Chemical Kinetics

Lecture notes edited by John Reif from PPT lectures by:

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Slides revised by Xin Song for Spring 2020 Term

What are Chemical Kinetics?

Chemical Kinetics

Kinetics – how fast does a reaction proceed?

Thermodynamics – does a reaction take place?

Reaction speed: 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

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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).

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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 temporature.
Mechanisms	Link between rate and molecular scale processes.

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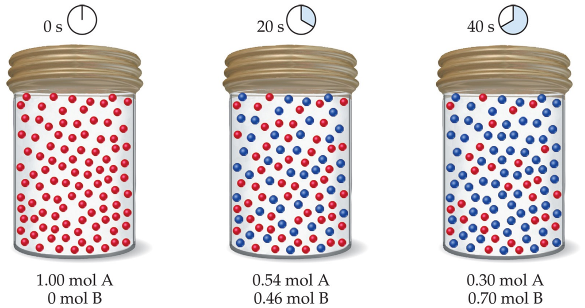
Reaction Rates

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**.

Notation for Stoichiometry:

[A] = concentration of reactant A

[B] = concentration of reactant B

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Reaction Rate

- For the reaction **A** → **B** there are two ways of **measuring rate**:

  (1) the speed at which the **reactants disappear**

  (2) the speed at which the **products appear**

- Reversible reactions: as products accumulates, 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.
- A general way of measuring the rate of the reaction is in terms of change in concentration per unit time…

Instantaneous rate = $\Delta[A]/\Delta t$ limits to $d[A]/dt$

Most Common Units… Rate = M/s

Where **Molarity (M)** = moles/Liter

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Chemical Kinetics

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

$$A \longrightarrow B$$

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

$\Delta[A]$ = 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, Δ[A] is negative.

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Reaction Rates and Stoichiometry

- To generalize, for the reaction

$$aA + bB \longrightarrow cC + dD$$

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

Reactants (decrease) Products (increase)

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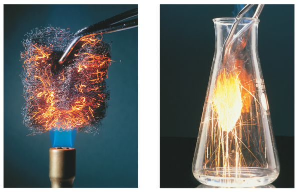
Factors Affecting Reaction Rate Constants

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 (in a particular orientation) 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**
   - More area for reactants to be in contact
5. **Pressure of gaseous reactants or products**
   - Increased number of collisions



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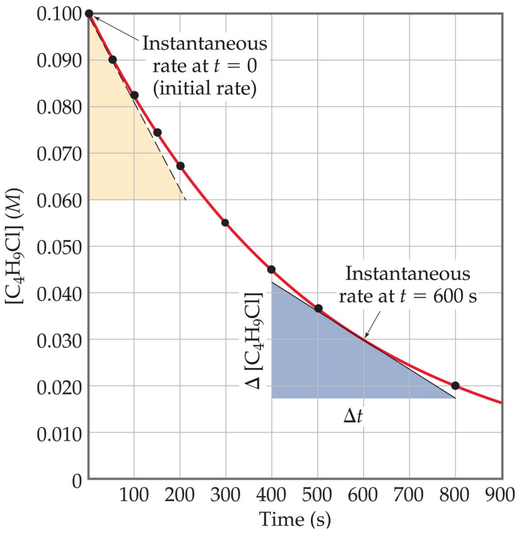
Reaction Rate Examples

An Example of Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$

- 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.

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

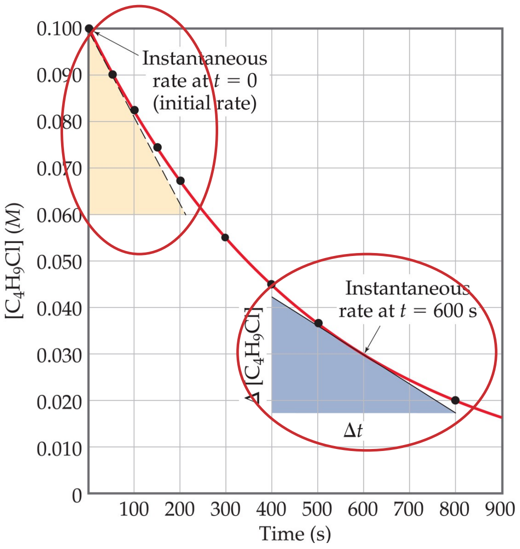


An Example of Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$

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

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



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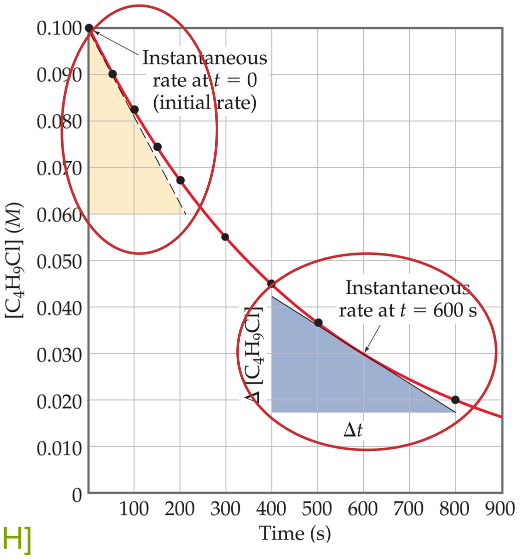
An Example of Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.
- Thus, the rate of *disappearance* of C_4H_9Cl is the same as the rate of *appearance* of C_4H_9OH.



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{D[C_4H_9OH]}{\Delta t}$$

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Reaction Rate Laws

Concentration and Rate

Each reaction has its own equation that expresses its **rate as a function of the concentrations** of the involved species (e.g., reactants, products, catalysts).

This is called its **Rate Law**

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.
- For reactions follow ***simple rate laws***:

$$v = k\,[A]^m\,[B]^n\ldots$$

  - [A], [B]: reactant concentrations
  - The exponents *m* and *n*: **reaction order** (w.r.t. specific reactant)
  - The constant *k*: **rate constant**
  - The **overall reaction order** is the sum of the reaction orders:

$$m + n$$

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Determination of Rate Laws

- Rate laws, rate constants, and orders are **determined *experimentally***.

