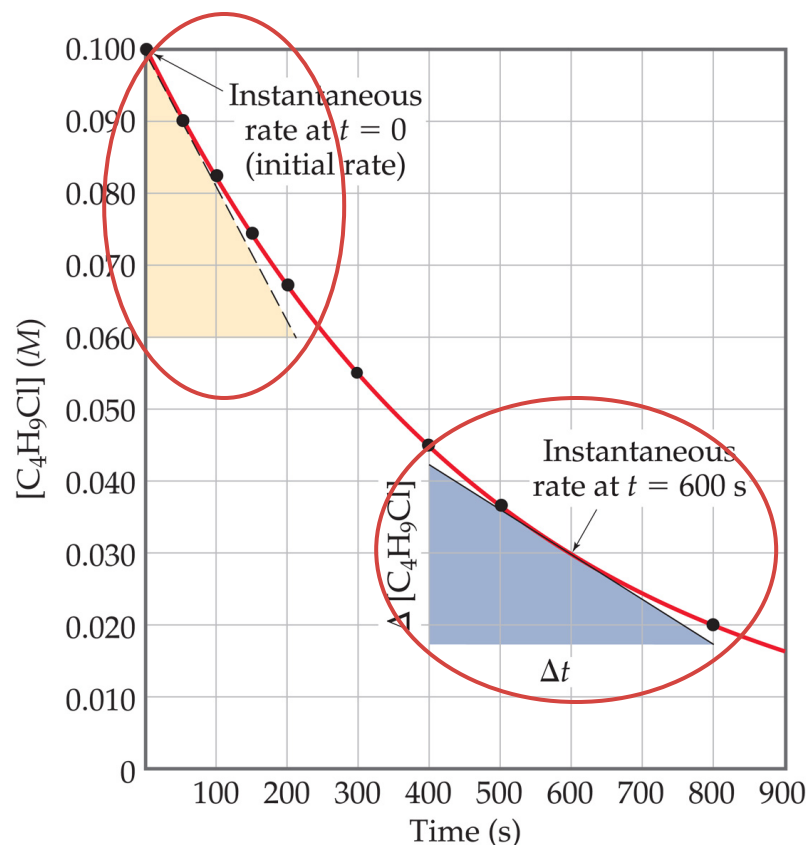


Reaction Rates



- The reaction slows down with time because the concentration of the reactants decreases.

$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$



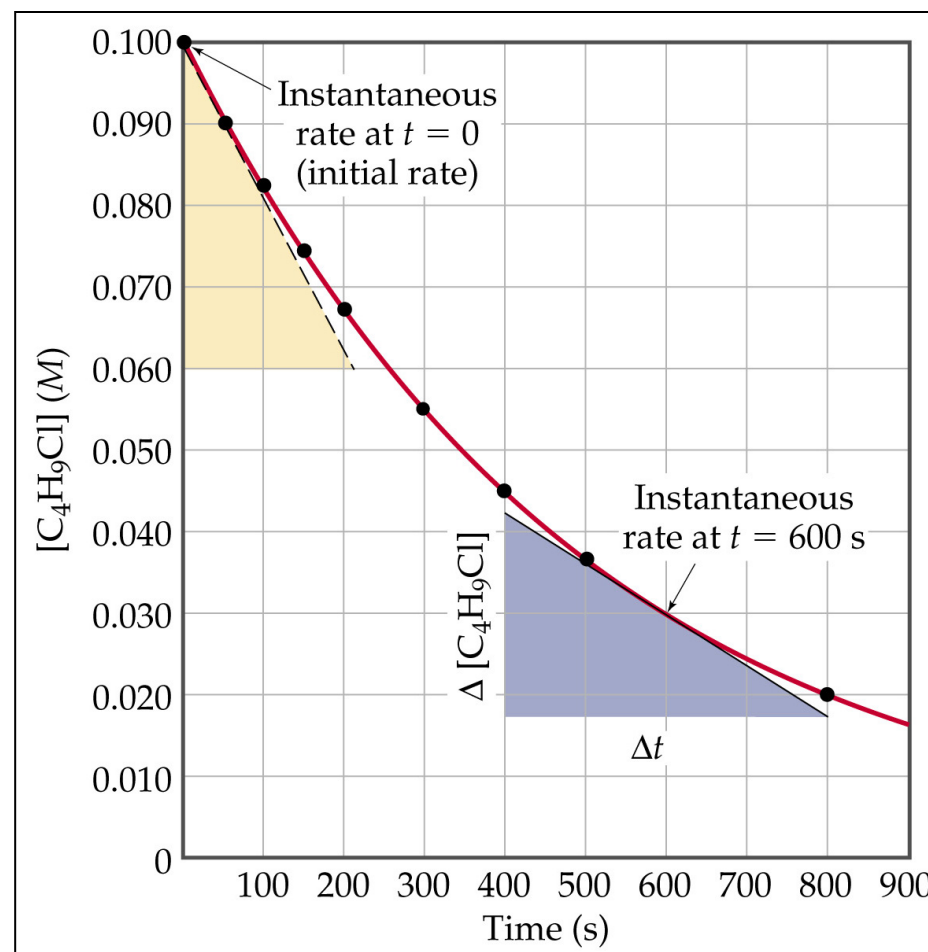
Reaction Rate

- Here's an example of a reaction...



- We can plot $[\text{C}_4\text{H}_9\text{Cl}]$ versus time...

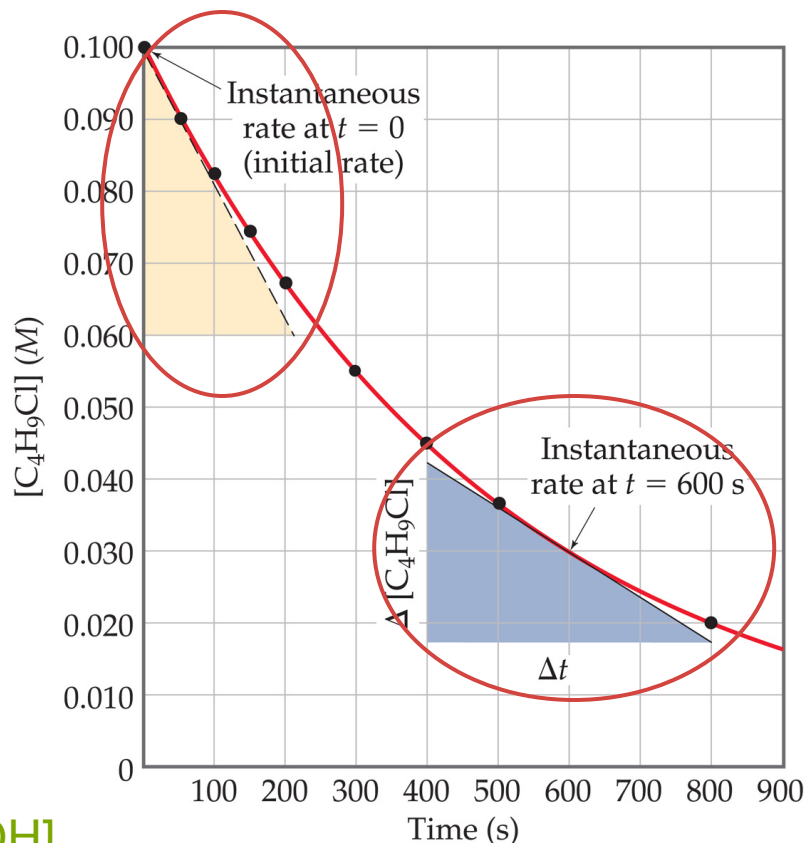
- The average rate of a reaction decreases with time.
- The rate at any instant in time (instantaneous rate) is the slope of the tangent to the curve.
- Instantaneous rate is different from average rate, so when we refer to the rate of a reaction, we will be assuming it's the instantaneous rate unless otherwise told.



Reaction Rates and Stoichiometry



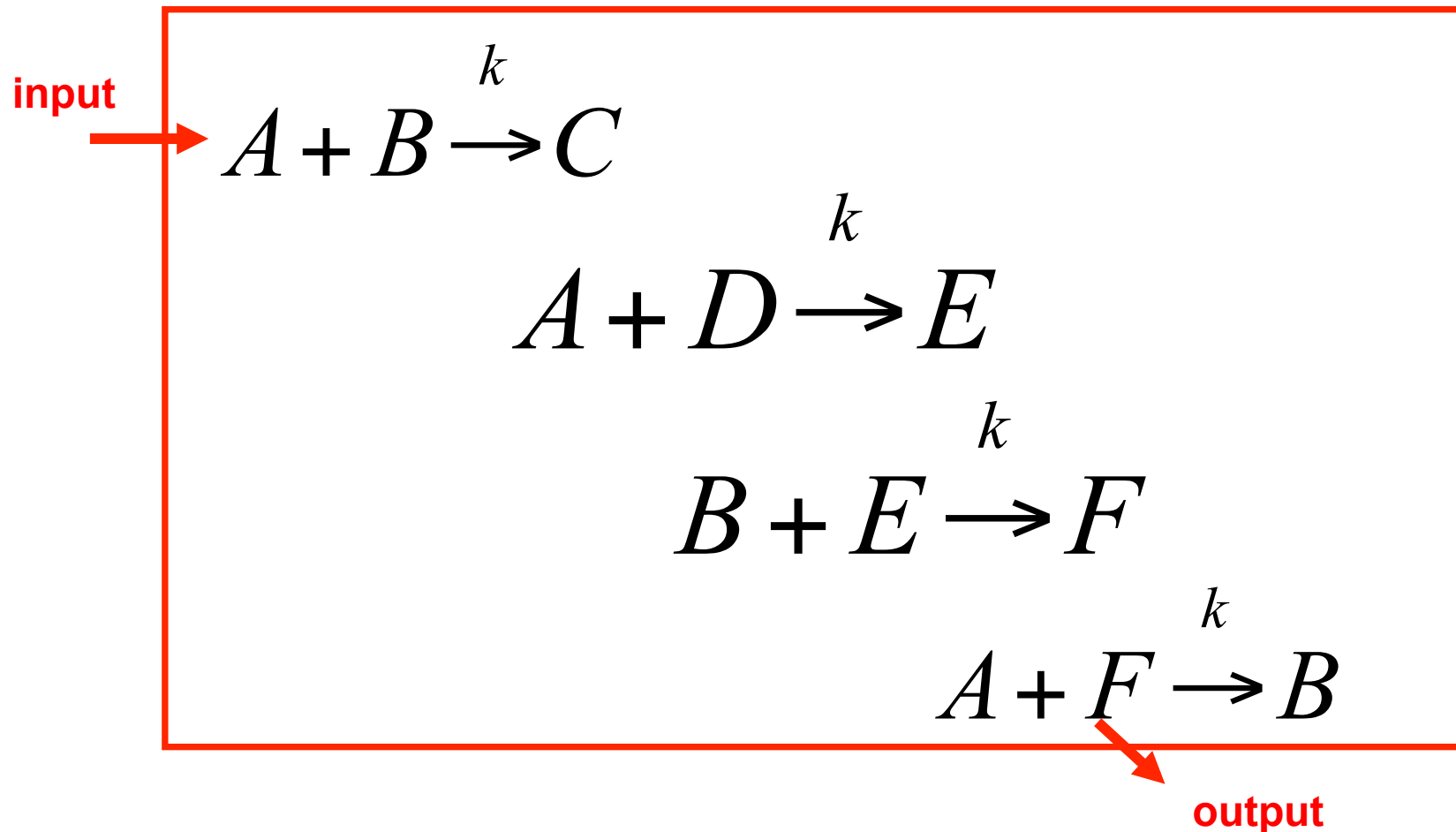
- In this reaction, the ratio of $\text{C}_4\text{H}_9\text{Cl}$ to $\text{C}_4\text{H}_9\text{OH}$ is 1:1.
- Thus, the rate of *disappearance* of $\text{C}_4\text{H}_9\text{Cl}$ is the same as the rate of *appearance* of $\text{C}_4\text{H}_9\text{OH}$.



$$\text{Rate} = \frac{-\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{D[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$

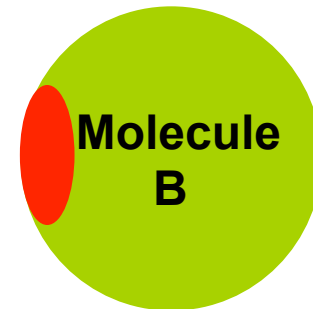
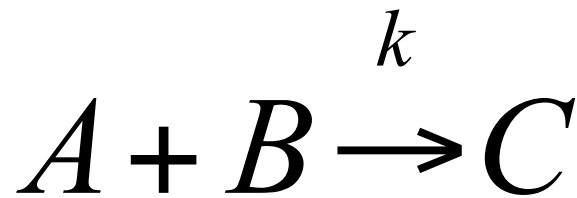
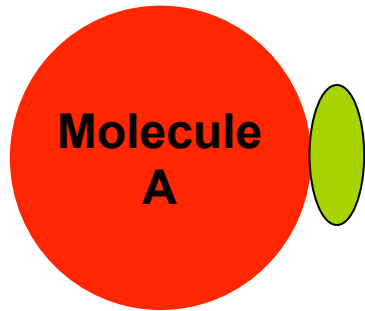
Simple Example Reactions

Simple Example Reaction Kinetics

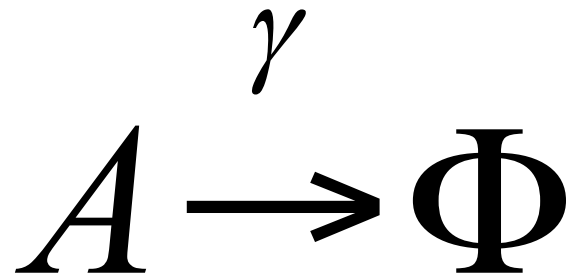


Given some initial concentrations, what is output give some prescribed input?

Example chemical reaction that models collisions of molecules A & B to form C



Example chemical reaction that models degradation of molecule A



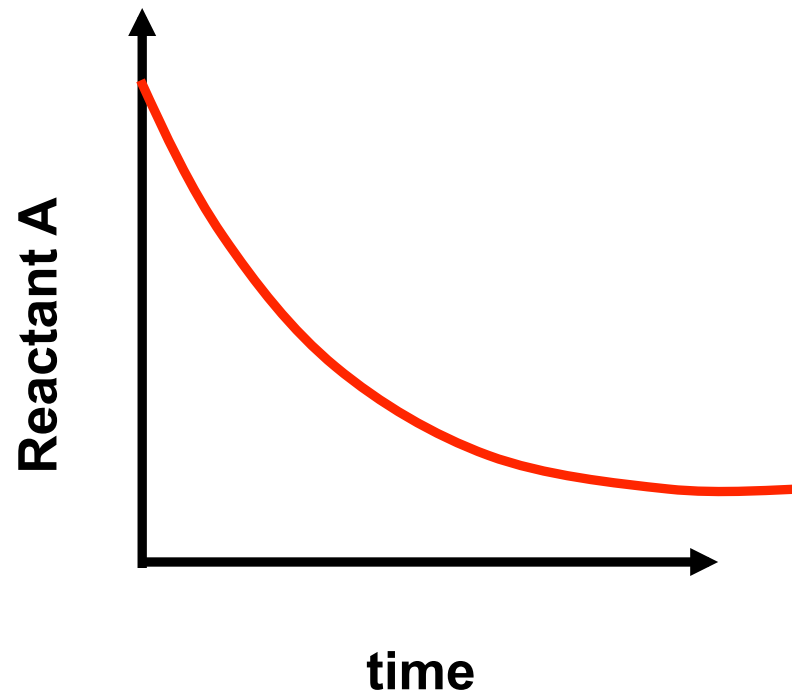
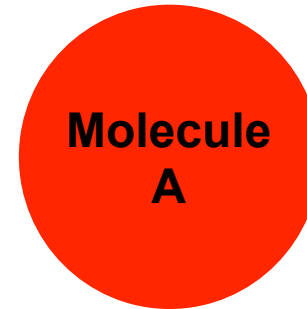
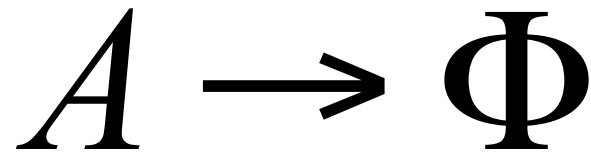
$$\frac{dA}{dt} = -\gamma[A]$$

Rate of change of A

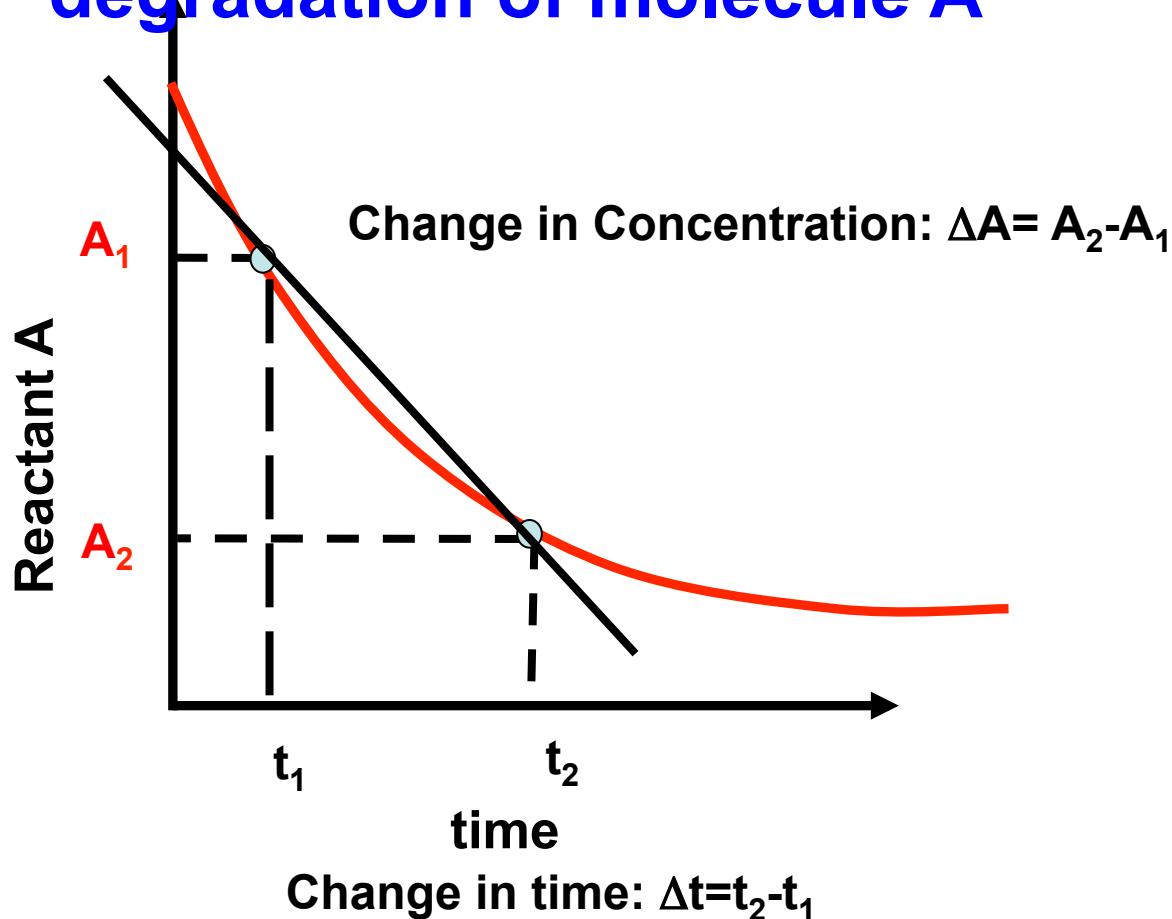
Concentration of A

Degradation constant

Example chemical reaction that models degradation of molecule A

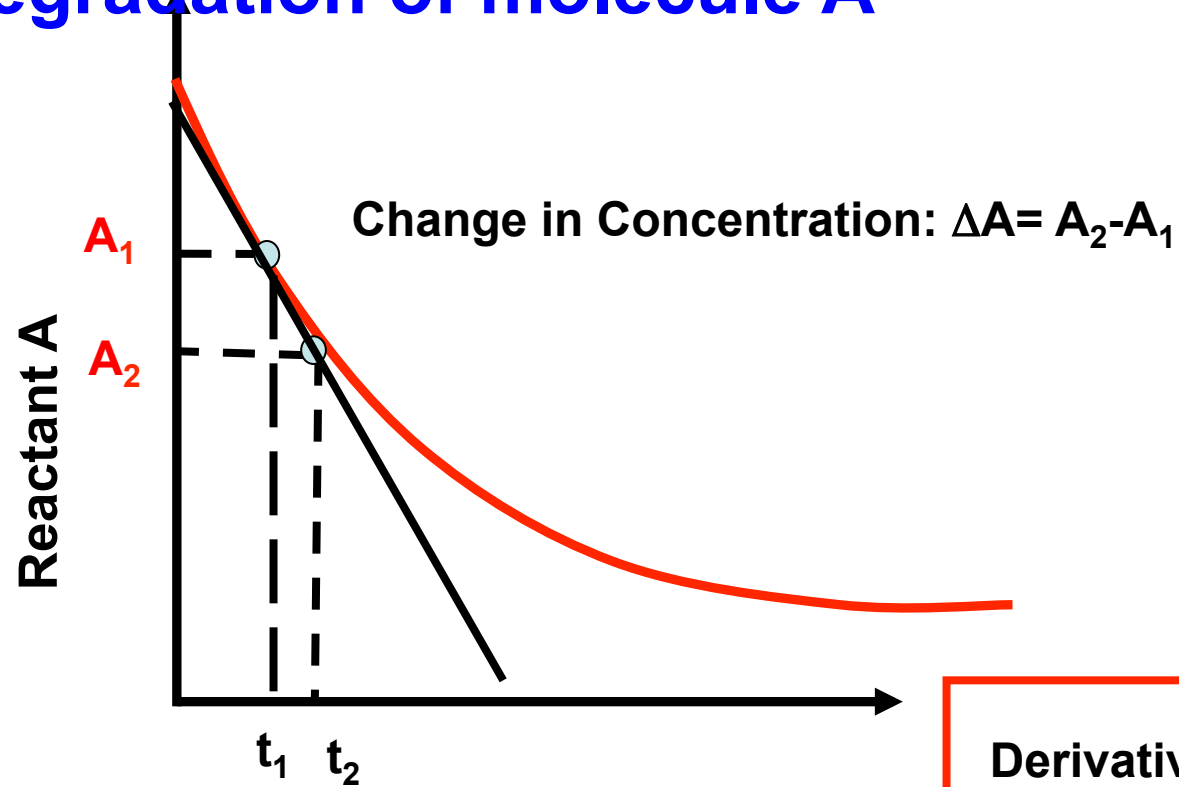


Example chemical reaction that models degradation of molecule A



Average rate of change in concentration during time $\Delta t = \frac{\Delta[A]}{\Delta t}$

