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Chapter 13

Chemical Kinetics

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Chemical Kinetics 1

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).

$$A \rightarrow B$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \Delta[A] = \text{change in concentration of A over time period } \Delta t$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t} \quad \Delta[B] = \text{change in concentration of B over time period } \Delta t$$

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

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Chemical Kinetics 2

$A \rightarrow B$

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

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

Number of molecules

t (s)

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Monitoring Kinetics

$\text{Br}_2^{\text{red-brown}}(aq) + \text{HCOOH}(aq) \rightarrow 2\text{Br}^-(aq) + 2\text{H}^+(aq) + \text{CO}_2(g)$

$\Delta[\text{Br}_2] \propto \Delta \text{Absorption}$

$t_1 < t_2 < t_3$

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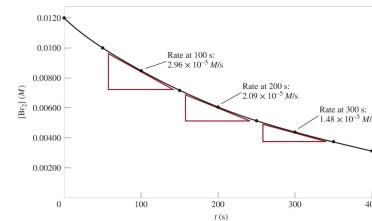
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Kinetic Rates 1



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



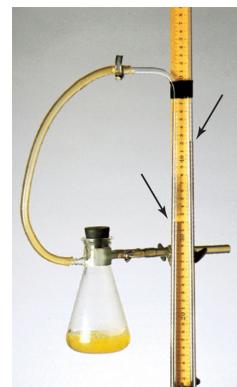
$$\text{average rate} = -\frac{\Delta[\text{Br}_2]}{\Delta t} = -\frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

instantaneous rate = rate for specific instance in time

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Kinetic Rates 2



$$PV = nRT$$

$$P = \frac{n}{V} RT = [\text{O}_2]\text{RT}$$

$$[\text{O}_2] = \frac{1}{RT} P$$

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$$

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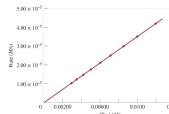
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Rates of Reaction

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 = $\frac{\text{rate}}{[\text{Br}_2]} (\text{s}^{-1})$
00	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

rate $\propto [\text{Br}_2]$
 rate = $k[\text{Br}_2]$
 $k = \frac{\text{rate}}{[\text{Br}_2]} = \text{rate constant}$
 $= 3.50 \times 10^{-3} \text{ s}^{-1}$



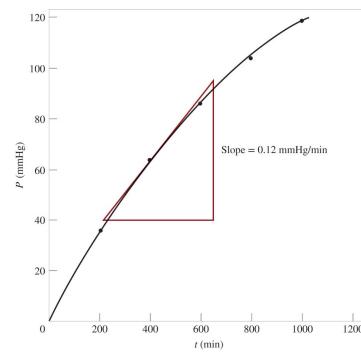
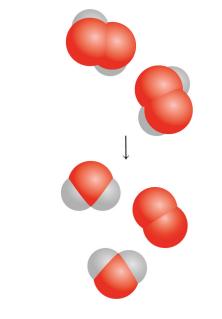
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Decomposition of H₂O₂

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Reaction Rates and Stoichiometry



Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

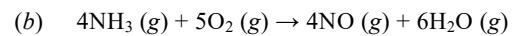
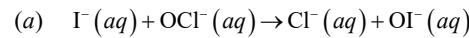
$$aA + bB \rightarrow cC + dD$$

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

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Example 13.1

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:


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Example 13.1₂

Strategy

To express the rate of the reaction in terms of the change in concentration of a reactant or product with time, we need to use the proper sign (minus or plus) and the reciprocal of the stoichiometric coefficient.

Solution

(a) Because each of the stoichiometric coefficients equals 1,

$$\text{rate} = -\frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{OCl}^-]}{\Delta t} = \frac{\Delta[\text{Cl}^-]}{\Delta t} = \frac{\Delta[\text{OI}^-]}{\Delta t}$$

(b) Here the coefficients are 4, 5, 4, and 6, so

$$\text{rate} = -\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

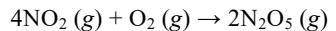
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Example 13.2₁

Consider the reaction



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s.

- a) At what rate is N₂O₅ being formed?
- b) At what rate is NO₂ reacting?

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Example 13.2₂

Strategy

To calculate the rate of formation of N₂O₅ and disappearance of NO₂, we need to express the rate of the reaction in terms of the stoichiometric coefficients as in Example 13.1:

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

We are given

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -0.024 \text{ M/s}$$

where the minus sign shows that the concentration of O₂ is decreasing with time.

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Example 13.2₃

Solution

- a) From the preceding rate expression we have

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Therefore

$$\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -2(-0.024 \text{ M/s}) = 0.048 \text{ M/s}$$

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Example 13.2 ₄

b) Here we have

$$-\frac{1}{4} \frac{\Delta [\text{NO}_2]}{\Delta t} = -\frac{\Delta [\text{O}_2]}{\Delta t}$$

So

$$\frac{\Delta [\text{NO}_2]}{\Delta t} = 4(-0.024 \text{ M/s}) = -0.096 \text{ M/s}$$

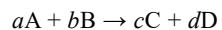
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The Rate Law ₁

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.