- The order of a reactant is **NOT** generally related to its stoichiometric coefficient in a balanced chemical equation.

$$F_2\,(g) + \boxed{2}ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$v = k\,[F_2][ClO_2]^{\boxed{1}}$$

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Expression of Rate Laws

Reactions with **simple rate laws**:

$H_2 + I_2 \rightarrow 2HI$	$\nu = k\,[H_2][I_2]$.
$3ClO^- \rightarrow ClO_3^- + 2Cl^-$	$\nu = k\,[ClO^-]^2$

Reactions with **complex rate laws***:

$H_2 + Br_2 \rightarrow 2HBr$ $\qquad$ $\nu = \dfrac{[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$

* imply multi-step reactions (sequence of elementary steps)

$Br_2 \rightarrow Br + Br$
$Br + H_2 \rightarrow H + HBr$
$H + Br_2 \rightarrow Br + HBr$
$Br + Br \rightarrow Br_2$

however, the overall rate cannot involve intermediate species

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Elementary reactions

Always follow simple rate laws

Unimolecular decomposition	$A \rightarrow B$	$\nu = k\,[A]$
Bimolecular reaction	$A + B \rightarrow P$	$\nu = k\,[A][B]$
	$A + A \rightarrow P$	$\nu = k\,[A][A] = k\,[A]^{2}$

Reactant **order** reflects **molecularity** (# of molecules involved in reaction)

More on this later…

Simple Example Reactions

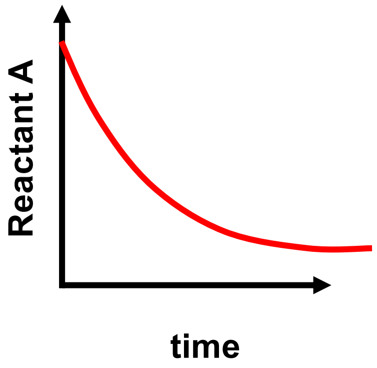
Example chemical reaction that models degradation of molecule A

$$A \xrightarrow{\gamma} \Phi$$

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

Rate of change of A

Degradation constant



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Example chemical reaction that models generation (from D) and degradation of molecule A

$$D \xrightarrow{k} A \xrightarrow{\gamma} \Phi$$

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

Rate of change of A

Production constant

Degradation constant

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

$$A + B \xrightarrow{k} C$$

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

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

$$nA + mB \xrightarrow{k} C$$

$$\frac{1}{n}\frac{d[A]}{dt} = -k[A]^{n}[B]^{m}$$

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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.
    - - extremely rare.

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Order of Reactions

Reaction	Order	Differential form	Integrated form
A → P	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
A → P	first	$\frac{d[A]}{dt} = -k\,[A]$	$\ln[A] = \ln[A]_0 - kt$
A + A → P	second	$\frac{1\,d[A]}{2\,dt} = -k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
A + B → P	second	$\frac{d[A]}{dt} = -k\,[A][B]$	$kt = \frac{1}{[B]_0-[A]_0}\ln\frac{[B]_0[A]}{[A]_0[B]}$

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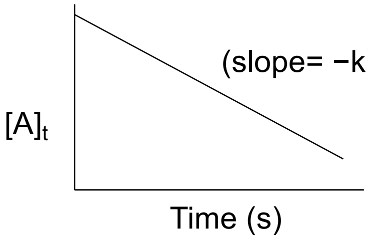
Zero-Order Processes

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

reaction rate $= -\frac{\Delta[A]_t}{\Delta t} = k$ **(constant)**

So… $[A]_t = -kt + [A]_0$

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



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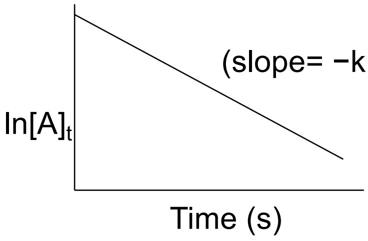
First-Order Processes

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
$[A]_o$ = initial concentration of A

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



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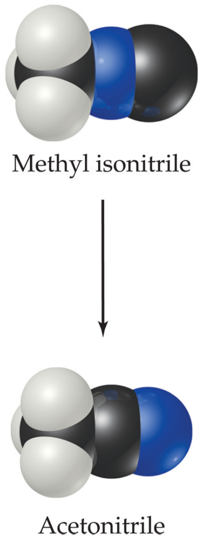
Example: First-Order Processes



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

$$CH_3NC \longrightarrow CH_3CN$$

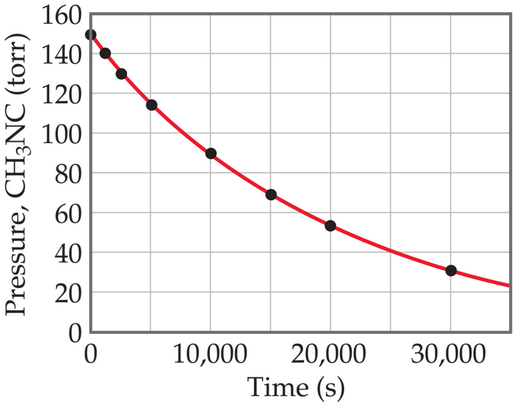
How do we know this is a first order reaction?

First-Order Processes

$$CH_3NC \longrightarrow CH_3CN$$

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

Does rate=k[CH_3NC] for all time intervals?