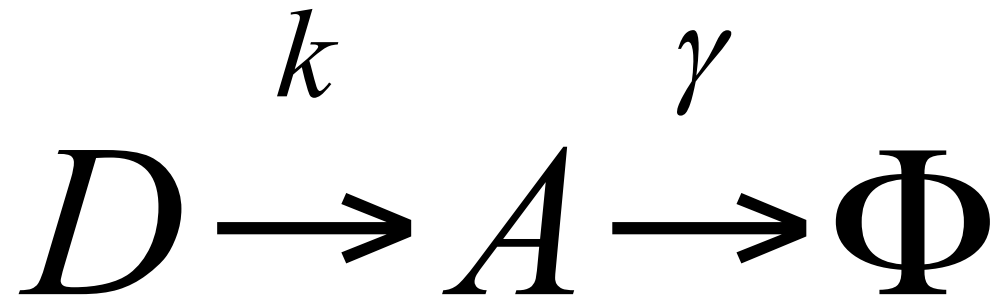
Example chemical reaction that models degradation of molecule A



Derivative of A with Respect to time

instantaneous rate of change in concentration during time $dt = \frac{d[A]}{dt}$

Example chemical reaction that models generation (from A) and degradation (to C) of molecule B



$$\frac{dA}{dt} = k[D] - \gamma[A]$$

Rate of change of A

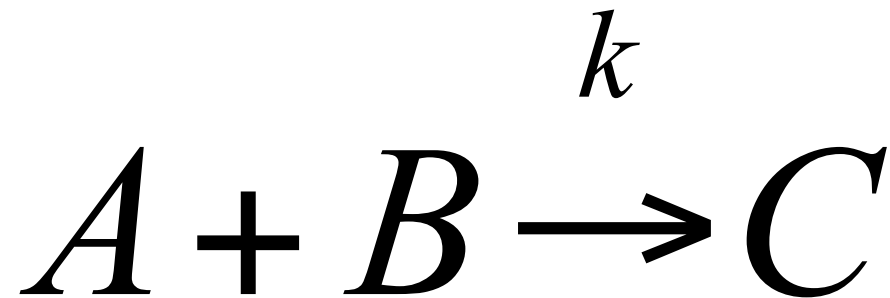
Concentration of D

Concentration of A

Production constant

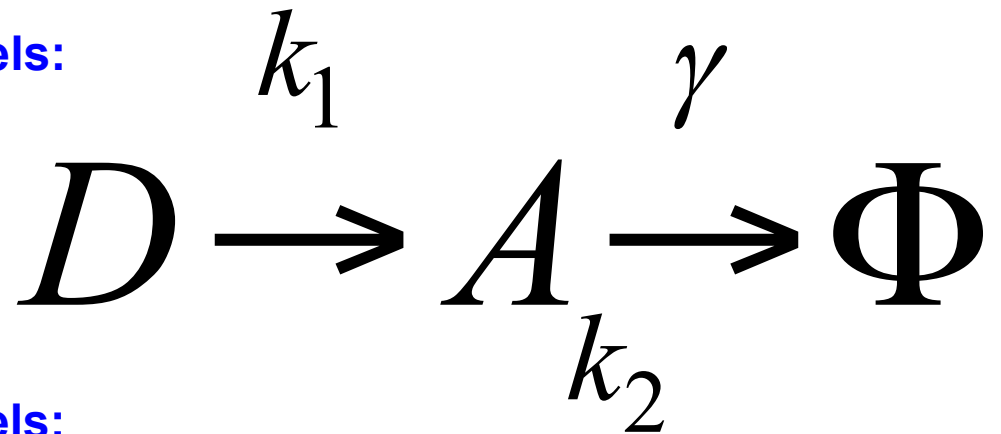
Degradation constant

**Example chemical reaction that models generation
(from A and B) of molecule C**

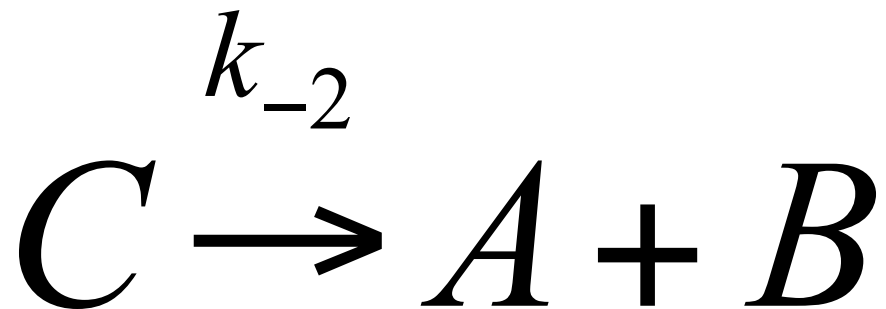
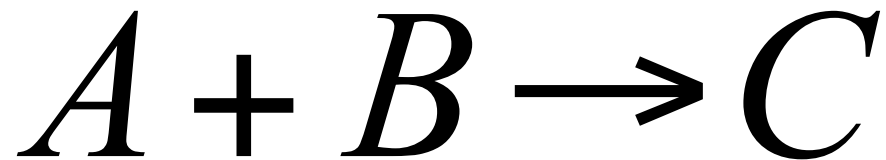


$$\frac{dA}{dt} = -k[A][B]$$

Example chemical reaction that models:
generation (from D) and degradation
(to C) of molecule B



Example chemical reaction that models:
generation and degeneration
(to and from from A and B)
of molecule C



$$\frac{d[A]}{dt} = k_1 [D] - \gamma [A]$$

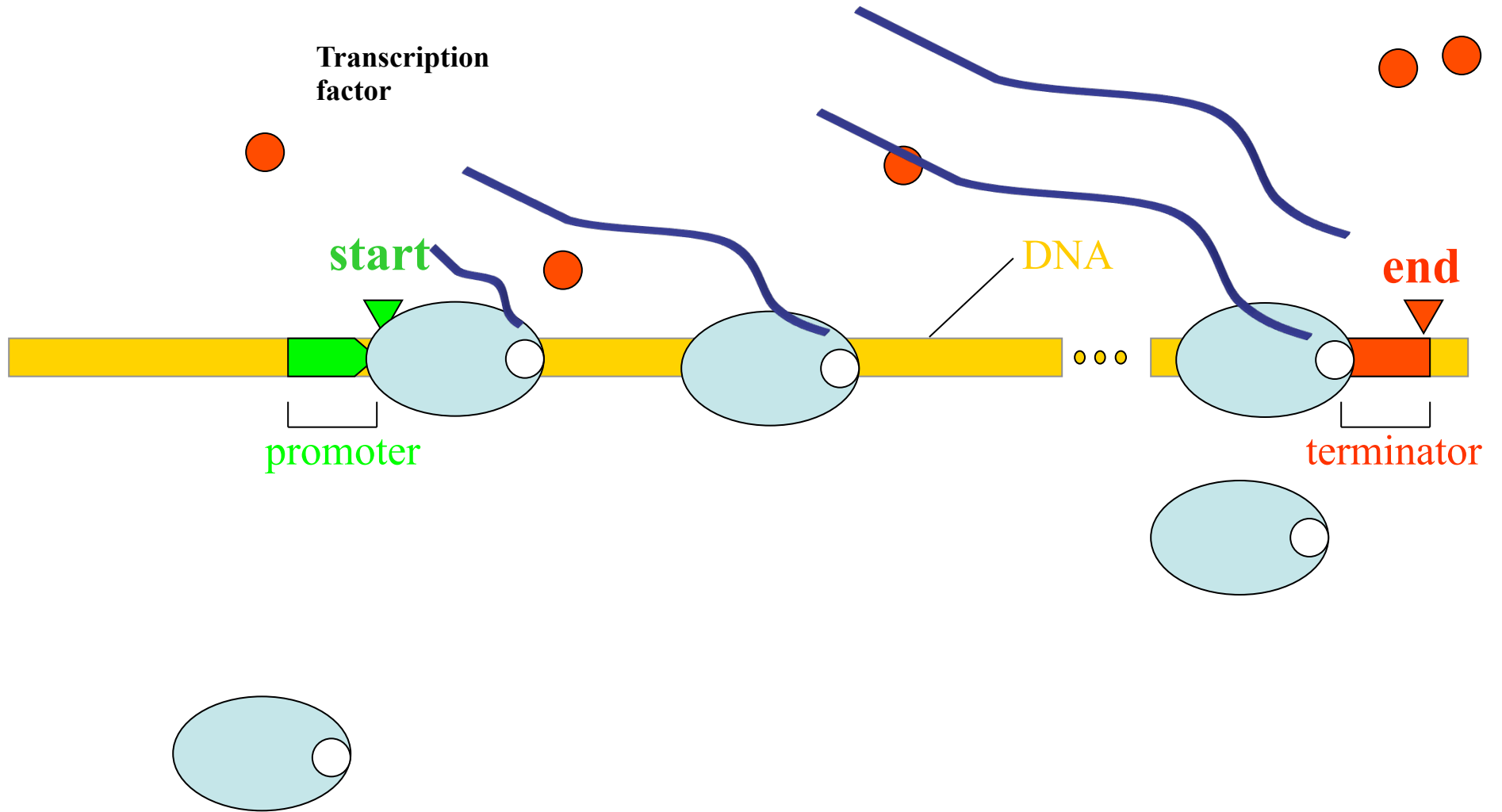
Example chemical reaction that models generation
(from n distinct A and m distinct B) of molecule C



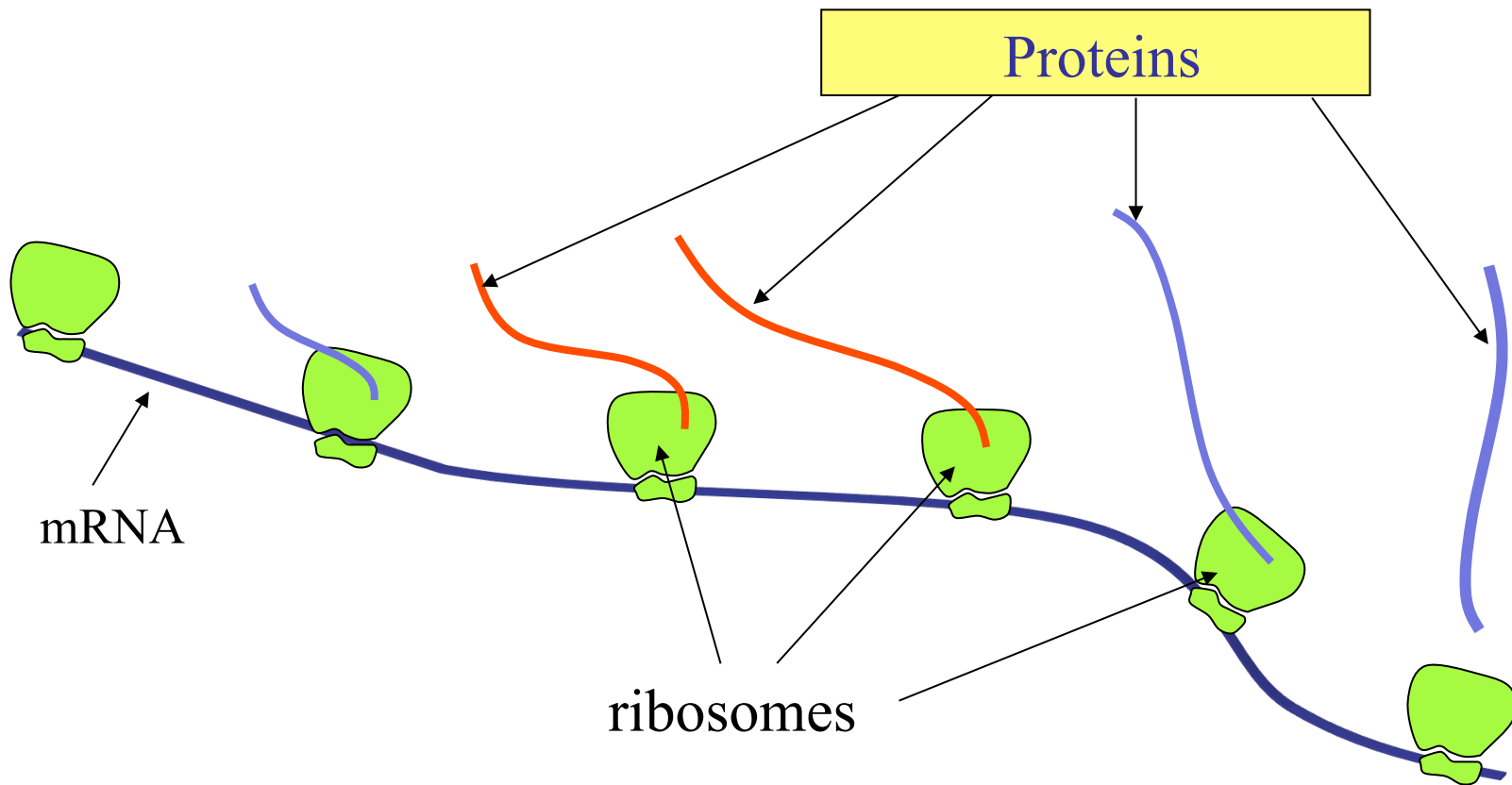
$$\frac{d[A]}{dt} = -k[A]^n[B]^m$$

Example of Transcription Reaction Kinetics

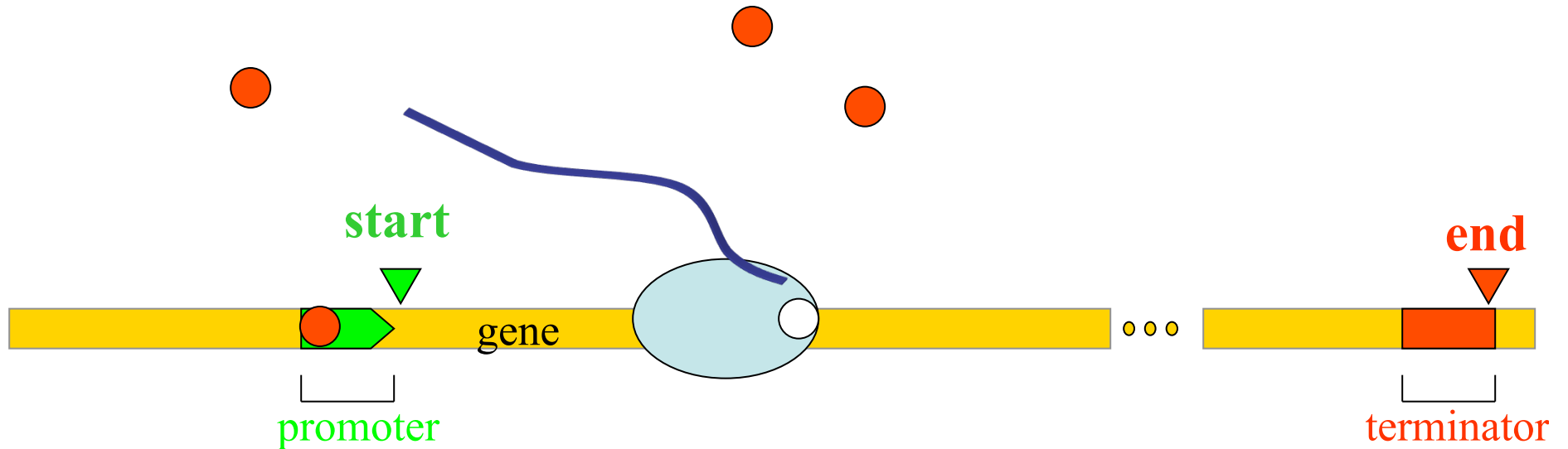
Transcription



mRNA Translation



Modeling activator binding and production of mRNA





$$\frac{d[A : DNA]}{dt} = k_1 \cdot A \cdot DNA - k_2 \cdot [A : DNA] = 0$$

$$k_1 \cdot A \cdot DNA = k_2 \cdot [A : DNA] \longrightarrow [A : DNA] = \frac{k_1 \cdot A \cdot DNA}{k_2}$$

but

$$DNA_{total} = DNA + [A : DNA] = DNA + \frac{k_1 \cdot A \cdot DNA}{k_2} = \left(1 + \frac{k_1 \cdot A}{k_2}\right) DNA$$

$$DNA = \frac{DNA_{total}}{\left(1 + \frac{k_1 \cdot A}{k_2}\right)}$$

$$DNA = \frac{DNA_{total}}{\left(1 + \frac{k_1 \cdot A}{k_2}\right)}$$

$$[A : DNA] = \frac{k_1 \cdot A \cdot DNA}{k_2}$$

$$[A : DNA] = \frac{\frac{k_1}{k_2} A}{1 + \frac{k_1}{k_2} A} DNA_{total}$$

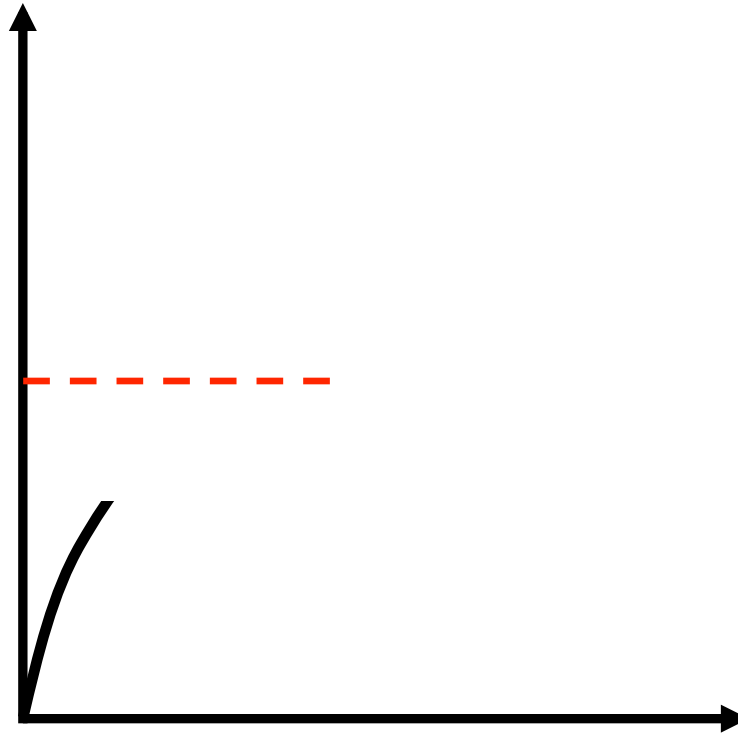
$$\frac{k_2}{k_1} = k_d$$

Dissociation constant

Hill Function

$$[A : DNA] = \frac{\frac{A}{k_d}}{1 + \frac{A}{k_d}} DNA_{total}$$

$[A : DNA]$



DNA_{total}

A

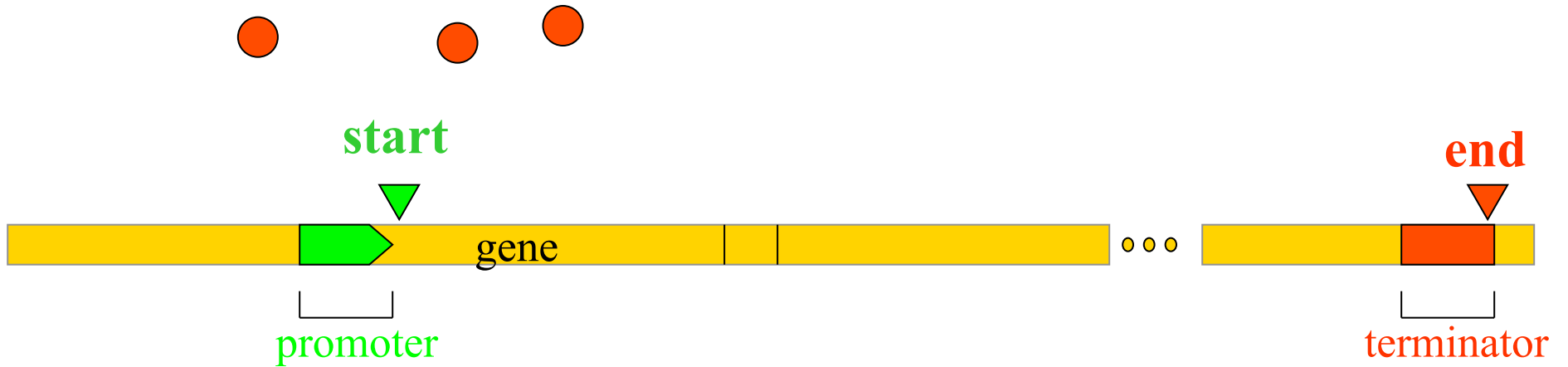


$$\frac{dmRNA}{dt} = k_3 \cdot [A : DNA] - \gamma_1 mRNA$$

$$[A : DNA] = \frac{\frac{A}{k_d}}{1 + \frac{A}{k_d}} DNA_{total}$$

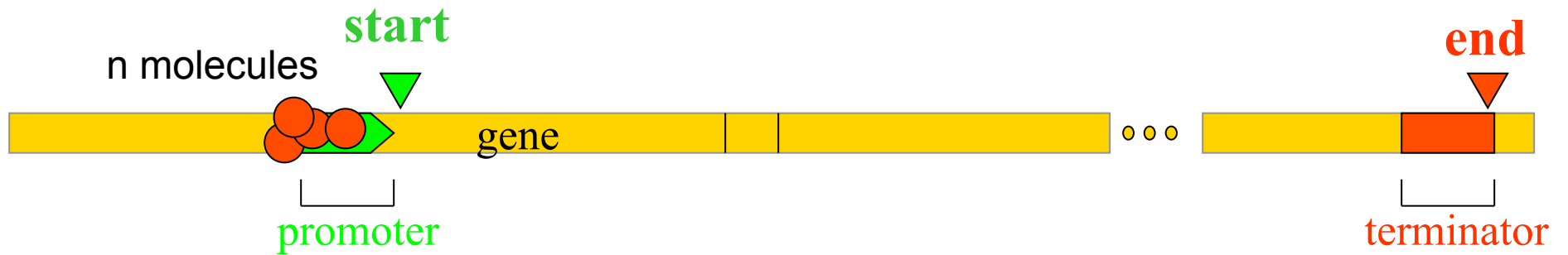
$$\frac{dmRNA}{dt} = k_3 \cdot \frac{\frac{A}{k_d}}{1 + \frac{A}{k_d}} DNA_{total} - \gamma_1 mRNA$$