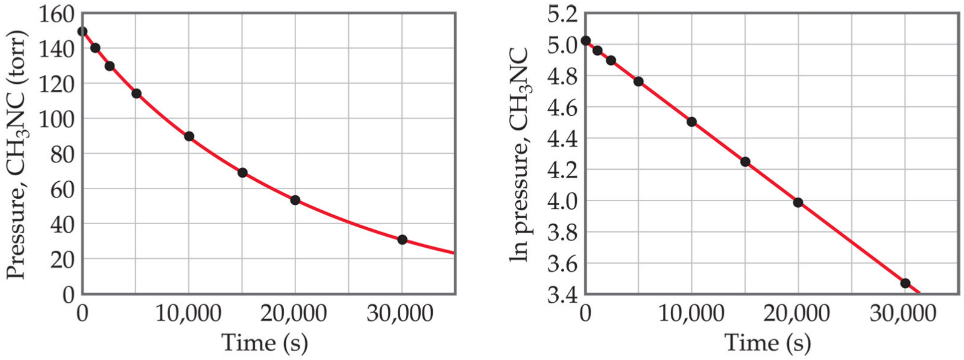
First-Order Processes

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

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



$$[A]_t = [A]_0\,e^{-kt} \qquad ln\,[A]_t = -kt + ln\,[A]_0$$

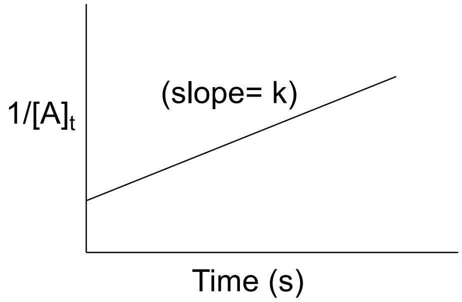
- When **ln[A]** is plotted as a function of time, a straight line results.
  - The process is first-order.
  - k is the negative slope: $5.1 \times 10^{-5}\ s^{-1}$.

Second-Order Processes

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
$[A]_o$ = initial concentration of A

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



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Half Life

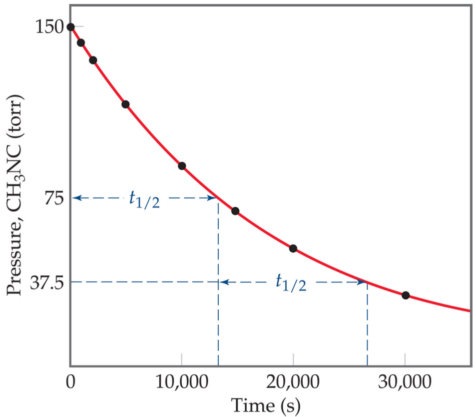
Half-Life

- Half-life is the time taken for the concentration of a reactant to drop to half its original value.
- Substitute into integrated rate laws: $t_{½}$ is the time taken for [A] to reach ½$[A]_0$

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

First order reaction $t_{1/2} = \frac{\ln 2}{k}$

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



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

Reaction Kinetics (Vallance)

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Half-Life - 1st order

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

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

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

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

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

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

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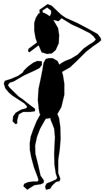
Half-Life - 1st order



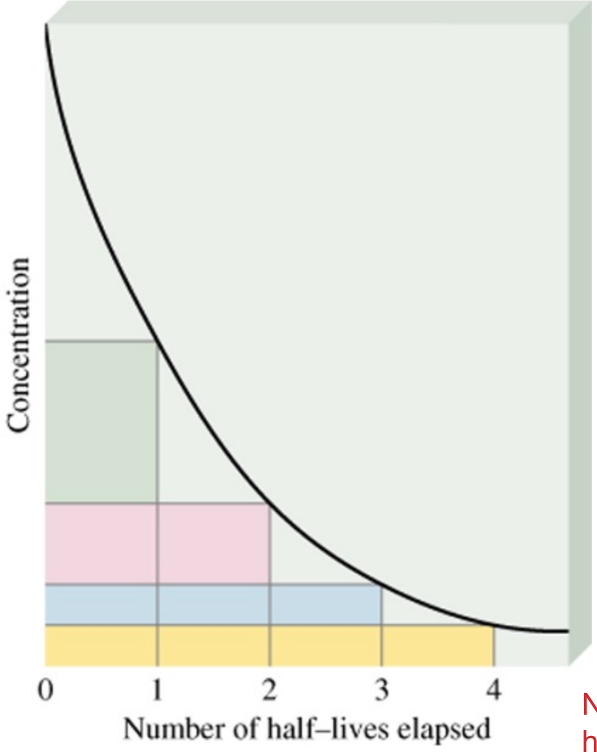
What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4}\ s^{-1}$?

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

How do you know decomposition is first order?

hint: units of *k* (s^{-1})