Cooperativity



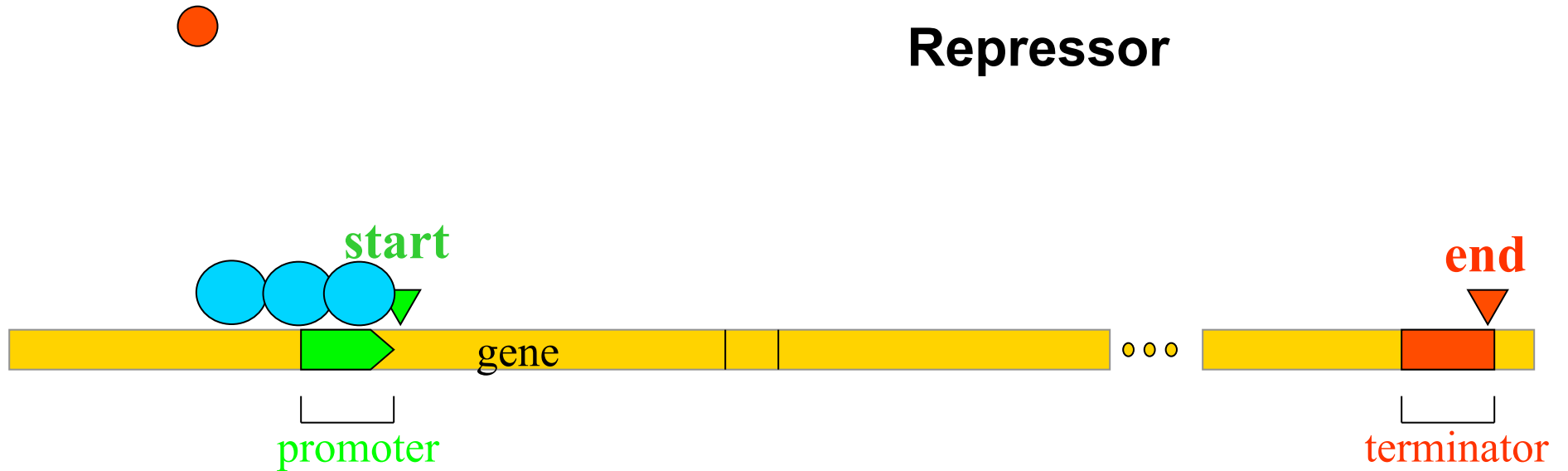
$$\frac{dmRNA}{dt} = k_3 \cdot \frac{\left(\frac{A}{k_d}\right)^3}{1 + \left(\frac{A}{k_d}\right)^3} DNA_{total} - \gamma_1 mRNA$$

Cooperativity



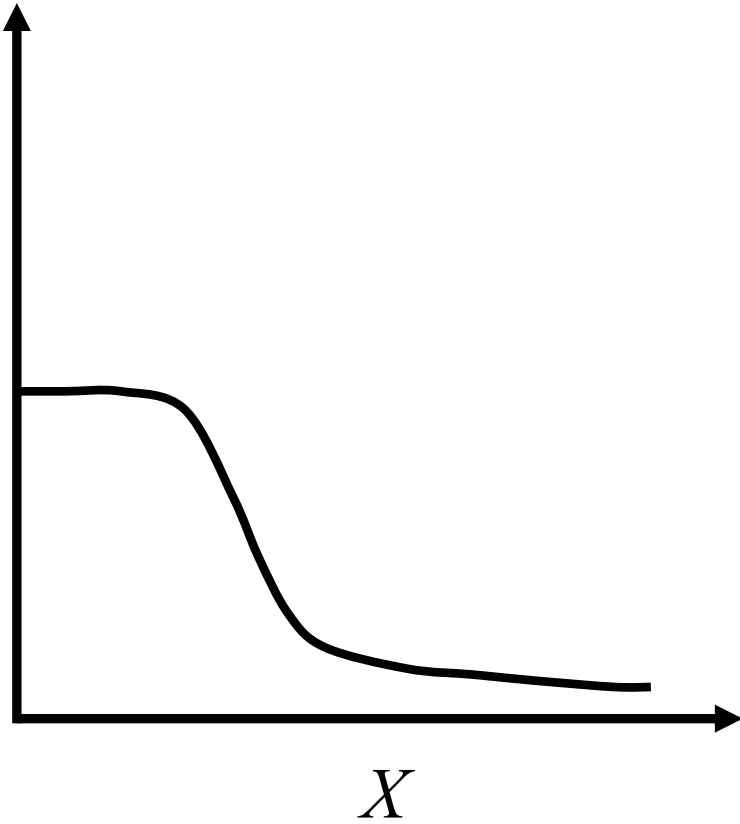
$$\frac{dmRNA}{dt} = k_3 \cdot \frac{\left(\frac{A}{k_d}\right)^n}{1 + \left(\frac{A}{k_d}\right)^n} DNA_{total} - \gamma_1 mRNA$$

Repressor



$$\frac{dmRNA}{dt} = k_3 \cdot \frac{1}{1 + \left(\frac{X}{k_d}\right)^n} DNA_{total} - \gamma_1 mRNA$$

$$k_3 \cdot \frac{1}{1 + \left(\frac{X}{k_d}\right)^n} DNA_{total}$$



Order of Reactions

Order of Reactions

- A reaction is **zero order** in a reactant if the change in concentration of that reactant produces no effect.
- A reaction is **1st order** if doubling the concentration causes the rate to double.
- A reaction is **2nd order** if doubling the concentration causes a quadruple increase in rate.
 - 3rd order**...doubling concentration leads to 2^3 (or 8 times) the rate.
- Note-- The rate constant, k , does not depend on concentration!
- Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations. (See Practice Problems for examples.)

Zero'th Order Reactions

Zero-Order Reactions

$$\text{rate} = - \frac{\Delta[A]_t}{\Delta t}$$

$$\text{rate} = k [A]_0 = k$$

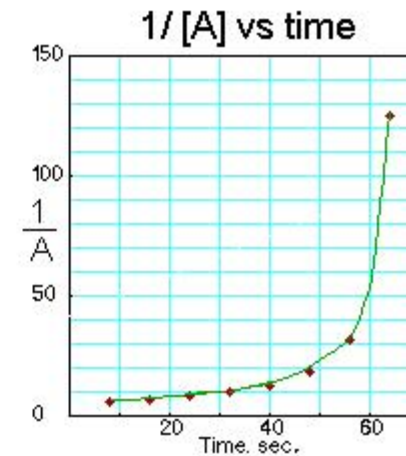
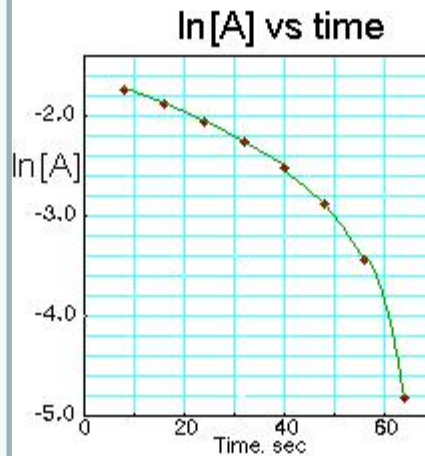
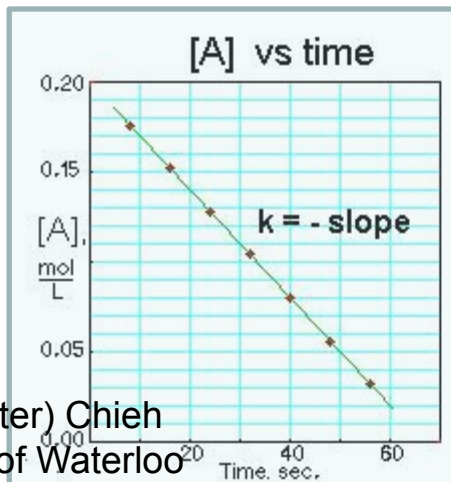
$$[A]_t - [A]_0 = kt$$

$[A]_t$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t=0$

Half life for zero order

$$t_{1/2} = t \text{ when } [A]_t = [A]_0/2$$

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



Change of Concentration with Time

For Zero order reactions:

$$\text{Rate} = k[A]_0 = k$$

Rate does not change with concentration.

$$\text{So... } [A]_t = -kt + [A]_0$$

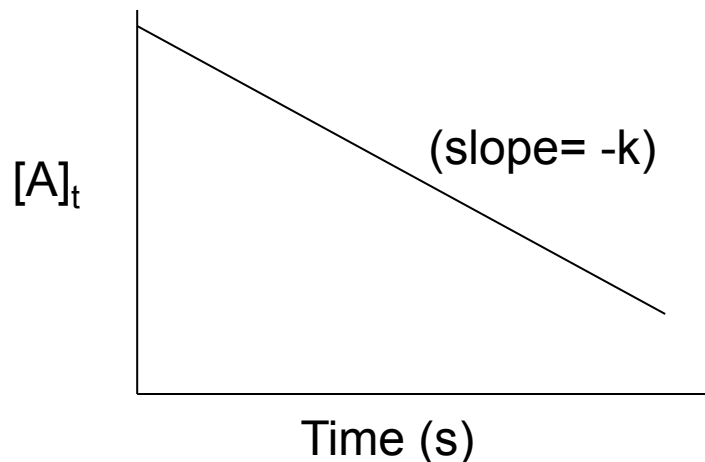
where $[A]_t$ = concentration of $[A]$ after some time, t

k = reaction rate constant in units of M/s

t = time in seconds

$[A]_0$ = initial concentration of A

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $[A]_t$ vs. t is a straight line with slope $(-k)$ and intercept $[A]_0$.



First Order Reactions

First-Order Processes

First order: $\ln [A]_t = -kt + \ln [A]_0$

If a reaction is first-order, a plot of $\ln [A]_t$ vs. t will yield a straight line with a slope of $-k$.

Change of Concentration with Time

- Goal: to convert the rate law into a convenient equation to give concentrations as a function of time...(the book has the derivation, and it involves calculus, so we will skip to the conclusion)...

For 1st order reactions: $\ln[A]_t = -kt + \ln[A]_0$

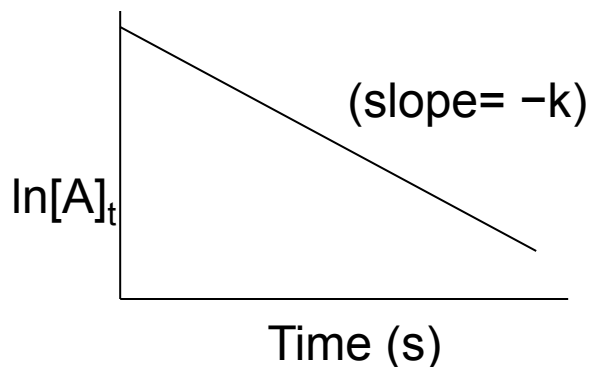
where $[A]_t$ = concentration of $[A]$ after some time, t

k = reaction rate constant in units of s^{-1}

t = time in seconds

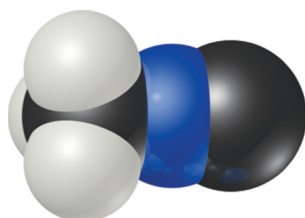
$[A]_0$ = initial concentration of A

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $\ln[A]_t$ vs. t is a straight line with slope $(-k)$ and intercept $\ln[A]_0$.



First-Order Processes

Consider the process in which methyl isonitrile is converted to acetonitrile.



Methyl isonitrile



Acetonitrile



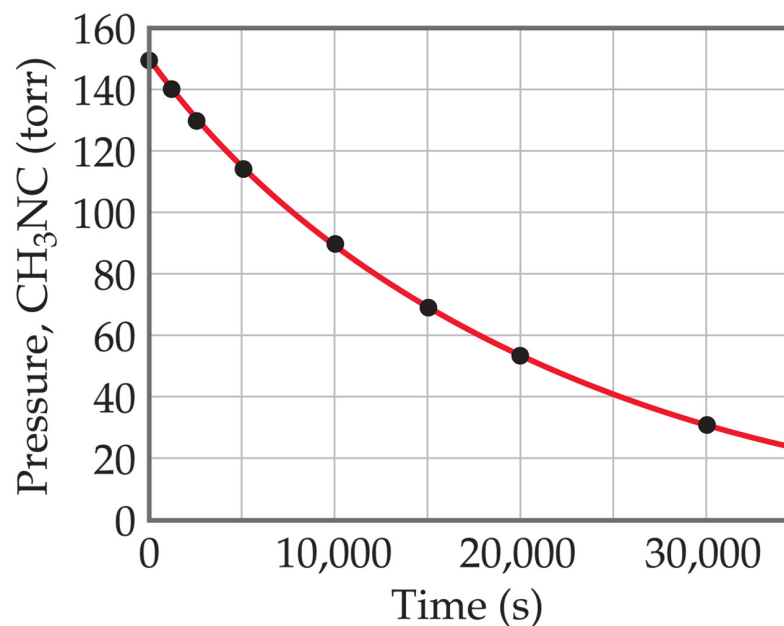
How do we know this is a first order reaction?

First-Order Processes



This data was collected for this reaction at 198.9°C.

Does
 $\text{rate} = k[\text{CH}_3\text{NC}]$
for all time intervals?



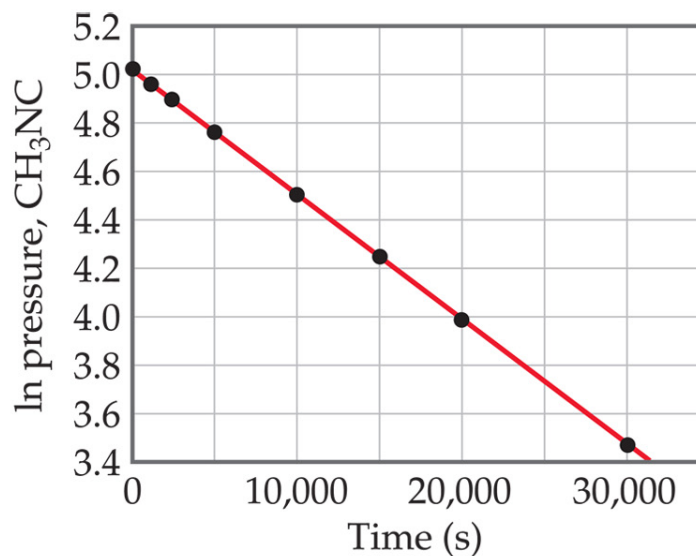
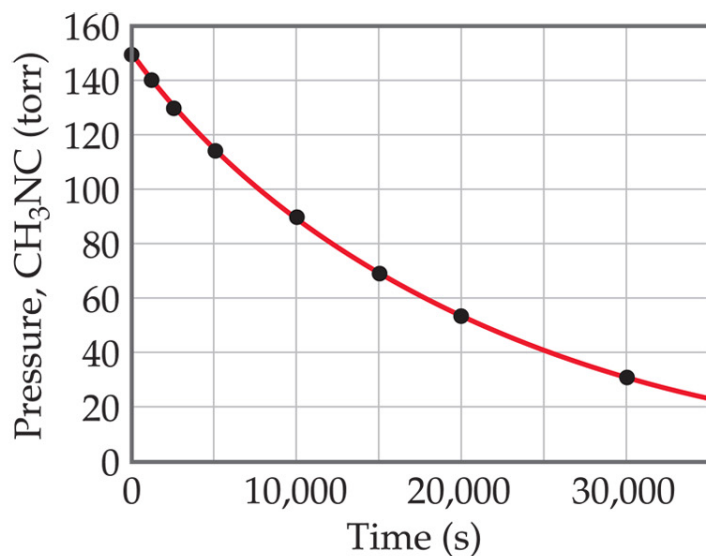
First-Order Processes

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

If a reaction is first-order:

a plot of $\ln [A]_t$ versus t will yield a straight line with a slope of $-k$.

First-Order Processes



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

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

- When $\ln P$ is plotted as a function of time, a straight line results.
 - The process is first-order.
 - k is the negative slope: $5.1 \times 10^{-5} \text{ s}^{-1}$.

Second Order Reactions

Second-Order Processes

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

So if a process is second-order in A, a plot of $1/[A]$ versus t will yield a straight line with a slope of k .

Change of Concentration with Time

For 2nd order reactions: $1/[A]_t = kt + 1/[A]_0$

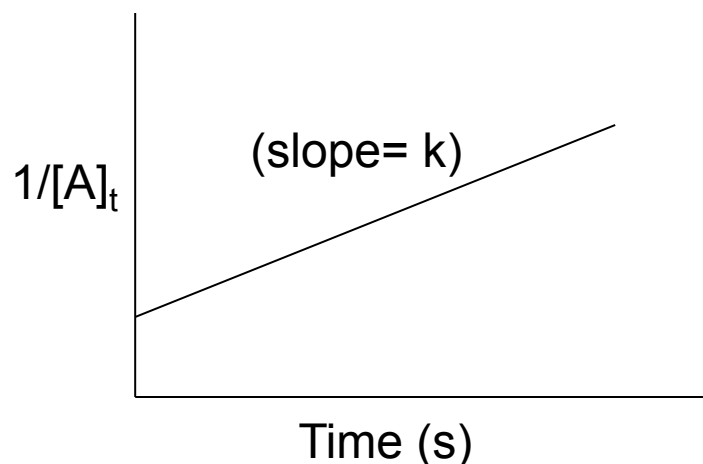
where $[A]_t$ = concentration of $[A]$ after some time, t

k = reaction rate constant in units of $M^{-1}s^{-1}$

t = time in seconds

$[A]_0$ = initial concentration of A

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $1/[A]_t$ vs. t is a straight line with slope (k) and intercept of $1/[A]_0$.



Second-Order Reactions

$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = k [A]_t^2$$

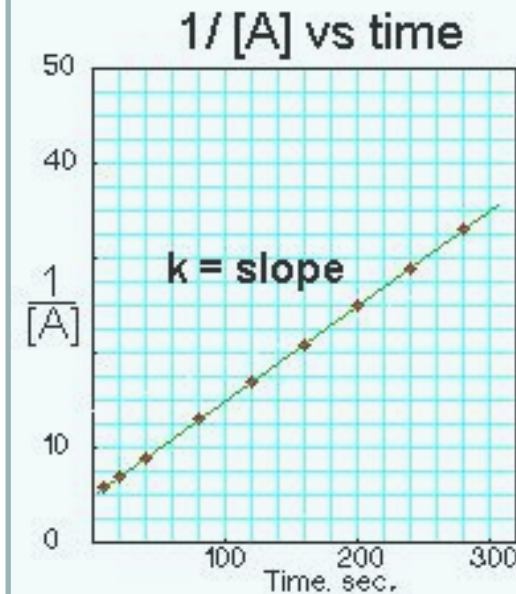
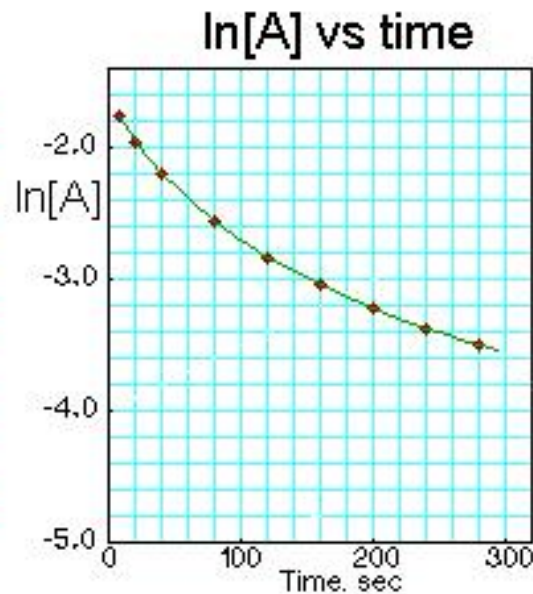
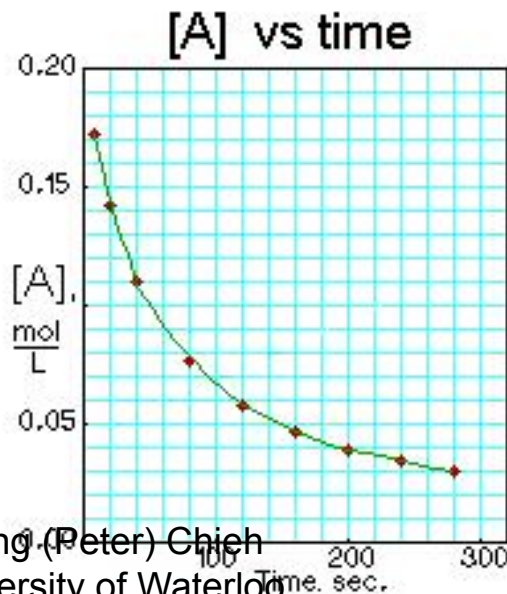
$[A]_t$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t=0$

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

Half life for second order

$$t_{1/2} = t \text{ when } [A]_t = [A]_0/2$$

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



Determining Reaction order

The decomposition of NO_2 at 300°C is described by the equation



and yields these data:

Time (s)	$[\text{NO}_2], M$
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

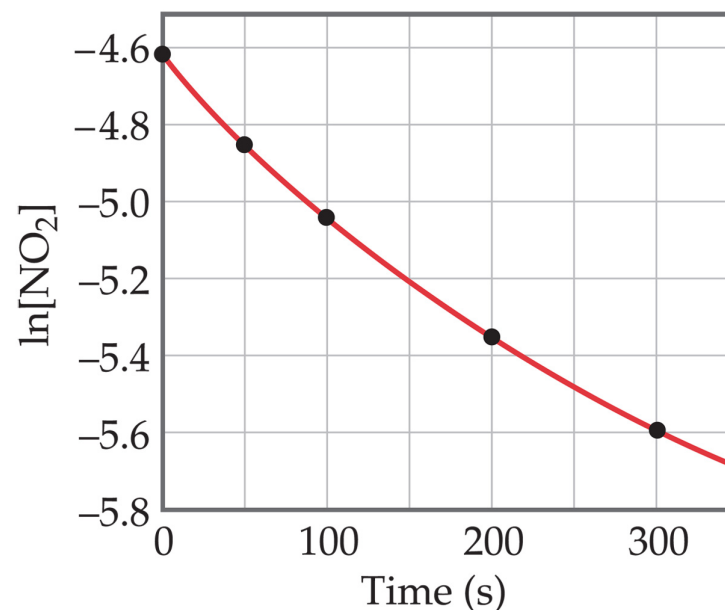
John D. Bookstaver

St. Charles Community College

Determining Reaction order

Graphing $\ln [\text{NO}_2]$ versus t yields:

- The plot is *not* a straight line, so the process is *not* first-order in $[\text{A}]$.



Does not fit:

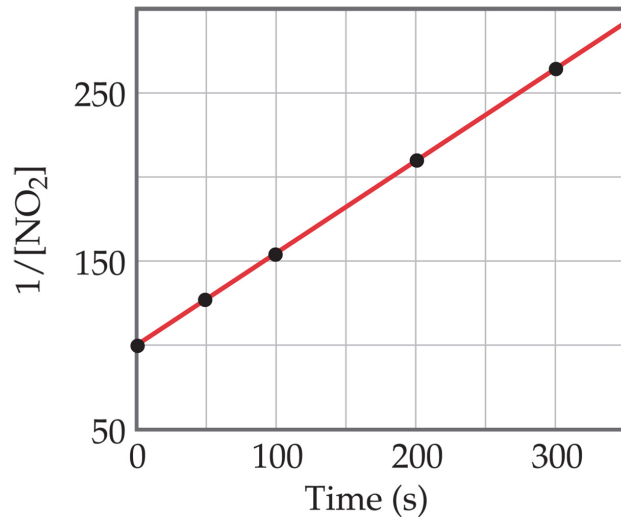
$$\ln [A]_t = -kt + \ln [A]_0$$

Time (s)	$[\text{NO}_2], M$	$\ln [\text{NO}_2]$
0.0	0.01000	-4.610
50.0	0.00787	-4.845
100.0	0.00649	-5.038
200.0	0.00481	-5.337
300.0	0.00380	-5.573

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Second-Order Processes



A graph of $1/[\text{NO}_2]$ vs. t gives this plot.

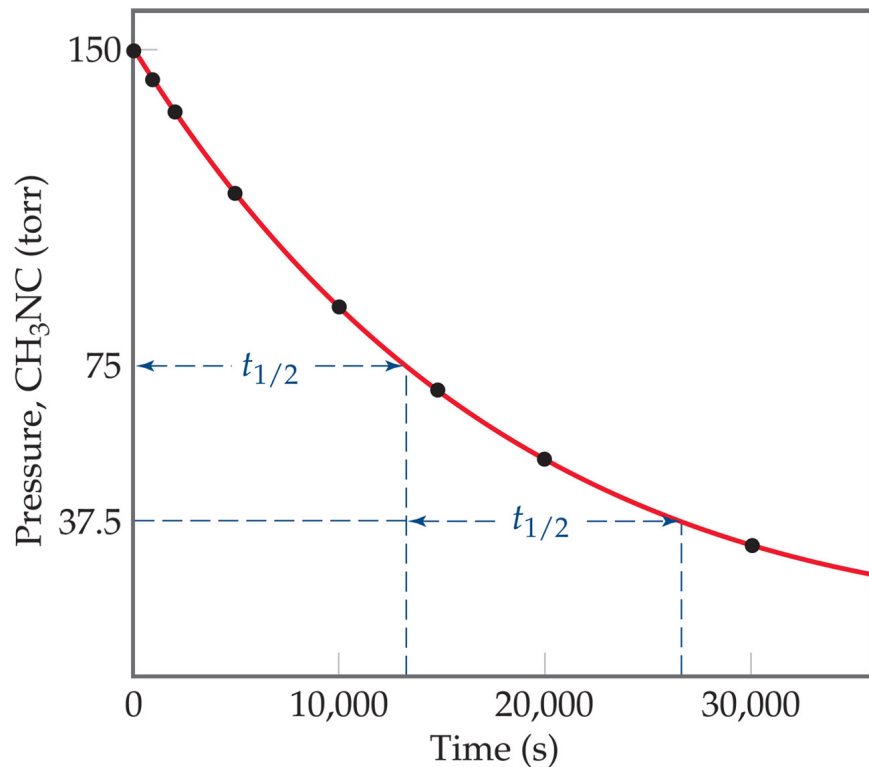
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Time (s)	$[\text{NO}_2]$, M	$1/[\text{NO}_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

- This is a straight line. Therefore, the process is second-order in $[\text{NO}_2]$.

Half Life

Half-Life



- Half-life is defined as the time required for one-half of a reactant to react.
- Because $[A]_t$ at $t_{1/2}$ is one-half of the original $[A]_0$,
$$[A]_t = 0.5 [A]_0.$$

Half-Life

- **Half-life** is the time taken for the concentration of a reactant to drop to half its original value.
- For a first order process, half life, $t_{1/2}$ is the time taken for $[A]_0$ to reach $\frac{1}{2}[A]_0$... (see the book for the next equation's derivation.)

$$t_{1/2} = \frac{-\ln(1/2)}{k} = \frac{0.693}{k} \quad \text{where } k = \text{the rate constant}$$

- For a 2nd order reaction, half-life depends on the reactant concentrations: $t_{1/2} = 1/k[A]_0$
- For Zero order reactions... $t_{1/2} = [A]_0 / 2k$

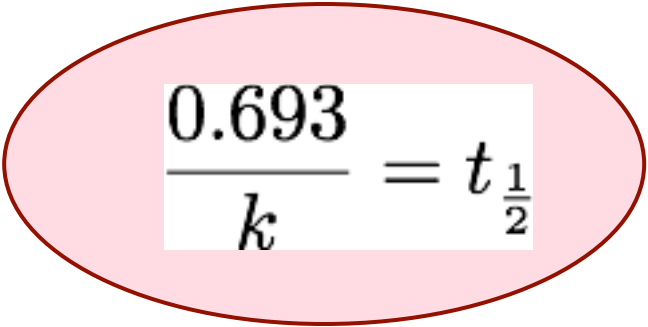
Half-Life

For a first-order process, set $[A]_t = 0.5 [A]_0$ in integrated rate equation:

$$\ln \frac{0.5 [A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$\ln(0.5) = -kt_{\frac{1}{2}}$$

$$\ln(2) = 0.693 = -kt_{\frac{1}{2}}$$


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

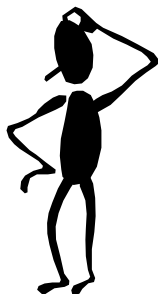
NOTE: For a first-order process, the half-life does not depend on $[A]_0$.

First-Order Reactions

The **half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

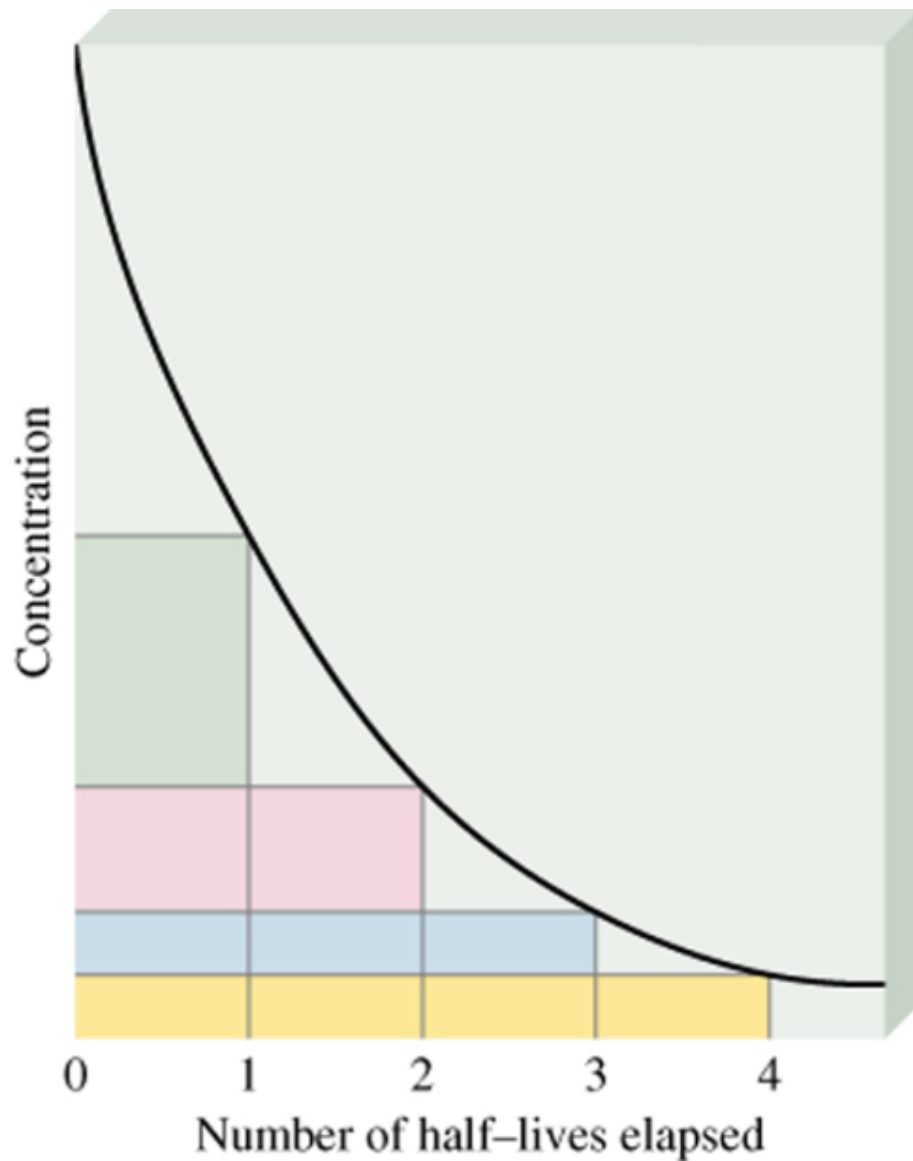
$$t_{1/2} = \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$



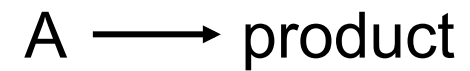
What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

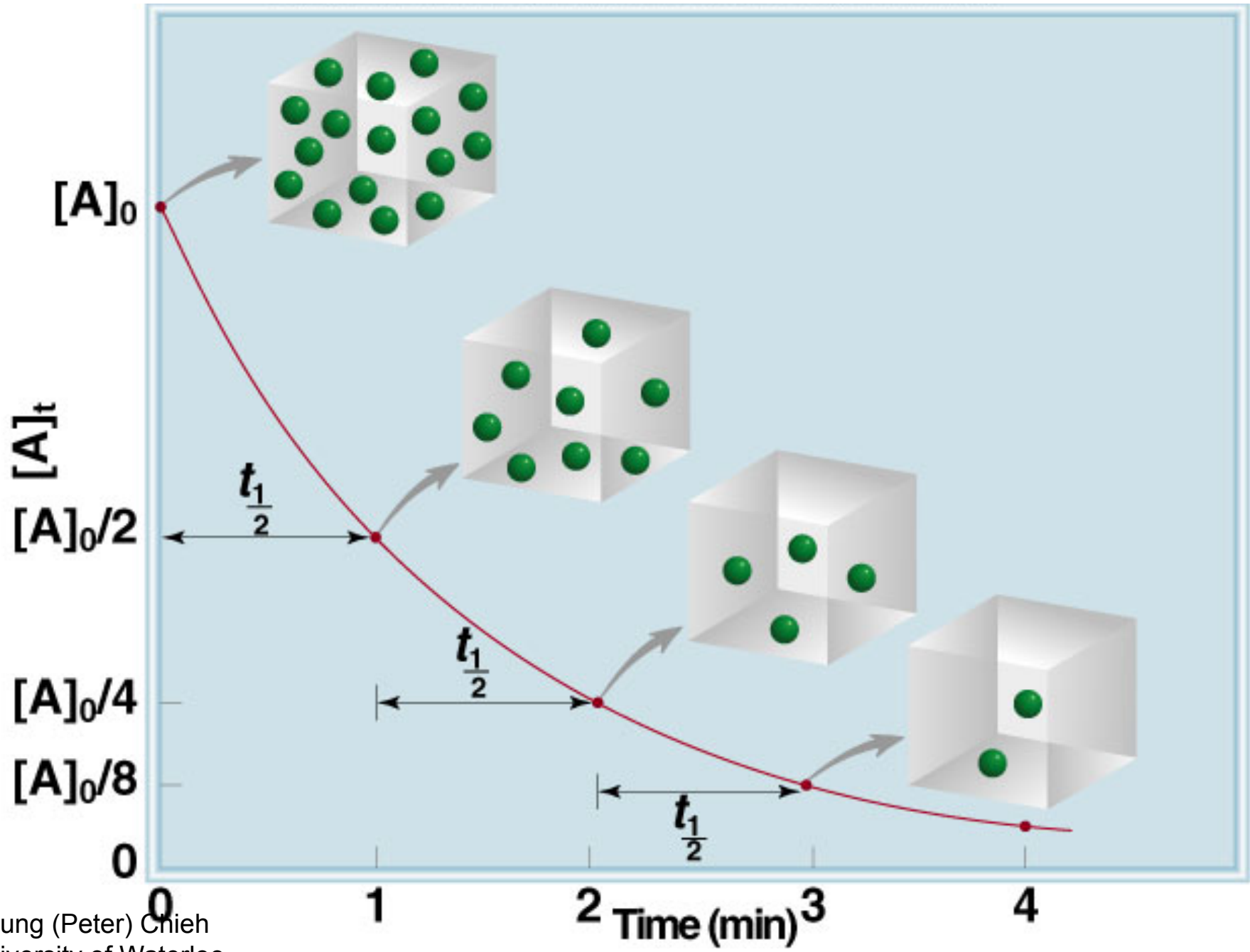
How do you know decomposition is first order?



First-order reaction



<u># of half-lives</u>	<u>$[A] = [A]_0/n$</u>
1	2
2	4
3	8
4	16



Chung (Peter) Chieh
University of Waterloo

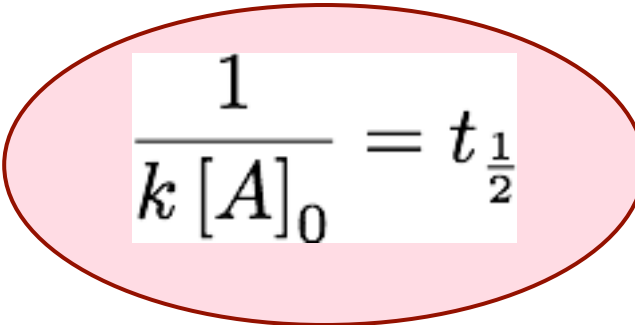
Half-Life- 2nd order

For a second-order process, set $[A]_t = 0.5 [A]_0$ in 2nd order equation.

$$\frac{1}{0.5 [A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{\frac{1}{2}}$$


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

Equations of Reactions of Various Orders

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] - [A]_0 = -kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k [A]$	$\ln[A] - \ln[A]_0 = -kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k [A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{1/2} = \frac{1}{k[A]_0}$

Summary of Kinetics

	First order	Second order (1 reactant)	General Second order
Rate Laws	$rate = -k [A]$	$rate = -k [A]^2$	$rate = -k [A] [B]$
Integrated Rate Laws	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	complicated
Half-life	$\frac{0.693}{k} = t_{\frac{1}{2}}$	$\frac{1}{k [A]_0} = t_{\frac{1}{2}}$	complicated

Summary of Kinetics

	First order	Second order (1 reactant)	General Second order
Rate Laws	$rate = -k [A]$	$rate = -k [A]^2$	$rate = -k [A] [B]$
Integrated Rate Laws	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	complicated
Half-life	$\frac{0.693}{k} = t_{\frac{1}{2}}$	$\frac{1}{k [A]_0} = t_{\frac{1}{2}}$	complicated
$k(T)$	$\ln(k) = -\frac{E_a}{RT} + \ln A$		

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Activation Energy

Activation Energy

- There is a minimum amount of energy required for a reaction: the **activation energy**, E_a .
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.



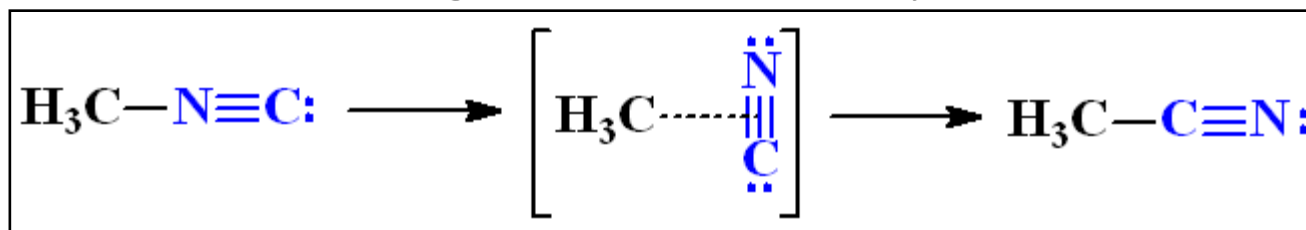
Activation Energy

- Molecules must possess a minimum amount of energy to react. Why?
 - In order to form products, bonds must be broken in the reactants. Bond breakage requires energy.
 - Molecules moving too slowly, with too little kinetic energy, don't react when they collide.
- **Activation energy, E_a** , is the minimum energy required to initiate a chemical reaction.
 - E_a will vary with the reaction.

Next we will look at an example of E_a .

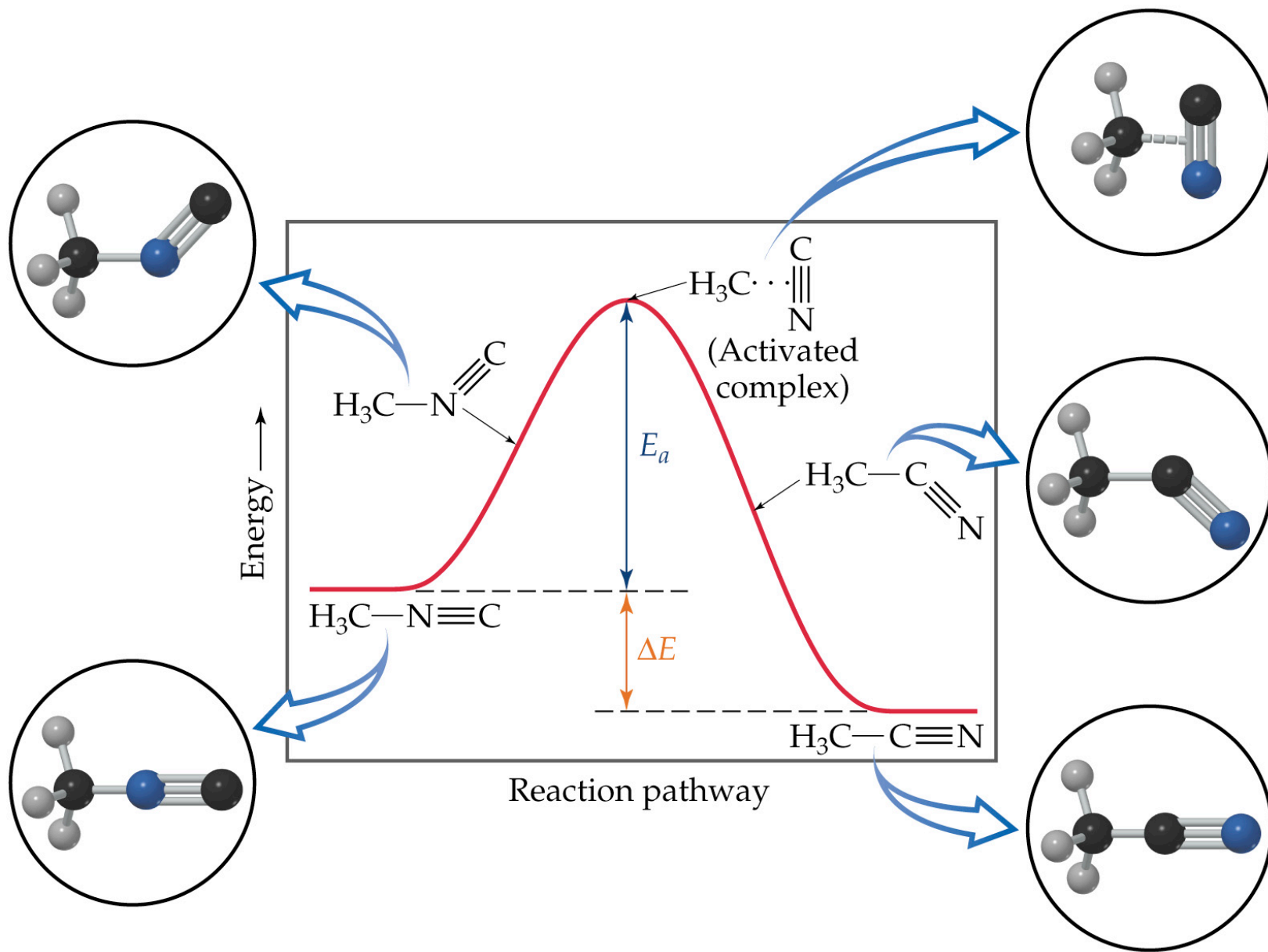
Activation Energy

- Consider the rearrangement of methyl isonitrile:



- In $\text{H}_3\text{C}-\text{N}\equiv\text{C}$, the $\text{C}-\text{N}\equiv\text{C}$ bond bends until the $\text{C}\equiv\text{N}$ bond breaks and the $\text{N}\equiv\text{C}$ portion is perpendicular to the H_3C portion. This structure is called the **activated complex** or **transition state**.
- The energy required for the above twist and break is the **activation energy**, E_a .
- Once the $\text{C}-\text{N}$ bond is broken, the $\text{N}\equiv\text{C}$ portion can continue to rotate forming a $\text{C}-\text{C}\equiv\text{N}$ bond.