Half-Life - 1st order



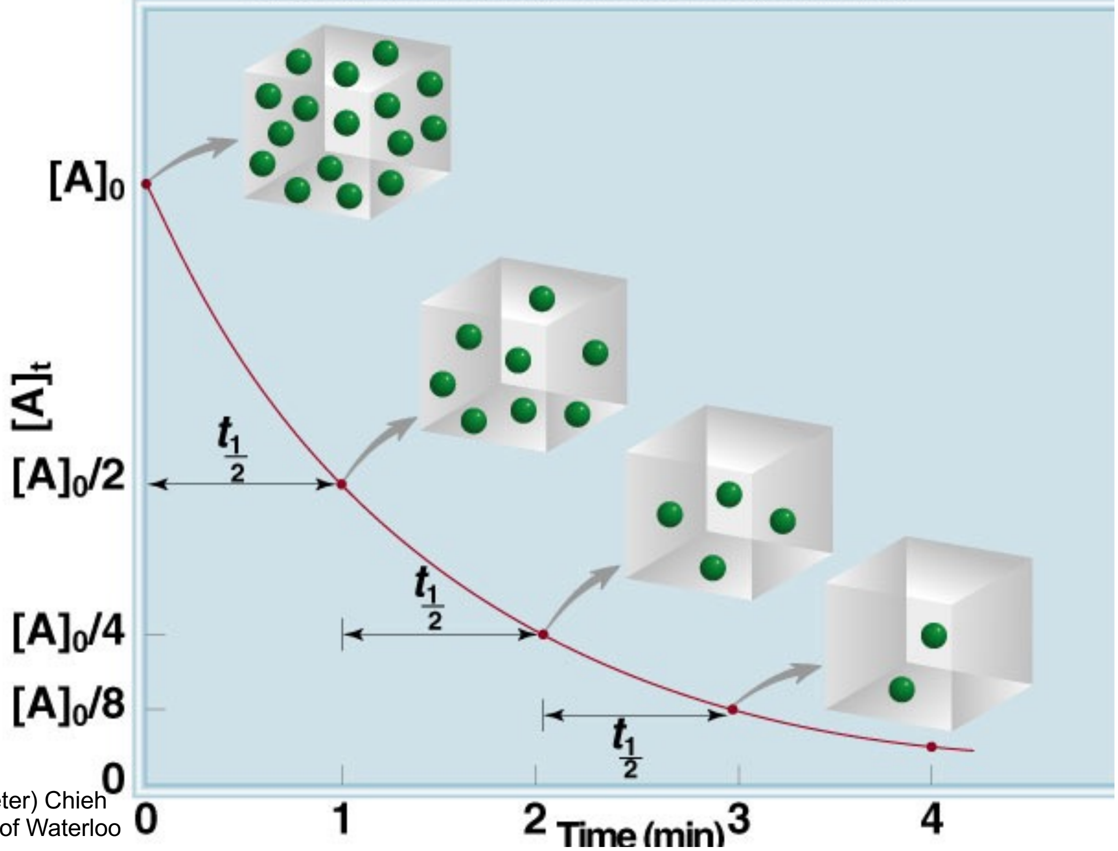
First-order reaction

$A \longrightarrow$ product

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

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

Half-Life - 1st order



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Half-Life - 2nd order

For a **second-order** process, set $[A]_t = 0.5\,[A]_0$ in 2nd order equation: $\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$

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

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

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

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

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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	$[A] - [A]_0 = -kt$	$t_{½} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\text{In}[A] - \text{In}[A]_0 = -kt$	$t_{½} = \frac{\text{Ln } 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{½} = \frac{1}{k[A]_0}$

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Summary of Kinetics

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

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Summary of Kinetics

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

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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.

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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***.

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

N_2O_2 is detected during the reaction!

$$\begin{array}{lrcl} \text{Elementary step:} & NO + NO & \longrightarrow & \cancel{N_2O_2} \\ +\ \text{Elementary step:} & \cancel{N_2O_2} + O_2 & \longrightarrow & 2NO_2 \\ \hline \text{Overall reaction:} & 2NO + O_2 & \longrightarrow & 2NO_2 \end{array}$$

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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.

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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.)

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Rate Laws of Elementary Steps

- Since this process occurs in one single step, the stoichiometry **can** be used to determine the rate law!

- **<u>Law of Mass Action</u>**: The rate of a **simple (one step) reaction** is directly proportional to the concentration of the reacting substances.

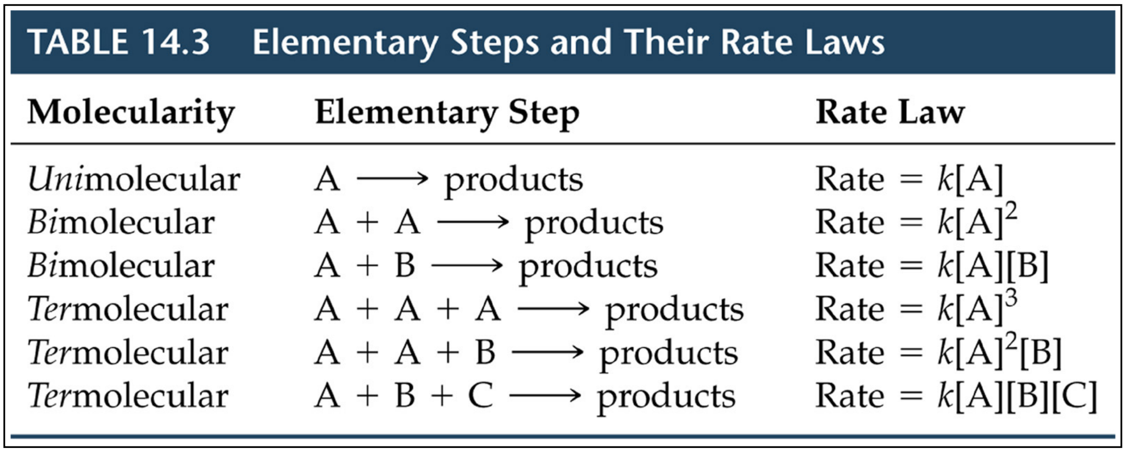

TABLE 14.3 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

- Notice that the coefficients become the exponents.

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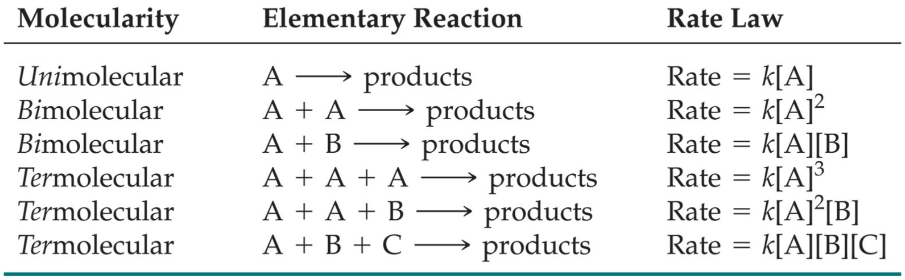
Reaction Mechanisms



Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ 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.

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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.

$$
\begin{array}{lrcl}
\text{Elementary step:} & NO + NO & \longrightarrow & \enclose{circle}{N_2O_2} \\
+\ \text{Elementary step:} & \enclose{circle}{N_2O_2} + O_2 & \longrightarrow & 2NO_2 \\
\hline
\text{Overall reaction:} & 2NO + O_2 & \longrightarrow & 2NO_2
\end{array}
$$

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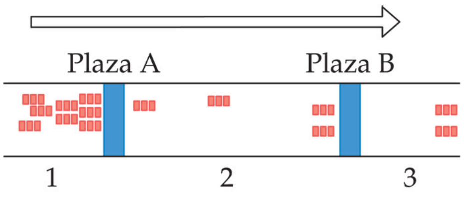
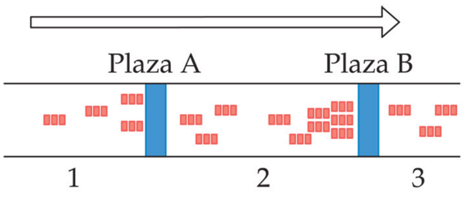
Multistep Mechanisms

- 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.