* Here's what the reaction looks like in terms of a graph of the energies that are involved in the process...

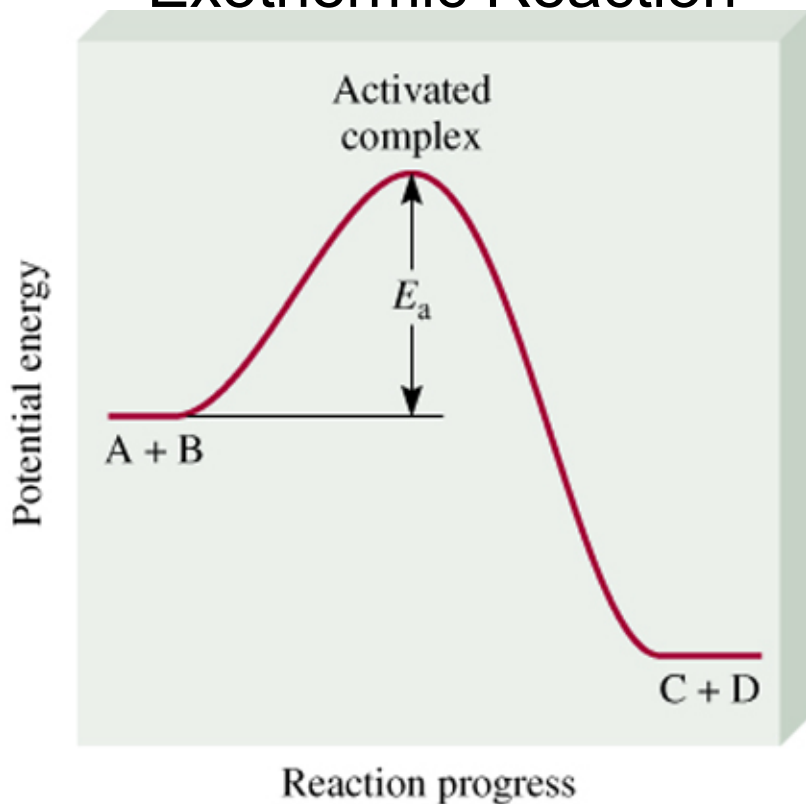


Activation Energy

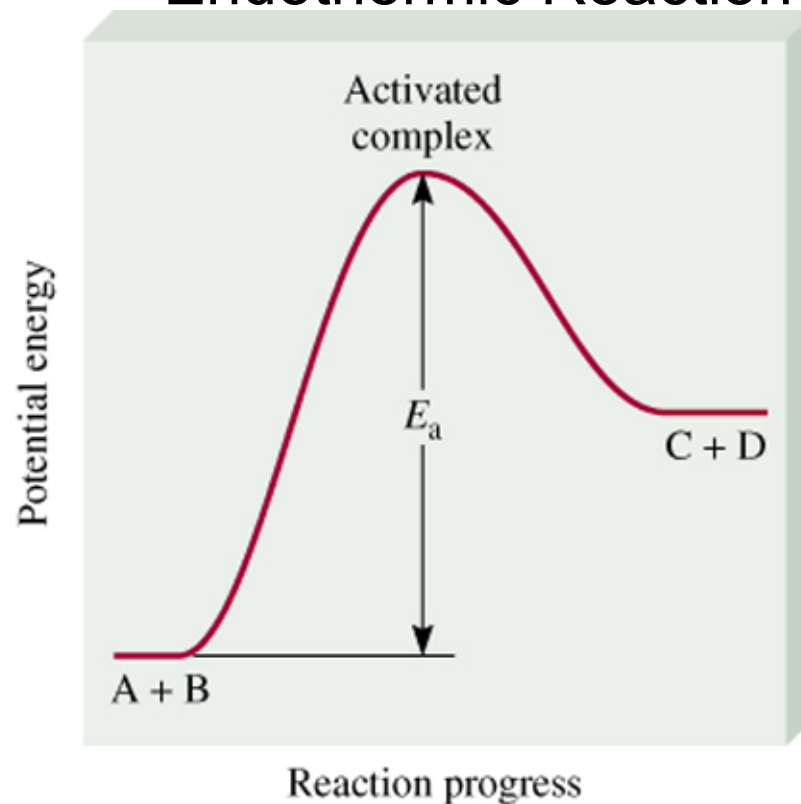
- The change in energy, ΔE , for the reaction is the difference in energy between CH_3NC and CH_3CN .
- The activation energy, E_a , is the difference in energy between reactants, CH_3NC , and the transition state.
- The rate depends on E_a . If the “hill” is taller, the reaction rate is slower. If the “hill” is shorter the rate is faster.
- Notice that if a forward reaction is exothermic... ($\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$), then the reverse reaction is endothermic... ($\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$).
- The methyl isonitrile molecule needs to gain enough energy to overcome the activation energy barrier.
- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases and the number of molecules with energy greater than E_a increases.
- So as long as the temperature is high enough, the reaction can make it “over the hill” and proceed.



Exothermic Reaction

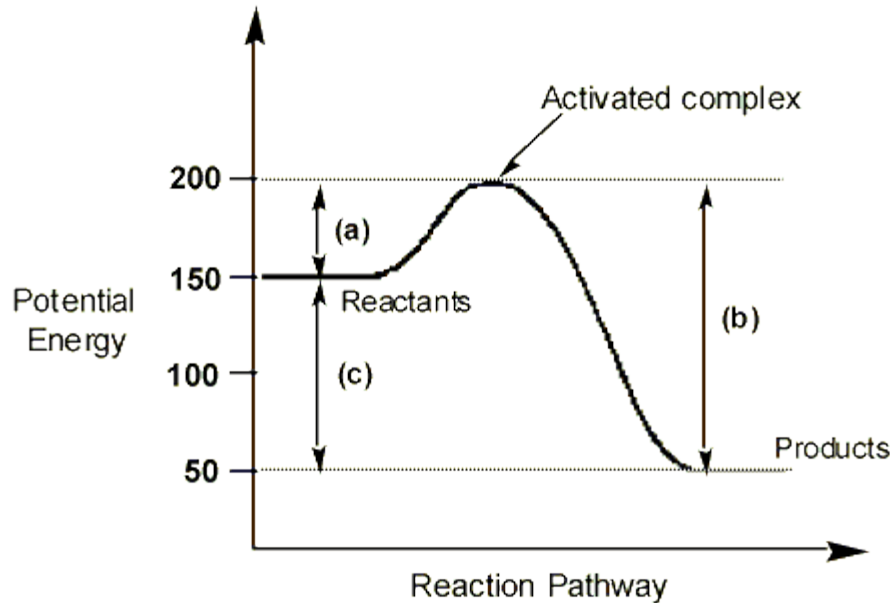


Endothermic Reaction

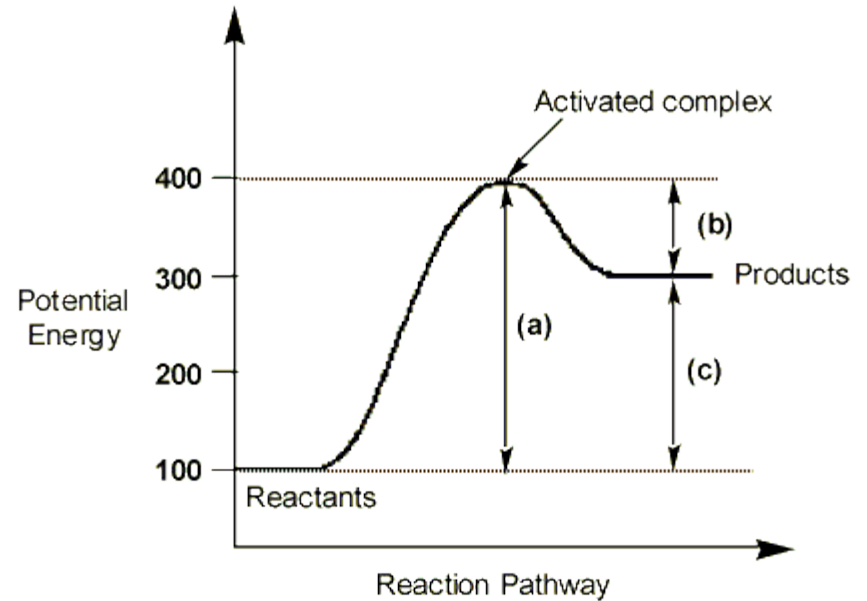


The **activation energy** (E_a) is the minimum amount of energy required to initiate a chemical reaction.

Energy Diagrams



Exothermic

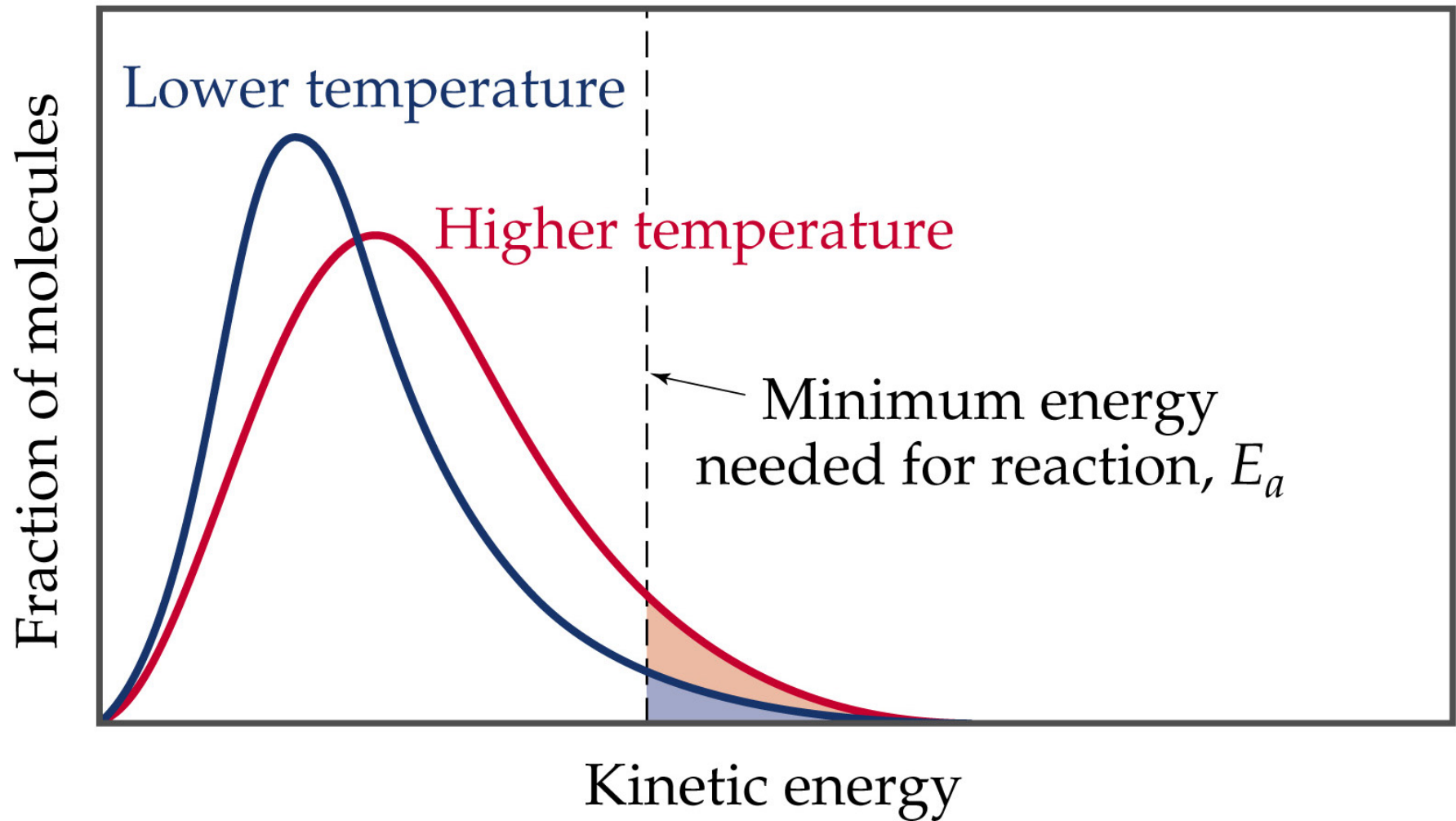


Endothermic

- (a) Activation energy (E_a) for the forward reaction
- (b) Activation energy (E_a) for the reverse reaction
- (c) ΔH

50 kJ/mol	300 kJ/mol
150 kJ/mol	100 kJ/mol
-100 kJ/mol	+200 kJ/mol

Temperature vs. Energy of Activation



Reaction Mechanisms

Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the **reaction mechanism**.

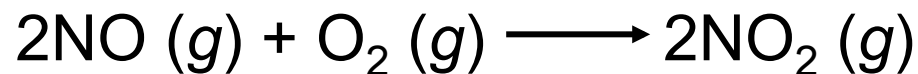
Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.

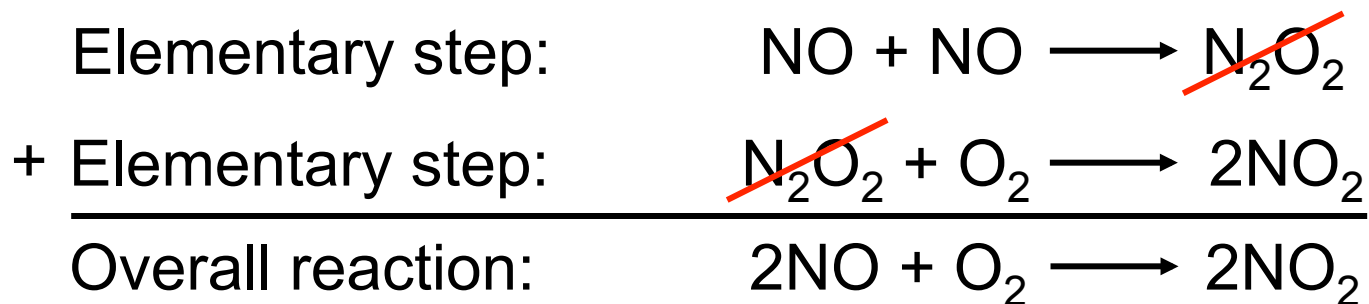
Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple ***elementary steps*** or ***elementary reactions***.

The sequence of ***elementary steps*** that leads to product formation is the ***reaction mechanism***.



N_2O_2 is detected during the reaction!

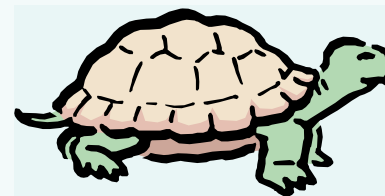


Rate Laws and Rate Determining Steps

Writing plausible reaction mechanisms:

- The sum of the elementary steps **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-determining step*** is the **slowest** step in the sequence of steps leading to product formation.



Rate Laws and Elementary 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 $A + A \rightarrow \text{products}$ $\text{rate} = k [A]^2$

Reaction Mechanisms

- Up until now, we have only been concerned with the reactants and products. Now we will examine what path the reactants took in order to become the products.
- The **reaction mechanism** gives the path of the reaction.
- Mechanisms provide a very detailed picture of which bonds are broken and formed during the course of a reaction.

Elementary Steps & Molecularity

- **Elementary step**: any process that occurs in a single step.
- **Molecularity**: number of molecules present in an elementary step.
 - **Unimolecular**: one molecule in the elementary step,
 - **Bimolecular**: two molecules in the elementary step, and
 - **Termolecular**: three molecules in the elementary step.

(It is uncommon to see termolecular processes...statistically improbable for an effective collision to occur.)

Rate Laws of Elementary Steps

- Since this process occurs in one single step, the stoichiometry can be used to determine the rate law!
- Law of Mass Action: The rate of a simple (one step) reaction is directly proportional to the concentration of the reacting substances.

TABLE 14.3 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
<i>Unimolecular</i>	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
<i>Bimolecular</i>	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
<i>Bimolecular</i>	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
<i>Termolecular</i>	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
<i>Termolecular</i>	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
<i>Termolecular</i>	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

- Notice that the coefficients become the exponents.

Reaction Mechanisms

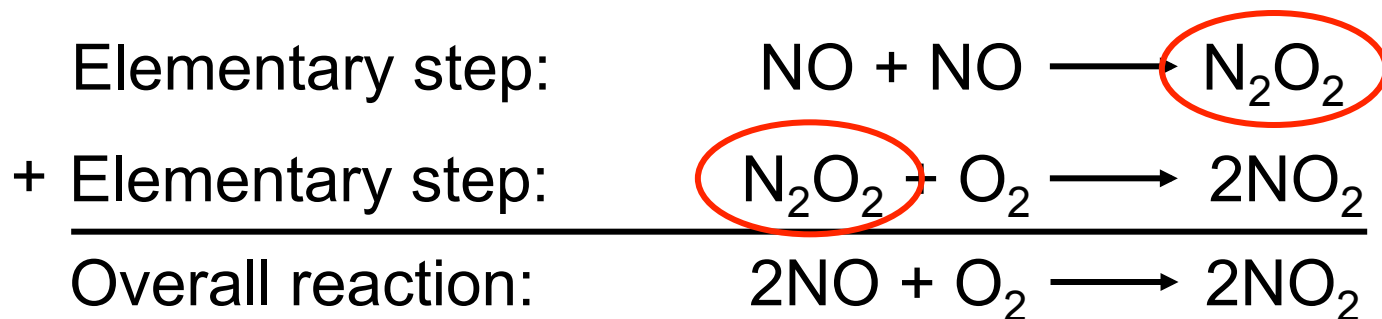
Molecularity	Elementary Reaction	Rate Law
<i>Unimolecular</i>	$A \longrightarrow \text{products}$	Rate = $k[A]$
<i>Bimolecular</i>	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
<i>Bimolecular</i>	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
<i>Termolecular</i>	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
<i>Termolecular</i>	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
<i>Termolecular</i>	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

- The **molecularity** of a process tells how many molecules are involved in the process.
- The rate law for an elementary step is written directly from that step.

Reaction Intermediates

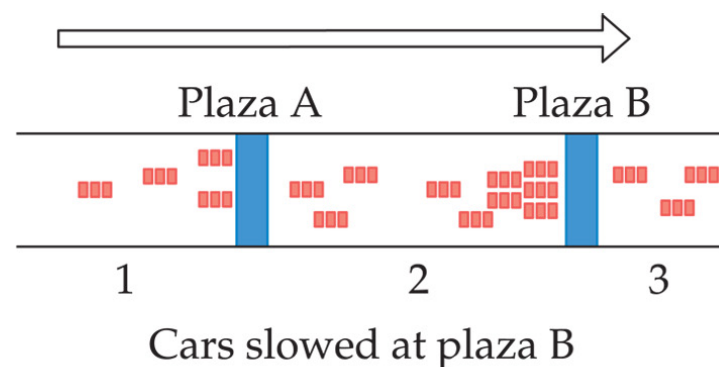
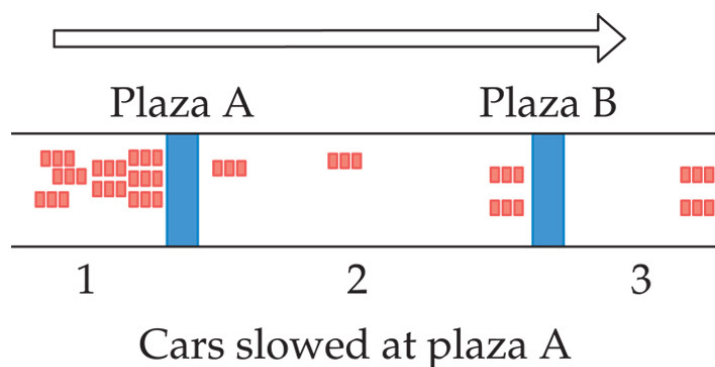
Intermediates are species that appear in a reaction mechanism **but not** in the overall balanced equation.

An **intermediate** is always formed in an early elementary step and consumed in a later elementary step.



Multistep Mechanisms

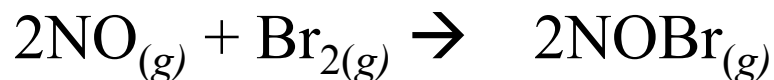
- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, **rate-determining step**.



Example of Slow & Fast Reaction Mechanisms

Rate Laws for Multistep Mechanisms

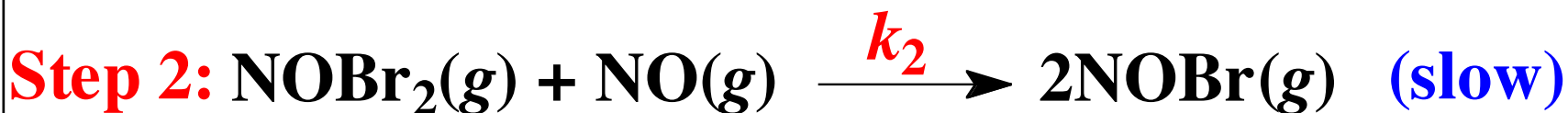
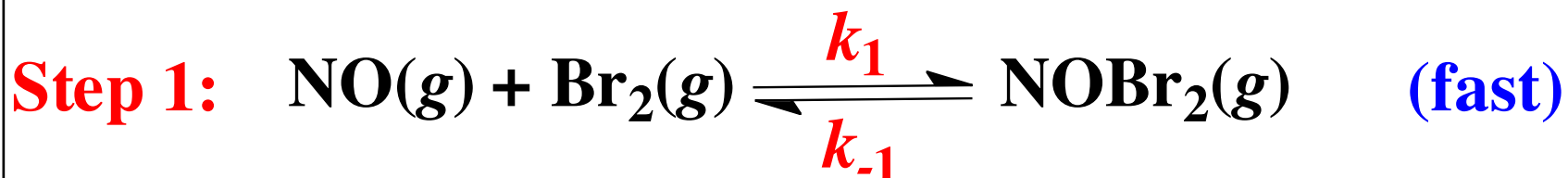
- Let's look at another example...



- The experimentally determined rate law is...

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

- Consider the following mechanism...



- The rate law is based on **Step 2**:

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}]$$

Slow Initial Step



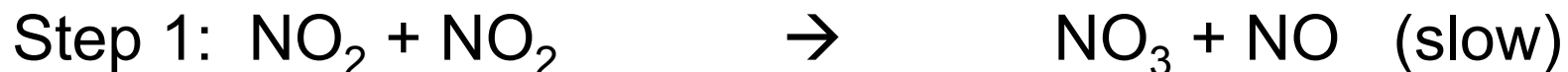
- The rate law for this reaction is found experimentally to be

$$\text{Rate} = k [\text{NO}_2]^2$$

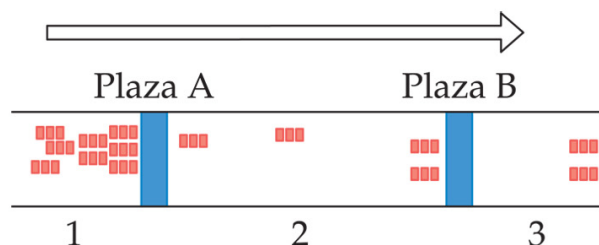
- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.

Slow Initial Step

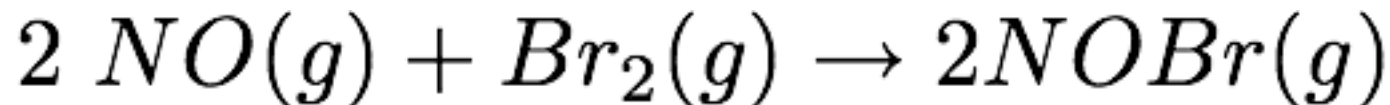
- A proposed mechanism for this reaction is



- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.



Fast Initial Step



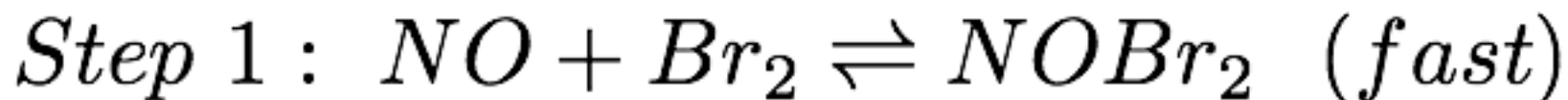
- The rate law for this reaction is found (experimentally) to be

$$\text{rate} = k [\text{NO}]^2 [\text{Br}_2]$$

- Because termolecular (= trimolecular) processes are rare, this rate law suggests a two-step mechanism.

Fast Initial Step

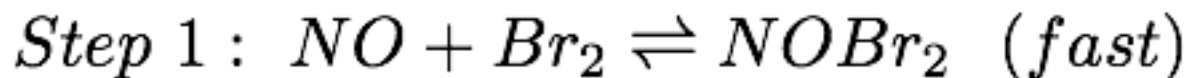
- A proposed mechanism is



Step 1 is an *equilibrium*:

it includes the forward *and* reverse reactions.

Fast Initial Step

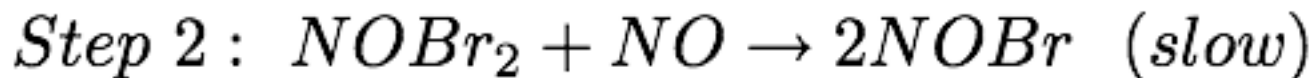
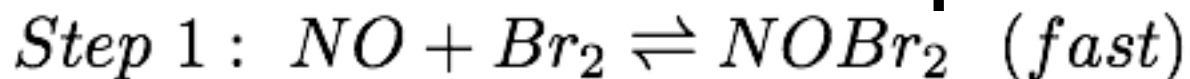


- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$\text{rate}_2 = k_2 [\text{NOBr}_2] [\text{NO}]$$

- But how can we find $[\text{NOBr}_2]$?

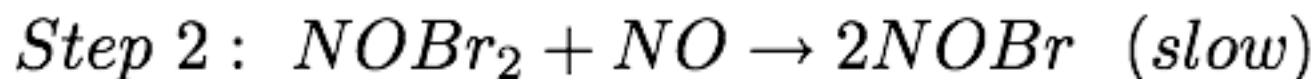
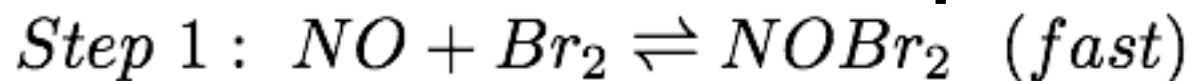
Fast Initial Step



- NOBr_2 can react two ways:
 - With NO to form NOBr
 - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$\text{Rate}_f = \text{Rate}_r$$

Fast Initial Step



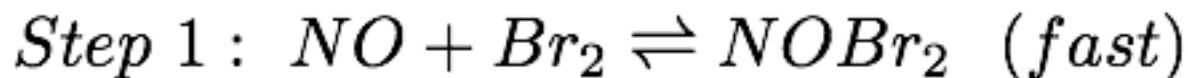
- Because $\text{Rate}_f = \text{Rate}_r$,

$$k_1 [\text{NO}] [\text{Br}_2] = k_{-1} [\text{NOBr}_2]$$

Solving for $[\text{NOBr}_2]$ gives us

$$\frac{k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$

Fast Initial Step



Substituting this expression for $[\text{NOBr}_2]$ in the rate law for the rate-determining step gives

$$\begin{aligned} \text{rate} &= \frac{k_2 k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] [\text{NO}] \\ &= \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{Br}_2] \end{aligned}$$

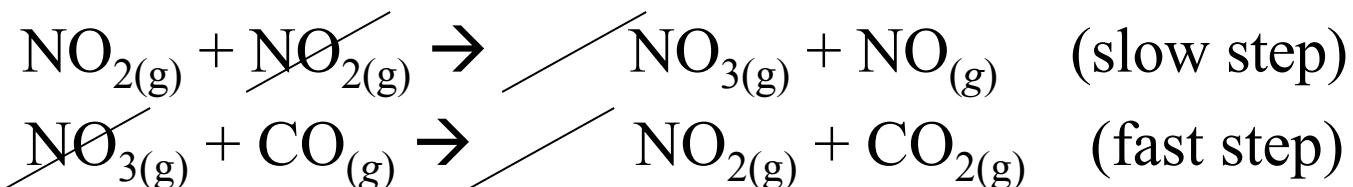
Rate Laws for Multistep Reactions

Rate Laws for Multistep Mechanisms

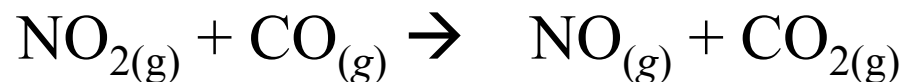
- Most reactions proceed through more than one step:



- A proposed mechanism is as follows...



- Notice that if we add the above steps, we get the overall reaction:



- If a reaction proceeds via several elementary steps, then the elementary steps must add to give the balanced chemical equation.
- **Intermediate:** a species which appears in an elementary step which is not a reactant or product. They are formed in one elementary step and consumed in another...Our Example: $\text{NO}_{3(g)}$

Rate Laws for Multistep Mechanisms

- Often one step is much slower than the others. The slow step limits the overall reaction rate.
- This is called the **rate-determining step** of the reaction.
- This step governs the overall rate law for the overall reaction.
- In our previous example, the theoretical rate law is therefore...

$$\text{Rate} = k[\text{NO}_2]^2$$

- The experimentally determined rate law is...

$$\text{Rate} = k[\text{NO}_2]^2$$

- This supports, (but does not prove), our mechanism.

Rate Laws for Multistep Mechanisms

- But we have a problem... This rate law depends on the concentration of an intermediate species.
- Intermediates are usually unstable and have low/unknown concentrations. We need to find a way to remove this term from our rate law.
- So we have to express $[\text{NOBr}_2]$ in terms of NO and Br_2 by assuming there is an equilibrium in **step 1**.
- In a dynamic equilibrium, the forward rate equals the reverse rate. Therefore, by definition of equilibrium we get:

$$k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$$

Rearranging...

$$[\text{NOBr}_2] = (k_1/k_{-1})[\text{NO}][\text{Br}_2]$$

Rate Laws for Multistep Mechanisms

- Now we substitute $[\text{NOBr}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2]$ into our previous rate law...

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}]$$

And we get...

$$\text{Rate} = (k_2k_1/k_{-1})[\text{NO}][\text{Br}_2][\text{NO}]$$

Combining terms...

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

- This matches the experimentally determined rate law equation, so this supports, (but does not prove) our reaction mechanism.

Arrhenius Equation

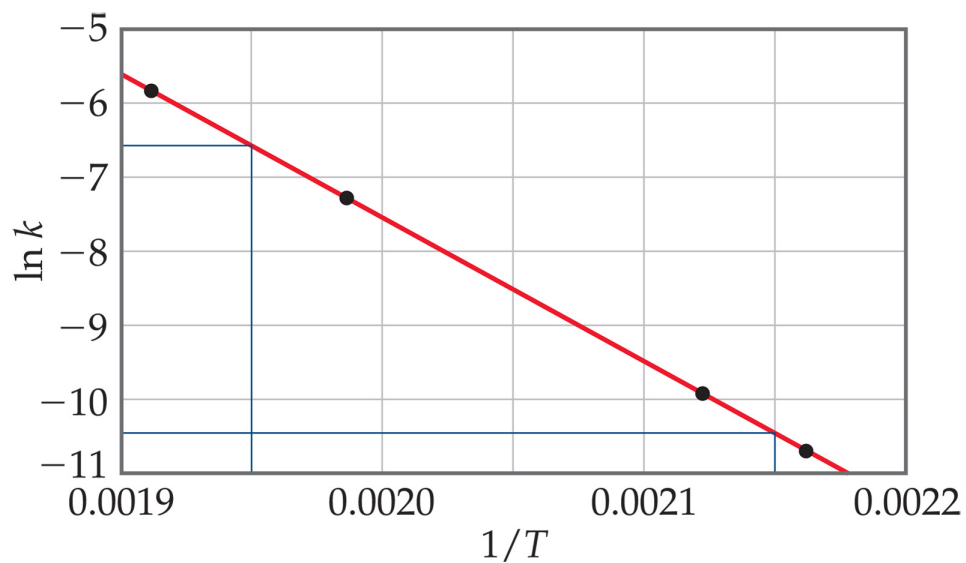
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a :

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

where A is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

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

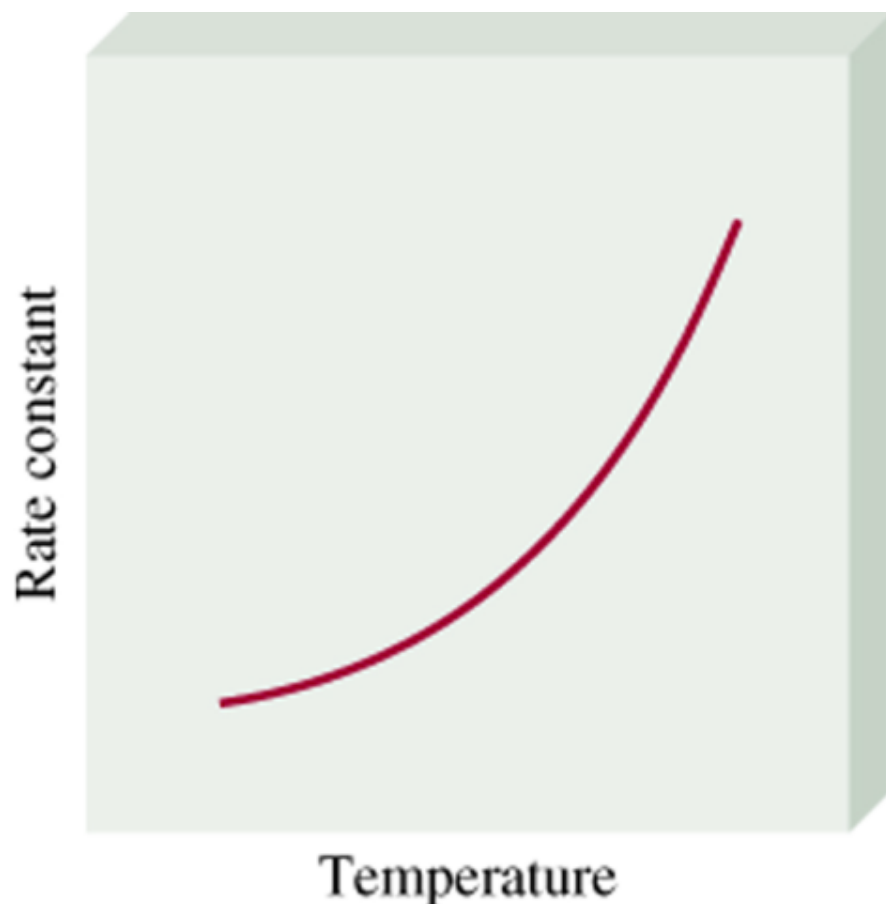
$$y = mx + b$$

When k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of $\ln k$ vs. $1/T$.

John D. Bookstaver

St. Charles Community College

Temperature Dependence of the Rate Constant



$$k = A \cdot \exp(-E_a/RT)$$

(Arrhenius equation)

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

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

Arrhenius Equation

- This is how the rate constant of a chemical reaction varies with respect to temperature and other variables.

$$\ln(k) = - E_a/R(1/T) + \ln(A)$$

where... k= rate constant

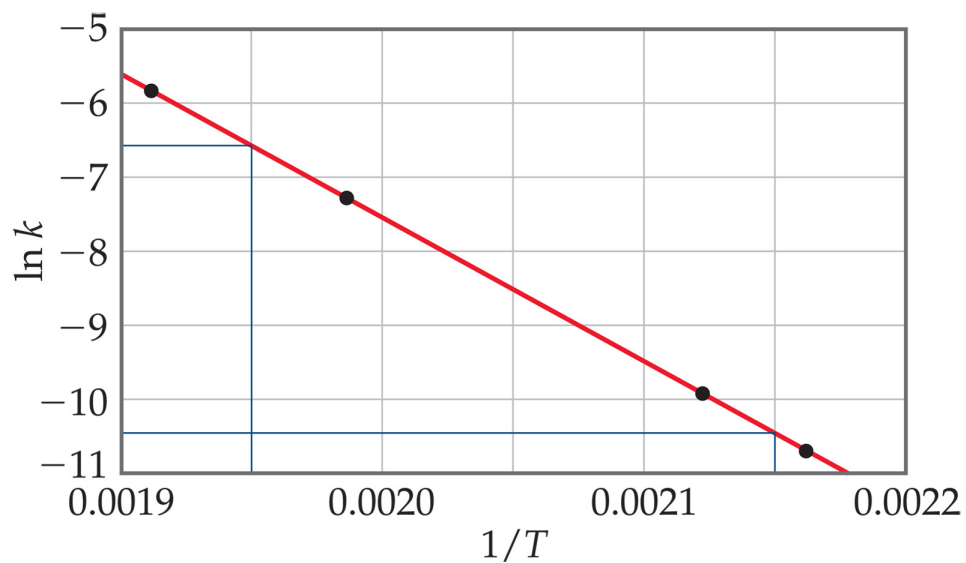
E_a = Activation Energy (in kJ/mole)

R = Gas Constant

T = Kelvin temperature

A = “Frequency Factor” -- a constant indicating how many collisions have the correct orientation to lead to products.

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

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

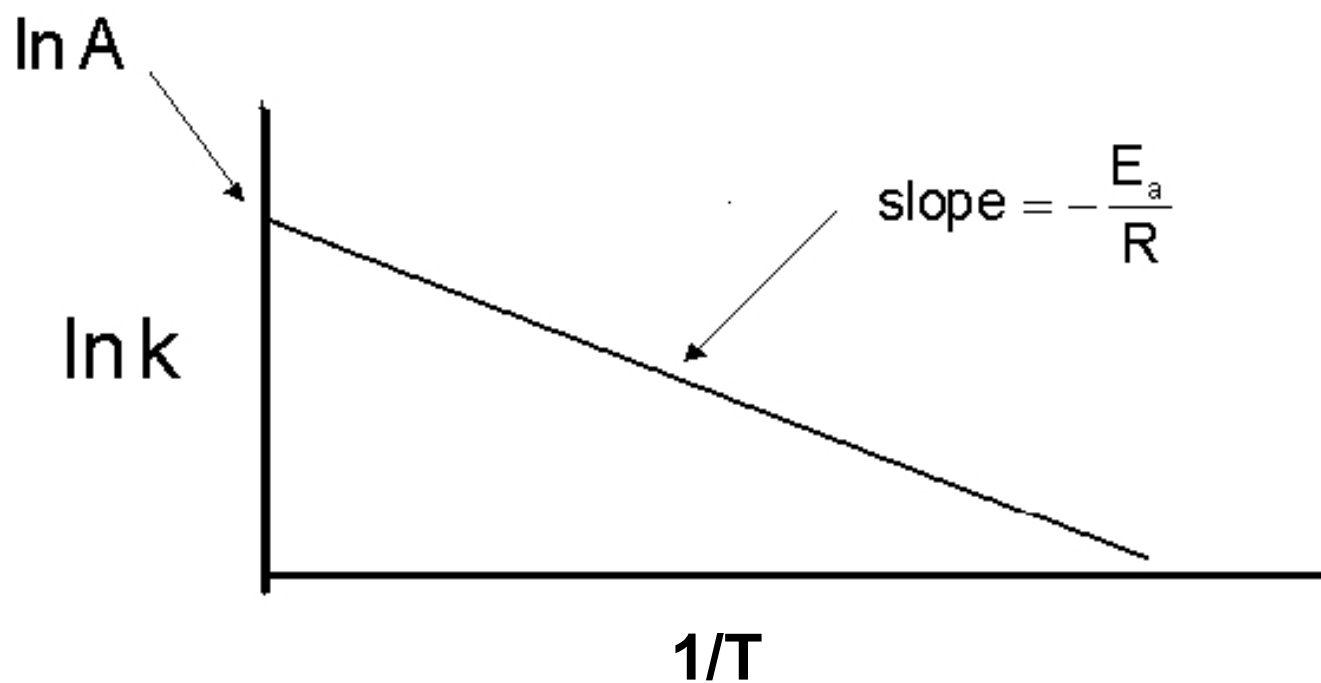
$$y = mx + b$$

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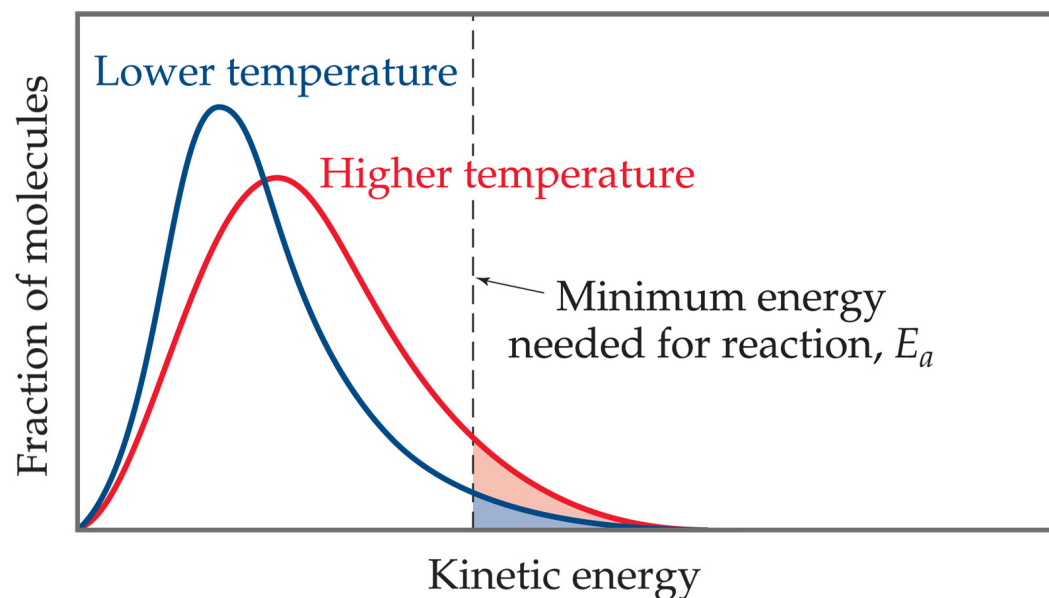
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Plot of Arrhenius Equation



Maxwell–Boltzmann Distributions

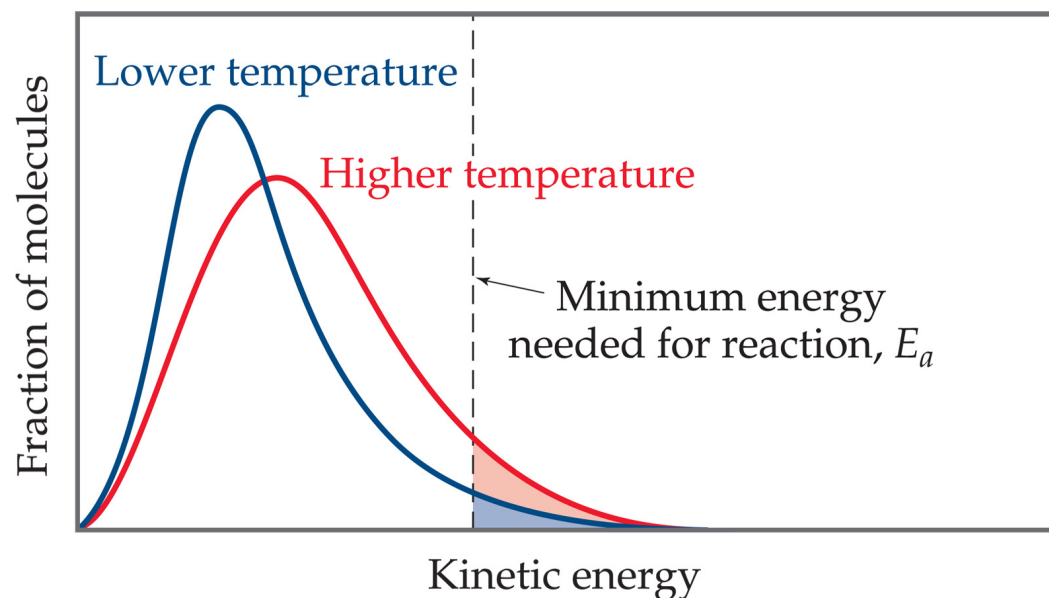
Maxwell–Boltzmann Distributions



- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

- At any temperature there is a wide distribution of kinetic energies.