Cars slowed at plaza A



Cars slowed at plaza B

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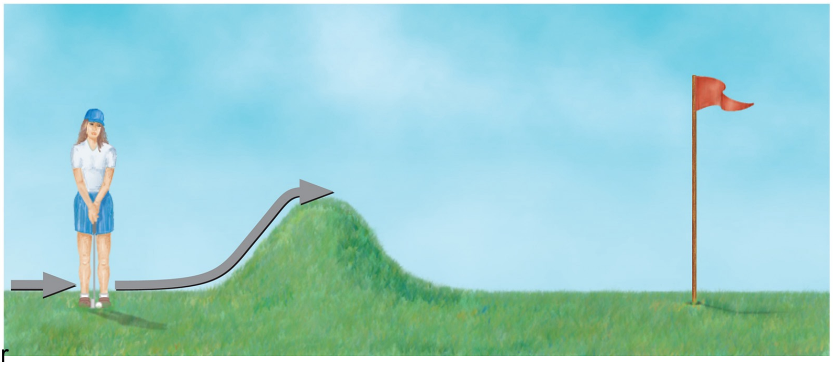
Activation Energy

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.



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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.

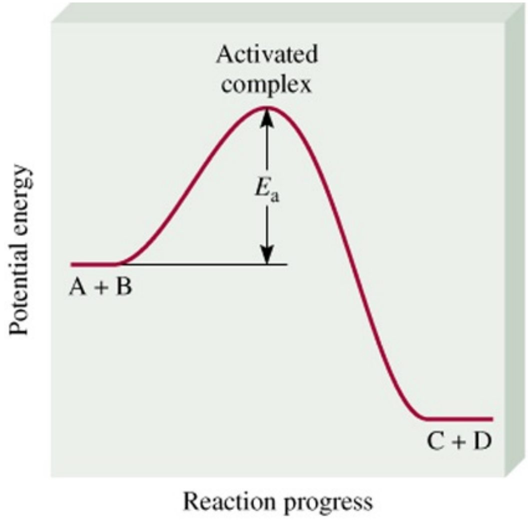
Next we will look at an example of E_a.

Activation Energy

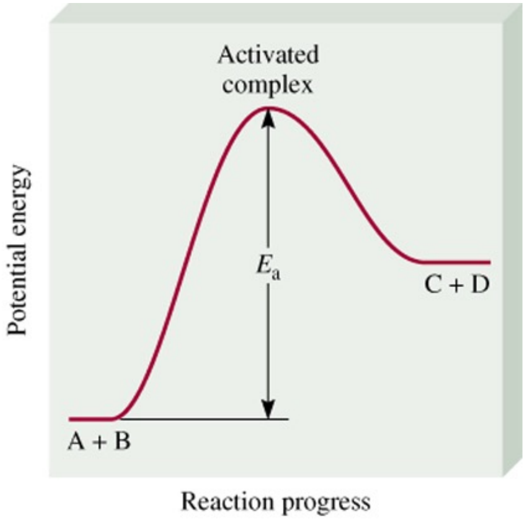
- The **change in energy** ΔE for the reaction is the difference in energy between CH_3NC (reactant) and CH_3CN (product).
- The **activation energy E_a** is the difference in energy between reactants, CH_3NC, and the transition state.
- The rate depends on E_a. If the "hill" is taller, the reaction rate is slower. If the "hill" is shorter the rate is faster.
- Notice that if a forward reaction is exothermic… ($CH_3NC \rightarrow CH_3CN$), then the reverse reaction is endothermic… ($CH_3CN \rightarrow CH_3NC$).
- 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.

$A + B \longrightarrow C + D$

Exothermic Reaction



Endothermic Reaction



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

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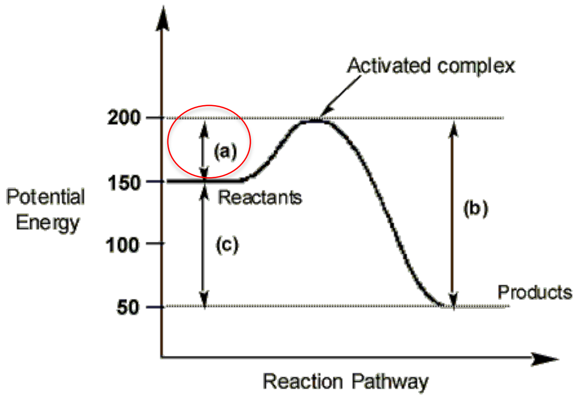
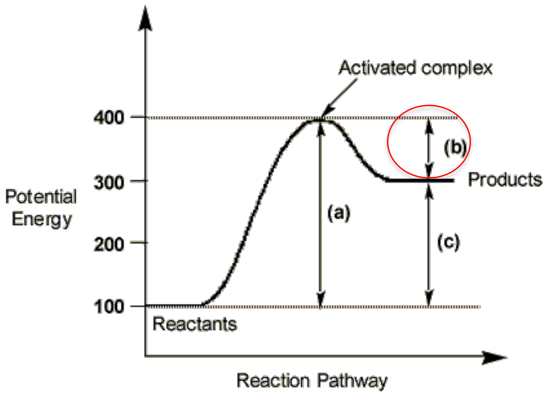
Energy Diagrams



Exothermic



Endothermic

(a) Activation energy (Ea) for the forward reaction	50 kJ/mol	300 kJ/mol
(b) Activation energy (Ea) for the reverse reaction	150 kJ/mol	100 kJ/mol
(c) Delta H	-100 kJ/mol	+200 kJ/mol