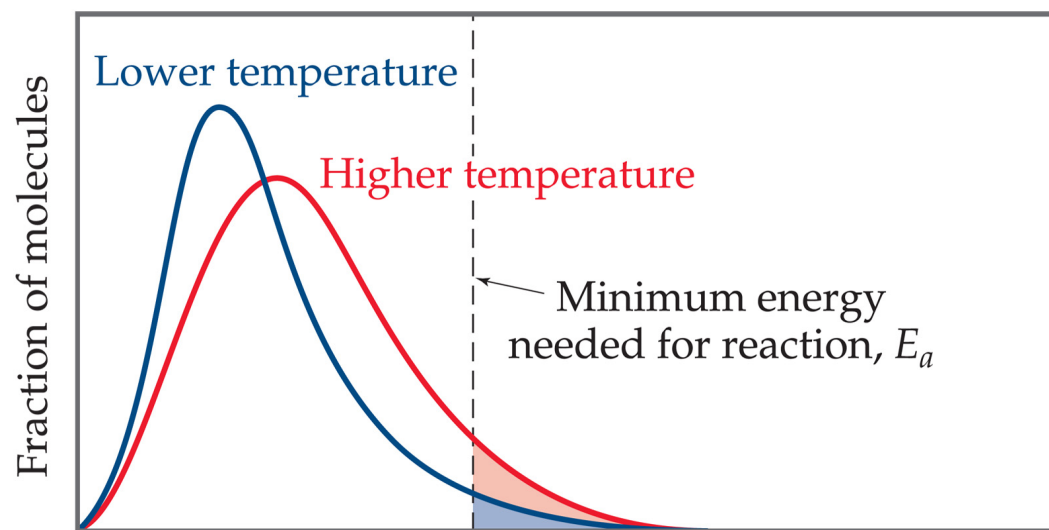
Maxwell–Boltzmann Distributions



- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.

Maxwell–Boltzmann Distributions

- If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.



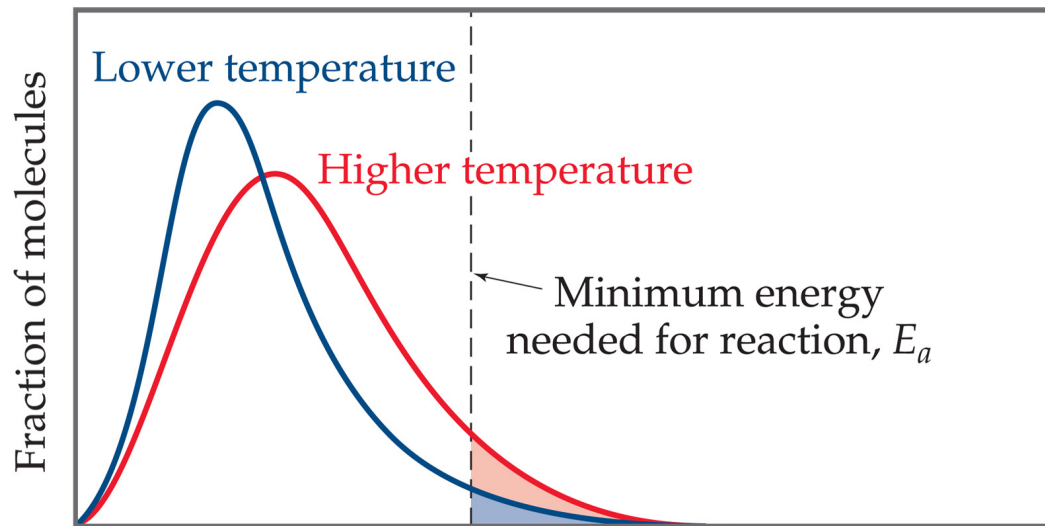
- As a result, the reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression:

$$f = e^{-\frac{E_a}{RT}}$$

where R is the gas constant and T is the temperature in Kelvin .

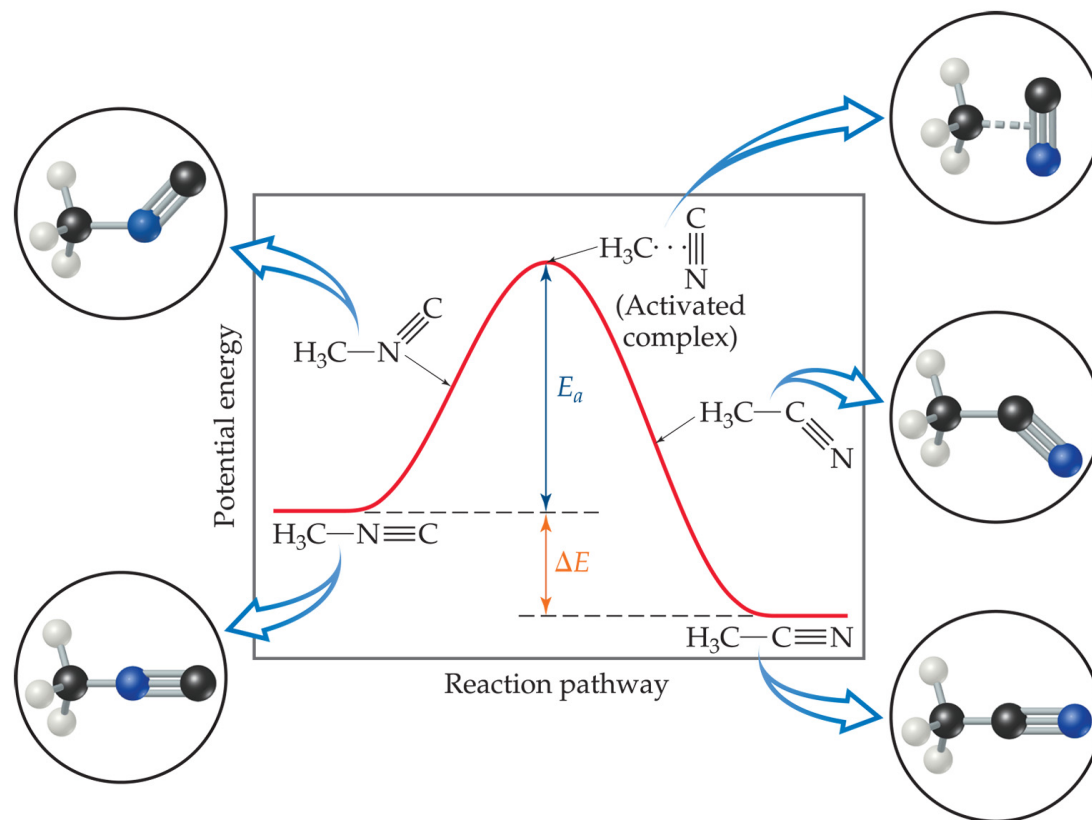


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Reaction Coordinate Diagrams

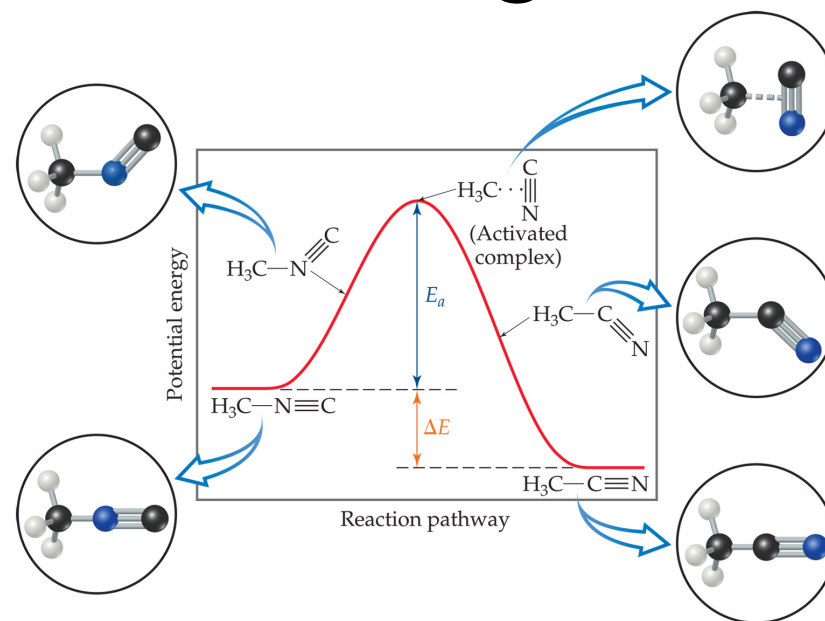
Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a **reaction coordinate diagram** like this one for the rearrangement of methyl isonitrile.



Reaction Coordinate Diagrams

- It shows the energy of the reactants and products (and, therefore, ΔE).
- The high point on the diagram is the **transition state**.



- The species present at the transition state is called the **activated complex**.
- The energy gap between the reactants and the activated complex is the **activation energy barrier**.

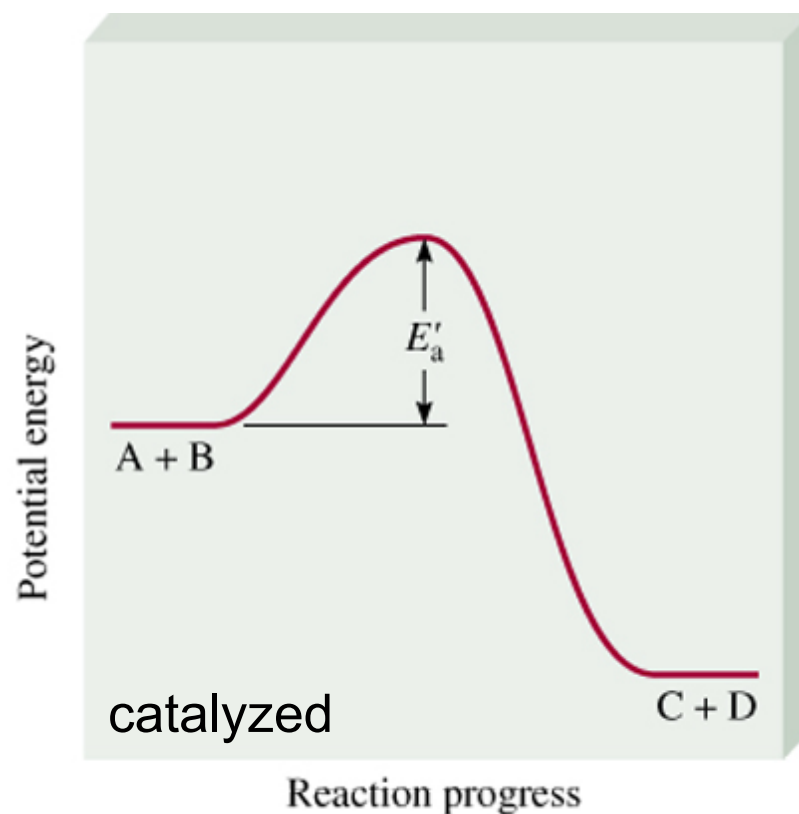
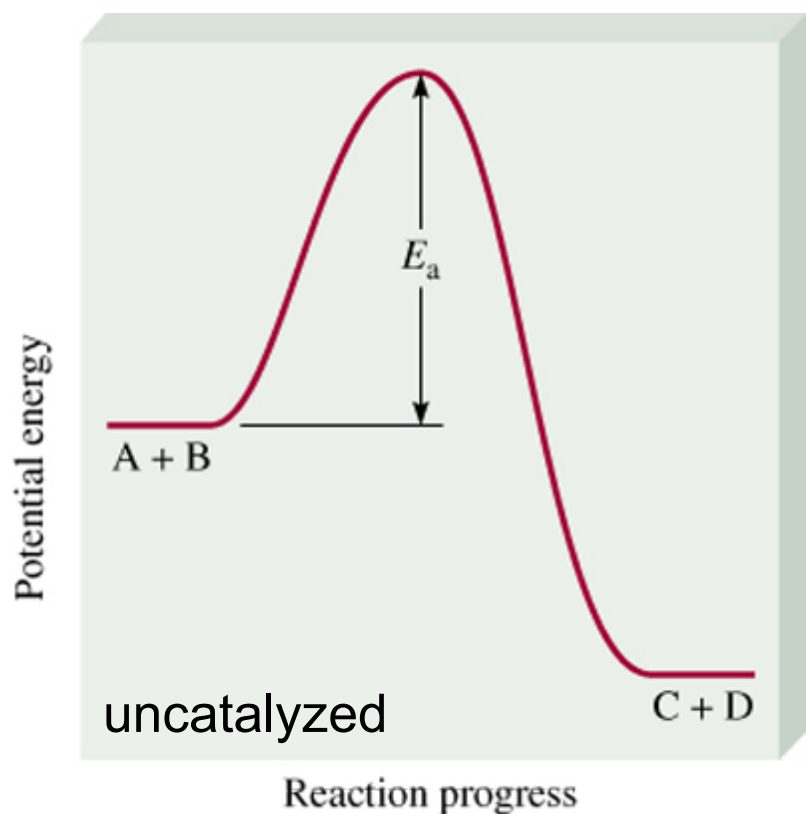
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Catalysts

A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

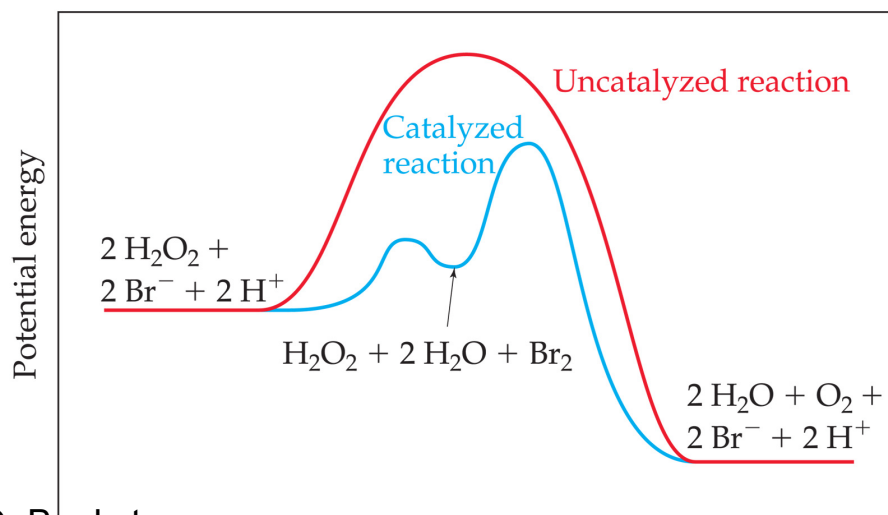
$$E_a \downarrow \quad k \uparrow$$



$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.

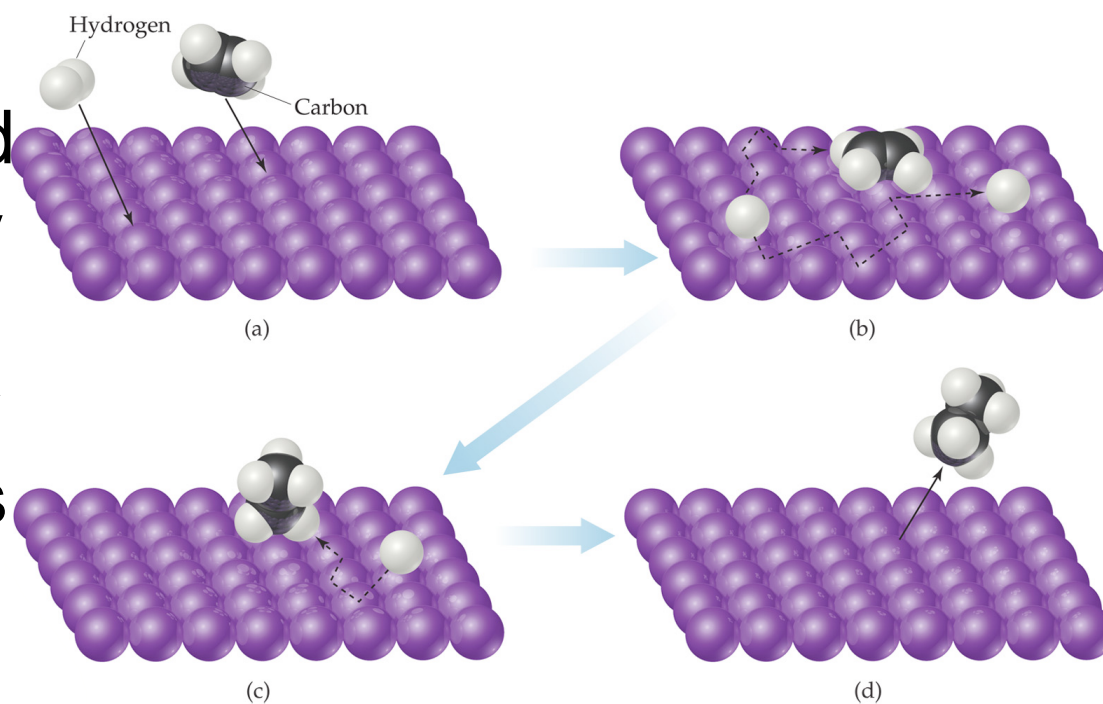


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Catalysts

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.



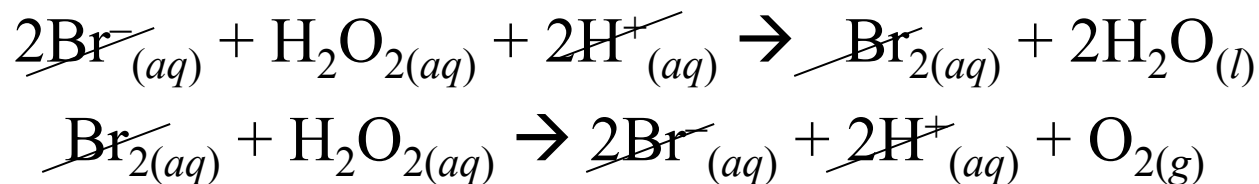
Catalysts

- A **catalyst** is a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.
- There are two types of catalyst: Heterogeneous--one that is present in a different phase as the reacting molecules. Homogeneous-- one that is present in the same phase as the reacting molecules.

Example: Hydrogen peroxide decomposes very slowly in the absence of a catalyst:



In the presence of bromide ions, the decomposition occurs rapidly in an acidic environment:



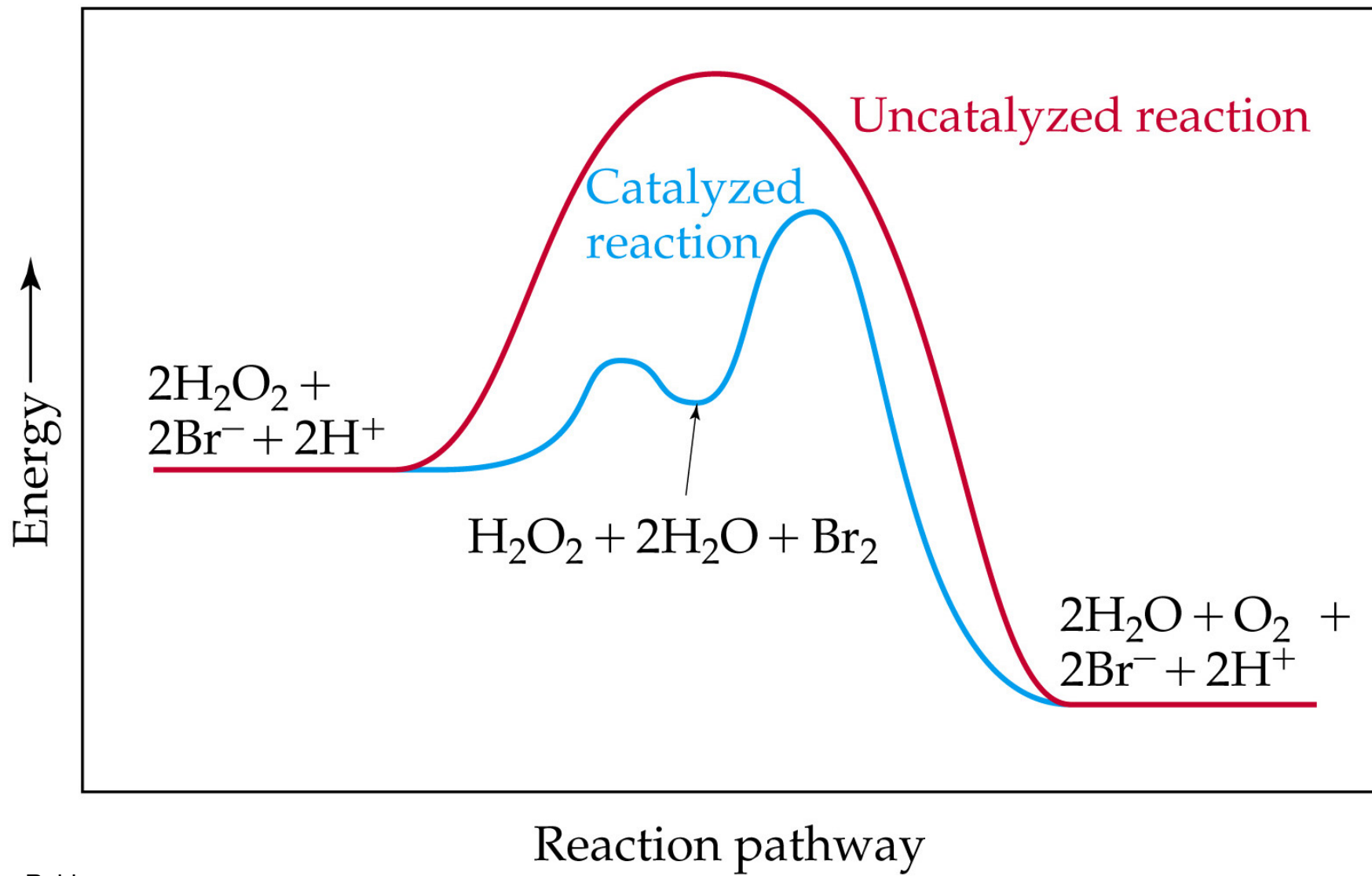
Br^- is a homogeneous catalyst because it is regenerated at the end of the reaction.

Catalysts and Reaction Rates

How do catalysts increase reaction rates?

- In general, catalysts operate by lowering the overall activation energy, E_a , for a reaction. (It lowers the “hill”.)
- However, catalysts can operate by increasing the number of effective collisions.
- A catalyst usually provides a completely different mechanism for the reaction.
- In the preceding peroxide decomposition example, in the absence of a catalyst, H_2O_2 decomposes directly to water and oxygen.
- In the presence of Br^- , $\text{Br}_{2(aq)}$ is generated as an **intermediate**.
- When a catalyst adds an intermediate, the activation energies for *both* steps must be lower than the activation energy for the uncatalyzed reaction.

Catalysts and Reaction Rates



Heterogeneous Catalysts

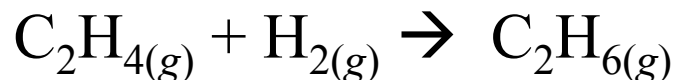
- Often we encounter a situation involving a solid catalyst in contact with gaseous reactants and gaseous products...
- Example: catalytic converters in cars.
 - Many industrial catalysts are heterogeneous.

How do they do their job?

- The first step is **adsorption** (the binding of reactant molecules to the catalyst surface).
- Adsorption occurs due to the high reactivity of atoms or ions on the surface of the solid.
- Molecules are adsorbed onto **active sites** on the catalyst surface.
- The number of active sites on a given amount of catalyst depends on several factors such as:
 - The nature of the catalyst.
 - How the catalyst was prepared.
 - How the catalyst was treated prior to use.

Heterogeneous Catalysts

Example:

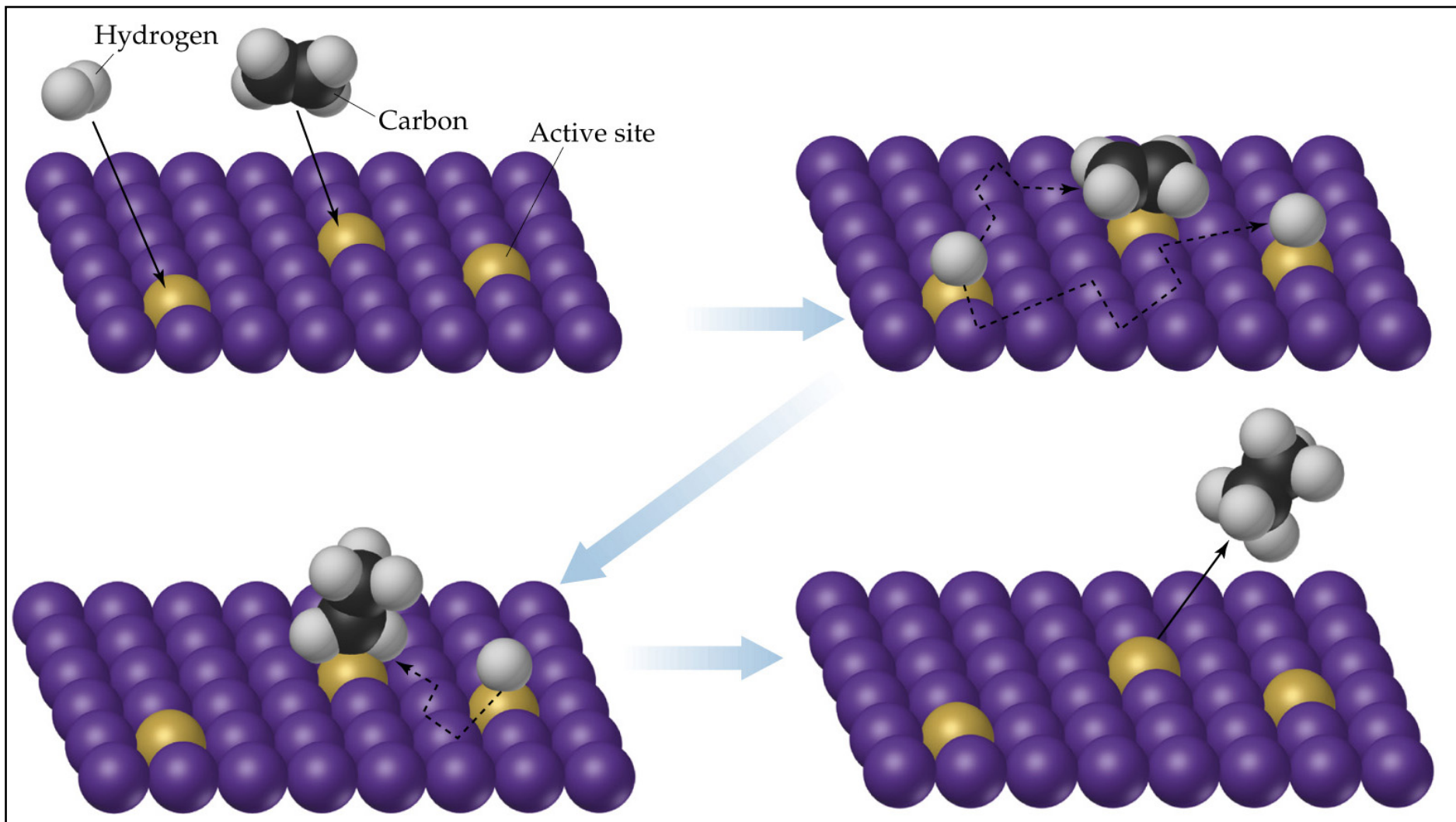


- In the presence of a metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.

Here are the steps...

- First, the ethylene and hydrogen molecules are adsorbed onto active sites on the metal surface.
- Second, the H–H bond breaks and the H atoms migrate about the metal surface and runs into a C₂H₄ molecule on the surface.
- Third, when an H atom collides with a C₂H₄ molecule on the surface, the C–C π-bond breaks and a C–H σ-bond forms.
- Lastly, When C₂H₆ forms it desorbs from the surface.
- When ethylene and hydrogen are adsorbed onto a surface, less energy is required to break the bonds.
- The E_a for the reaction is lowered, thus the reaction rate increases.

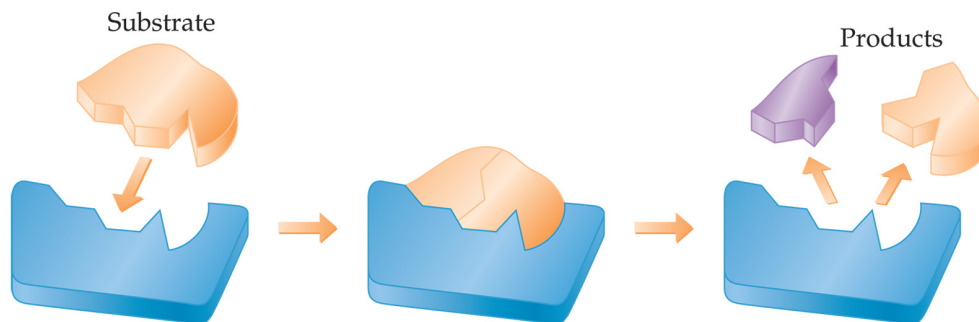
Heterogeneous Catalysts



Examples of Catalysts: Enzymes

Enzymes

- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.



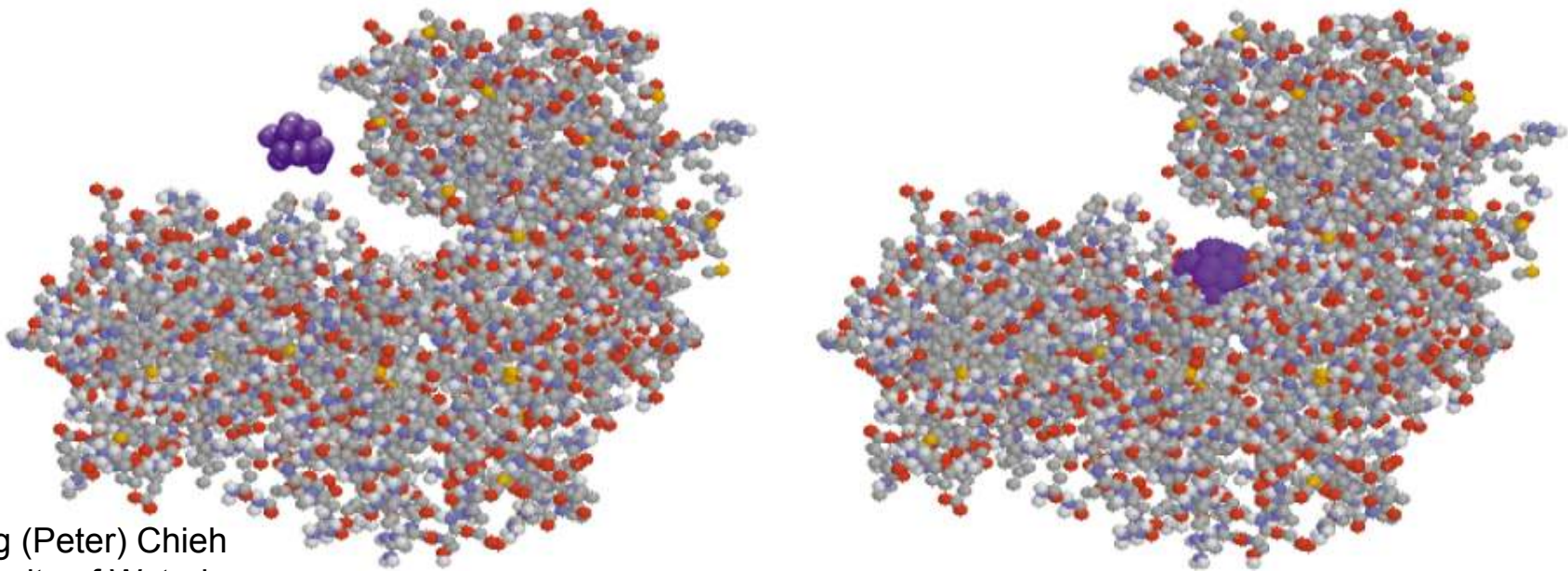
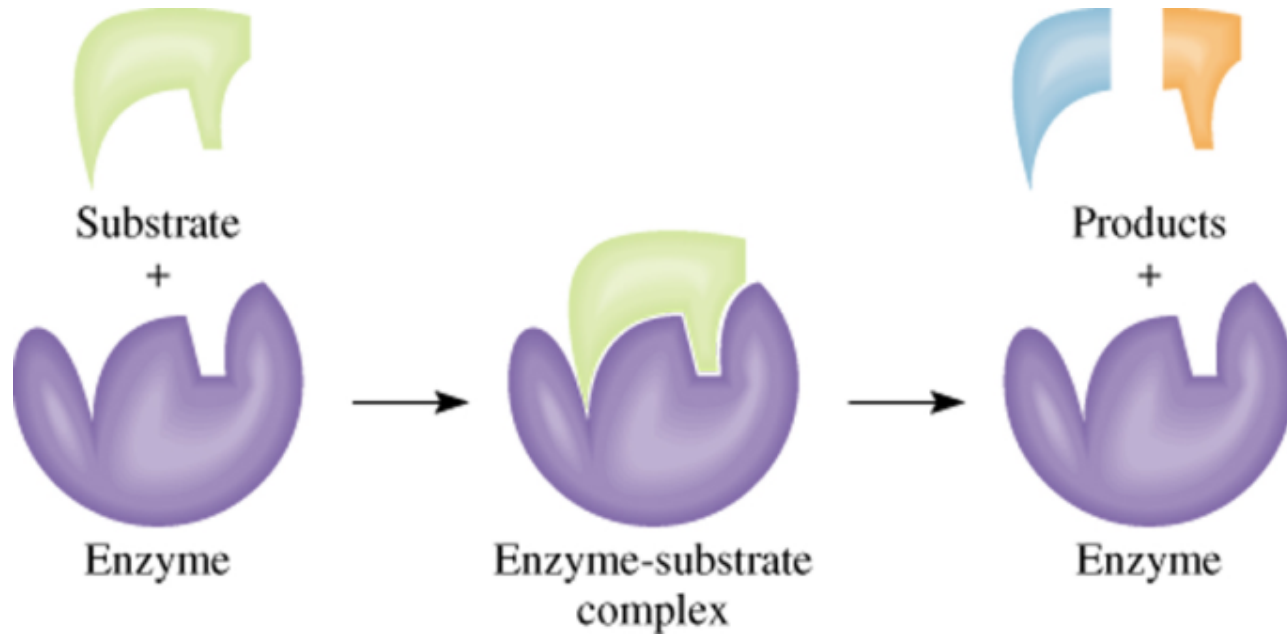
Enzyme Catalysts

- **Enzymes** are biological catalysts. There may be as many as 30,000 enzymes in the human body. (Ex: Lactase)
- Most enzymes are protein molecules with large molecular masses (10,000 to 10^6 amu).
- Enzymes have very specific shapes.
- Most enzymes catalyze very specific reactions.
- The substances that undergo reaction at the active site on enzymes are called **substrates**.
- A substrate locks into an enzyme and a fast reaction occurs. The products then move away from the enzyme.

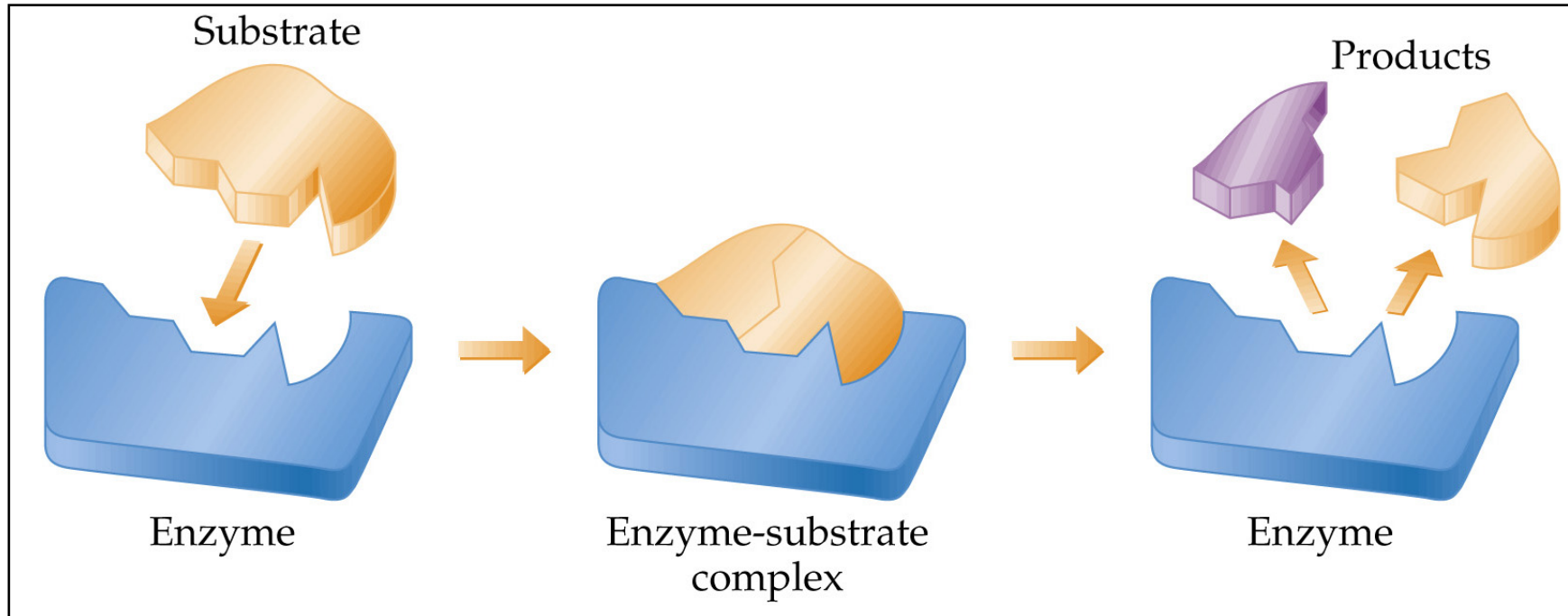
Enzyme Catalysts

- Only substrates that fit into the enzyme lock can be involved in the reaction.
 - If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (**enzyme inhibitors**).
 - Many poisons act by binding to the active site blocking the binding of substrates. The binding can also lead to changes in the enzyme.
 - Enzymes are extremely efficient catalysts.
 - The number of individual catalytic events occurring at an active site per unit time is called the *turnover number*.
 - Large turnover numbers correspond to very low E_a values.
- For enzymes, turnover numbers are very large $\approx 10^3$ to 10^7 /sec

Enzyme Catalysis



Enzyme Catalysts

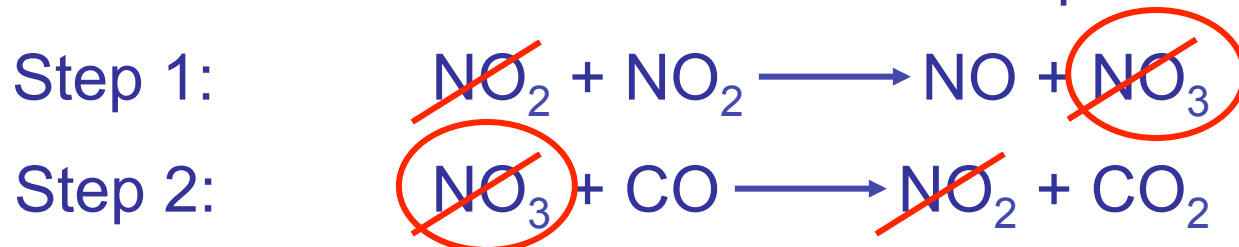


Another example...Nitrogen gas cannot be used in the soil for plants or animals. Nitrogen compounds, NH_3 , NO_2^- , and NO_3^- are used in the soil. The conversion between N_2 and NH_3 is a process with a high activation energy (the $\text{N}\equiv\text{N}$ triple bond needs to be broken). Nitrogenase, an enzyme in bacteria that lives in root nodules of legumes such as clover and alfalfa, catalyses the reduction of nitrogen to ammonia. It lowers the E_a , and the reaction proceeds.

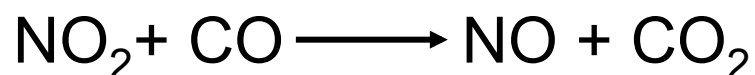
Other Examples of Catalysts



The experimental rate law for the reaction between NO_2 and CO to produce NO and CO_2 is $\text{rate} = k[\text{NO}_2]^2$. The reaction is believed to occur via two steps:



What is the equation for the overall reaction?



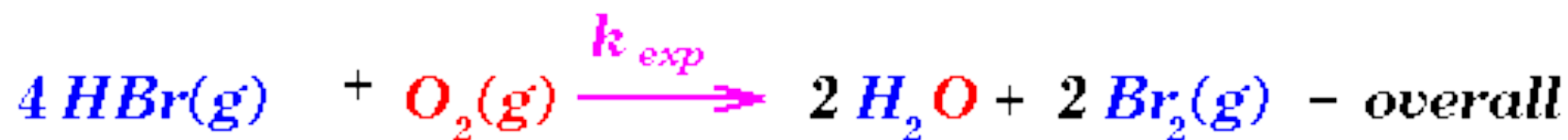
What is the intermediate? Catalyst?



What can you say about the relative rates of steps 1 and 2?

$\text{rate} = k[\text{NO}_2]^2$ is the rate law for step 1 so
step 1 must be slower than step 2

Proposed Mechanism:



Write the rate law for this reaction.

$$\text{Rate} = k [\text{HBr}] [\text{O}_2]$$

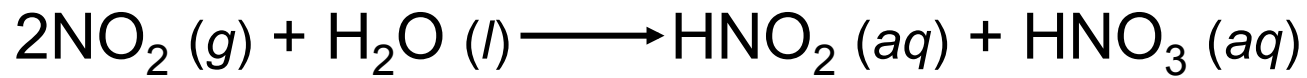
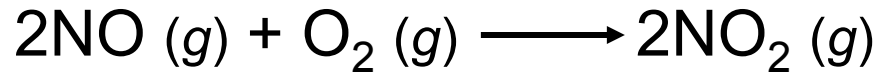
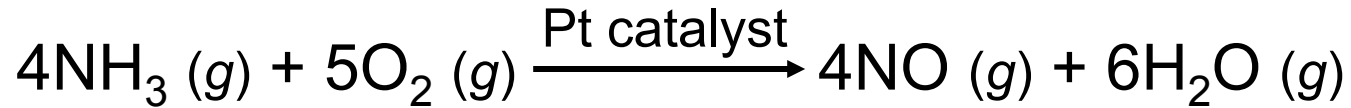
List all intermediates in this reaction.

HOBr, HOBr

List all catalysts in this reaction.

None

Ostwald Process



Pt-Rh catalysts used
in Ostwald process



Hot Pt wire
over NH₃ solution

Catalytic Converters