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Arrhenius Equation

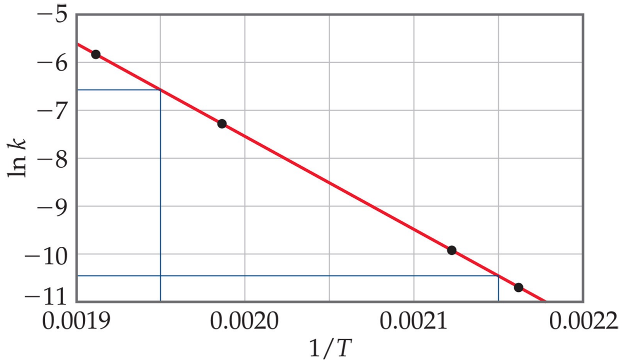
Arrhenius Equation

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

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

$$y \quad = \quad mx + b$$

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

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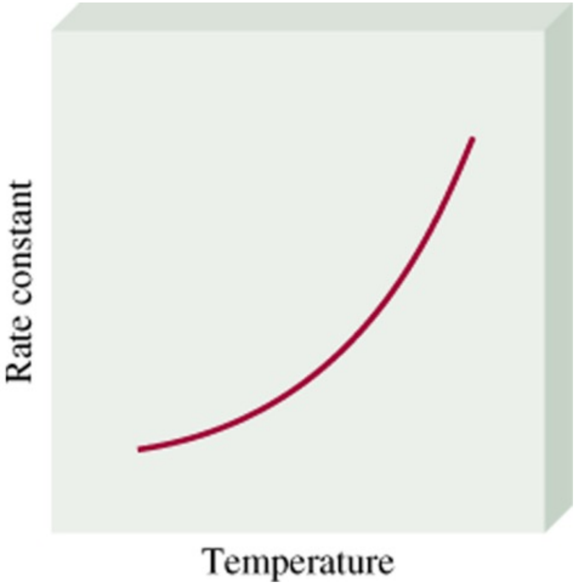
Temperature Dependence of the Rate Constant



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

(Arrhenius equation)

k is the rate constant

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the Kelvin temperature

A is the frequency factor

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

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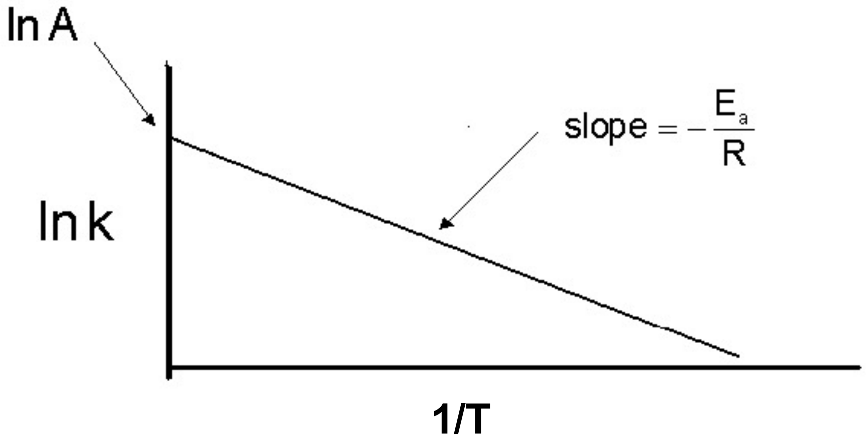
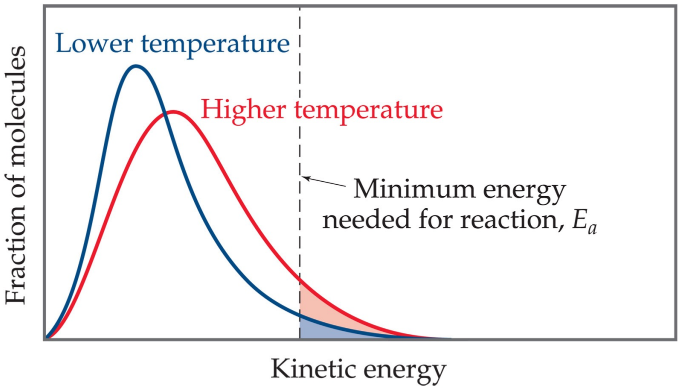
Plot of Arrhenius Equation



Maxwell–Boltzmann Distributions

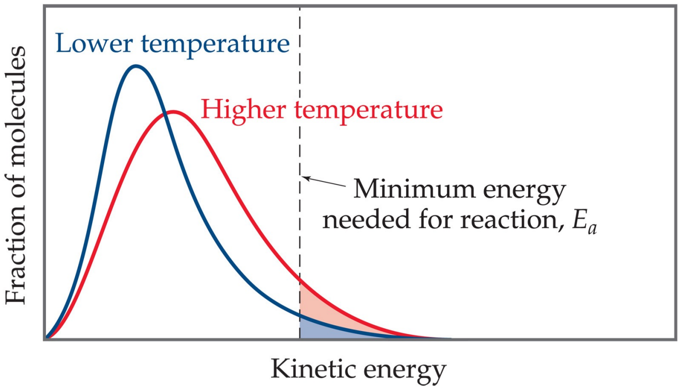
Maxwell–Boltzmann Distributions



- 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**.

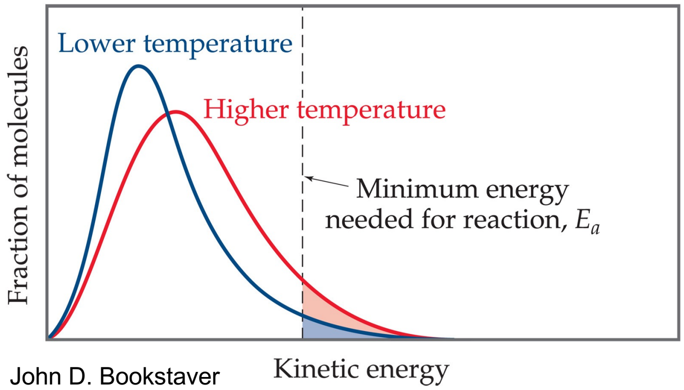
Maxwell–Boltzmann Distributions



- 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.



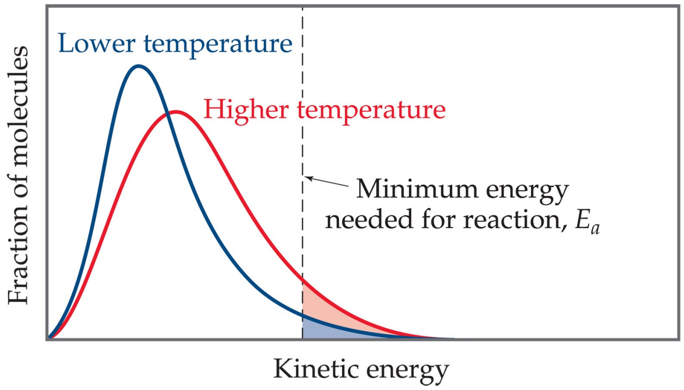
- As a result, the **reaction rate increases.**

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression:

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

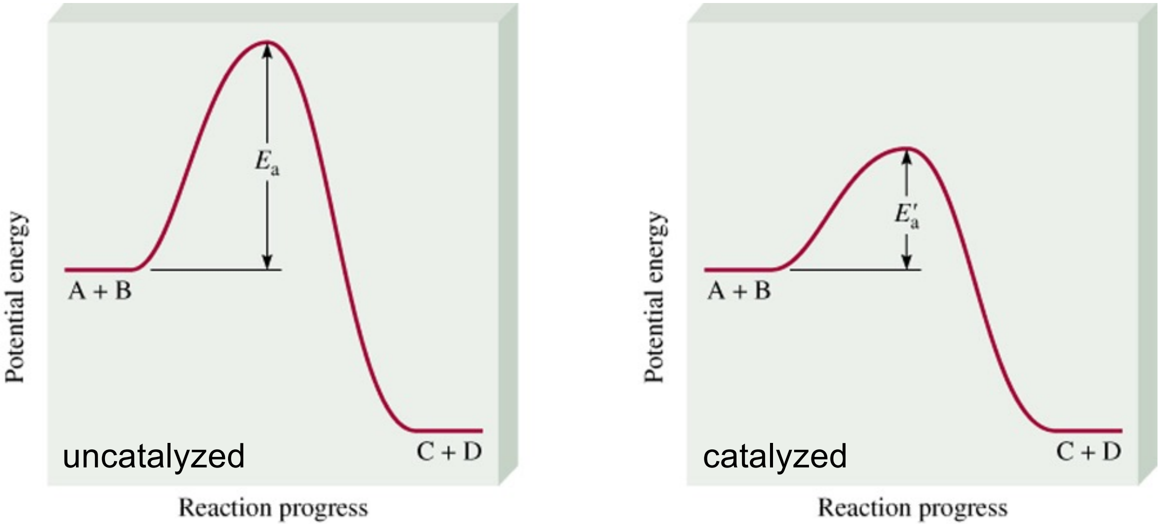
where *R* is the gas constant and *T* is the temperature in Kelvin.



Catalysts

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

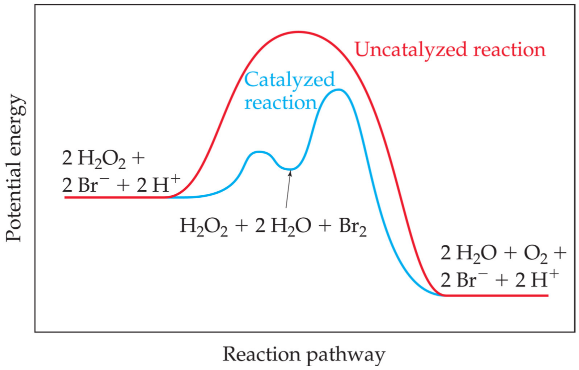
E_a ↓ k ↑



$$\mathbf{rate_{catalyzed} > rate_{uncatalyzed}}$$

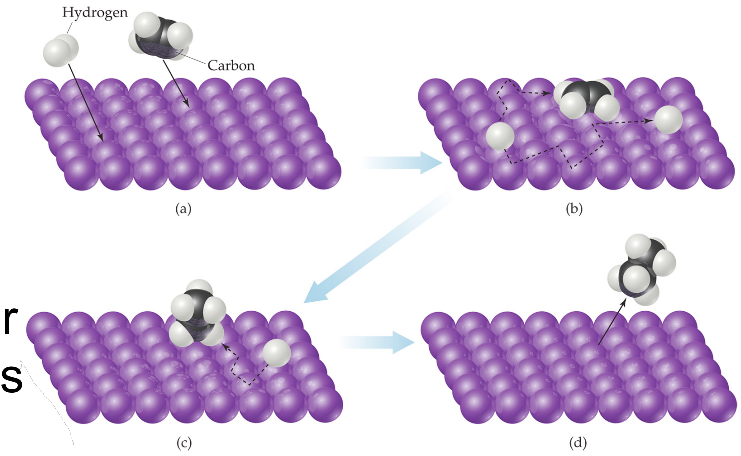
Catalysts

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



Catalysts

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



Catalysts

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:

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

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

$$\boxed{\cancel{2Br^-}_{(aq)}} + H_2O_{2(aq)} + \cancel{2H^+}_{(aq)} \rightarrow \cancel{Br}_{2(aq)} + 2H_2O_{(l)}$$

$$\cancel{Br}_{2(aq)} + H_2O_{2(aq)} \rightarrow \boxed{\cancel{2Br^-}_{(aq)}} + \cancel{2H^+}_{(aq)} + O_{2(g)}$$

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

The net reaction is still…$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

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^-, $Br_{2(aq)}$ 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.

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: $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$

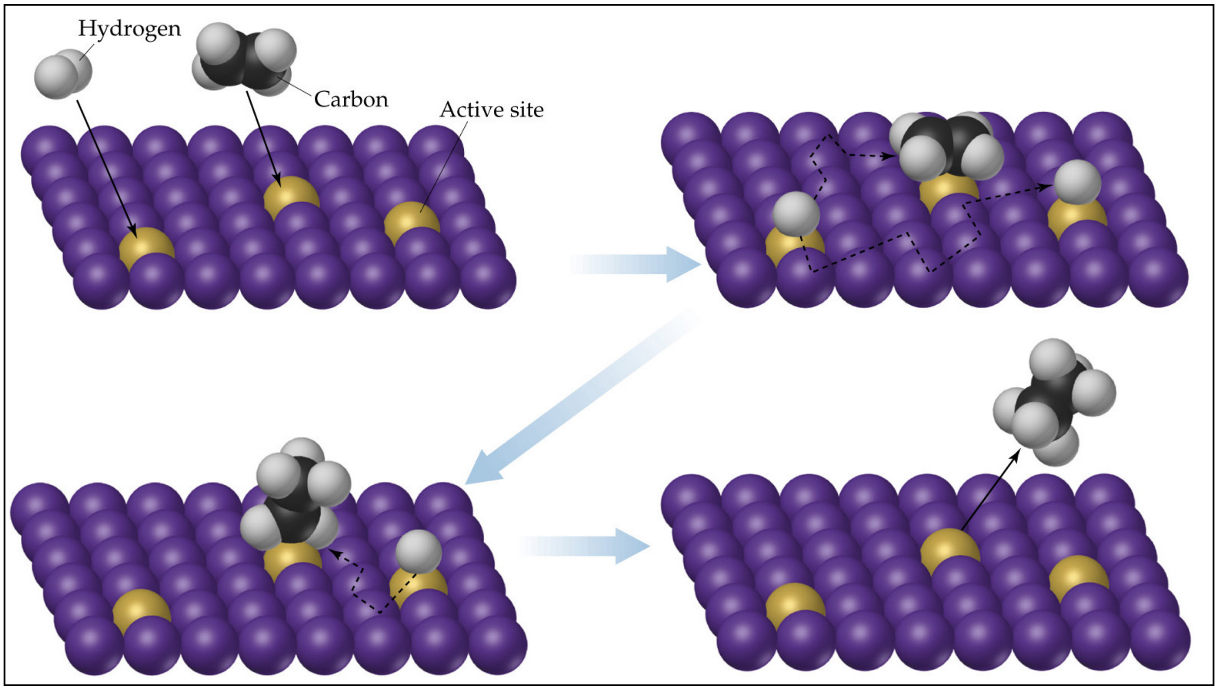
- In the presence of a metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.

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 C_2H_4 molecule on the surface.
- Third, when an H atom collides with a C_2H_4 molecule on the surface, the C−C π-bond breaks and a C–H σ-bond forms.
- Lastly, When C_2H_6 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



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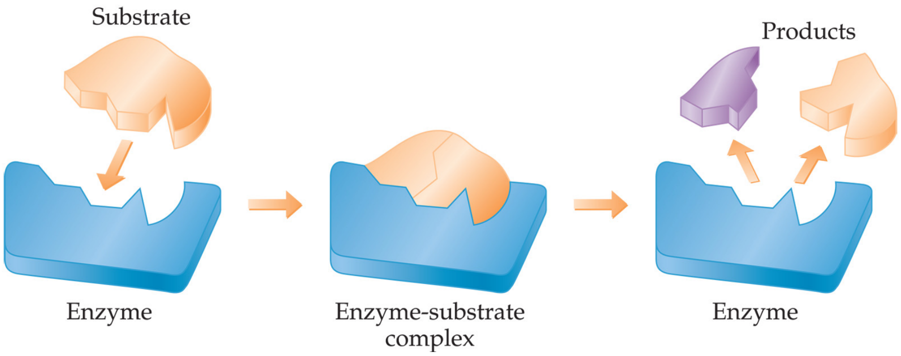
Examples of Catalysts: Enzymes

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.



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Enzyme Catalysts

- Enzymes are biological catalysts. There may be as many as 30,000 enzymes in the human body. (e.g., 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.

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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

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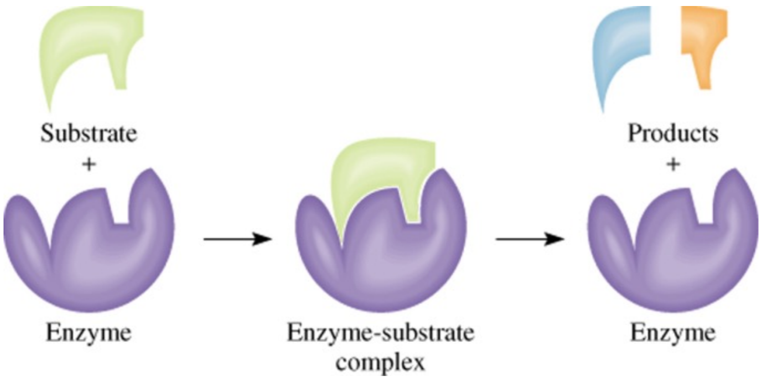
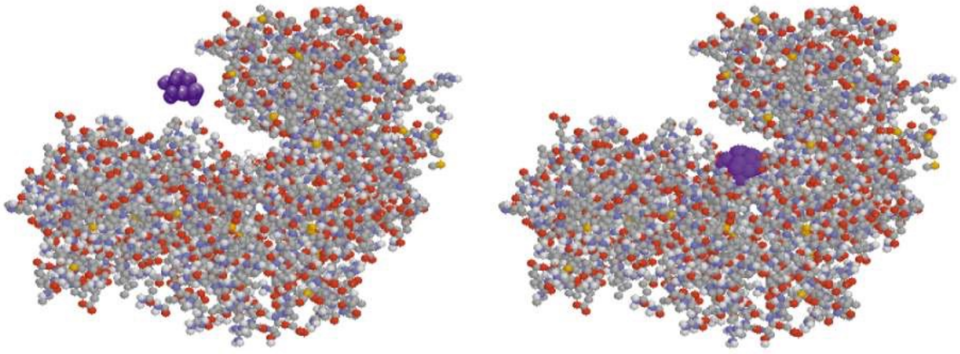
Enzyme Catalysis





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