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

Reaction is **x^{th} order** in A

Reaction is **y^{th} order** in B

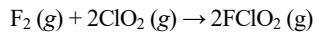
Reaction is **$(x+y)^{\text{th}}$ order overall**

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The Rate Law₂



$$\text{rate} = k [F_2]^x [ClO_2]^y$$

Table 13.2 Rate data for reaction between F₂ and ClO₂

	[F ₂] (M)	[ClO ₂] (M)	Initial Rates (M/s)
	1.010	0.010	1.2 × 10 ⁻³
Double [F ₂] with [ClO ₂] constant	2.010	0.040	4.8 × 10 ⁻³
Rate Doubles	3.020	0.10	2.4 × 10 ⁻³

x = 1

Quadruple [ClO₂] with [F₂] constant

$$\text{rate} = k [F_2][ClO_2]$$

Rate Quadruples

y = 1

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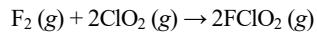
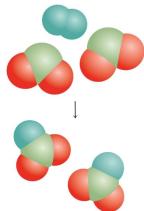
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Rate Laws

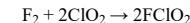
Rate laws are **always** determined experimentally.

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.



$$\text{rate} = k [F_2][ClO_2]$$

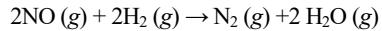


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Example 13.3 ₁

The reaction of nitric oxide with hydrogen at 1280°C is



From the following data collected at this temperature, determine

- a) the rate law
- b) the rate constant
- c) the rate of the reaction when $[\text{NO}] = 12.0 \times 10^{-3} \text{ M}$ and $[\text{H}_2] = 6.0 \times 10^{-3} \text{ M}$

Experiment	$[\text{NO}](\text{M})$	$[\text{H}_2](\text{M})$	Initial Rates(M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

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Example 13.3 ₂

Strategy

We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant.

We assume that the rate law takes the form

$$\text{rate} = k[\text{NO}]^x[\text{H}_2]^y$$

How do we use the data to determine x and y ?

Once the orders of the reactants are known, we can calculate k from any set of rate and concentrations.

Finally, the rate law enables us to calculate the rate at any concentrations of NO and H₂.

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Example 13.3₃

Solution

(a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H₂, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5} \text{ M/s}}{1.3 \times 10^{-5} \text{ M/s}} \approx 4 = \frac{k(10.0 \times 10^{-3} \text{ M})^x (2.0 \times 10^{-3} \text{ M})^y}{k(5.0 \times 10^{-3} \text{ M})^x (2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(10.0 \times 10^{-3} \text{ M})^x}{(5.0 \times 10^{-3} \text{ M})^x} = 2^x = 4$$

or x = 2, that is, the reaction is second order in NO.

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Example 13.3₄

Experiments 2 and 3 indicate that doubling [H₂] at constant [NO] doubles the rate. Here we write the ratio as

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5} \text{ M/s}}{5.0 \times 10^{-5} \text{ M/s}} = 2 = \frac{k(10.0 \times 10^{-3} \text{ M})^x (4.0 \times 10^{-3} \text{ M})^y}{k(10.0 \times 10^{-3} \text{ M})^x (2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(4.0 \times 10^{-3} \text{ M})^y}{(2.0 \times 10^{-3} \text{ M})^y} = 2^y = 2$$

or y = 1, that is, the reaction is first order in H₂. Hence the rate law is given by

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

which shows that it is a (2 + 1) or third-order reaction overall.

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Example 13.3 ₅

- b) The rate of constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

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

The data from experiment 2 give us

$$\begin{aligned} k &= \frac{5.0 \times 10^{-5} \text{ M/s}}{(10.0 \times 10^{-3} \text{ M})^2 (2.0 \times 10^{-3} \text{ M})} \\ &= 2.5 \times 10^2 / \text{M}^2 \cdot \text{s} \end{aligned}$$

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Example 13.3 ₆

- c) Using the known rate constant and concentrations of NO and H₂, we write

$$\begin{aligned} \text{rate} &= (2.5 \times 10^2 / \text{M}^2 \cdot \text{s})(12.0 \times 10^{-3} \text{ M})^2 (6.0 \times 10^{-3} \text{ M}) \\ &= 2.2 \times 10^{-4} \text{ M/s} \end{aligned}$$

Comment

Note that the reaction is first order in H₂, whereas the stoichiometric coefficient for H₂ in the balanced equation is 2. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

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First-Order Reactions

$A \rightarrow \text{product}$

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

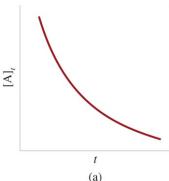
$$k = \frac{\text{rate}}{[A]} = \frac{M/\text{s}}{M} = 1/\text{s or s}^{-1}$$

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

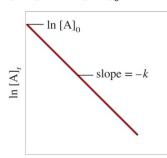
$[A]$ is the concentration of A at any time t
 $[A]_0$ is the concentration of A at time $t = 0$

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

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



(a)



(b)

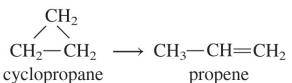
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Example 13.4

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C .



- If the initial concentration of cyclopropane was 0.25 M , what is the concentration after 8.8 min ?
- How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M ?
- How long (in minutes) will it take to convert 74 percent of the starting material?

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Example 13.4₂

Strategy

The relationship between the concentrations of a reactant at different times in a first-order reaction is given by Equation (13.3) or (13.4).

In (a) we are given $[A]_0 = 0.25 M$ and asked for $[A]$ after 8.8 min.

In (b) we are asked to calculate the time it takes for cyclopropane to decrease in concentration from 0.25 M to 0.15 M.

No concentration values are given for (c). However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be (100% – 74%), or 26%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]/[A]_0 = 26\%/100\%$, or 0.26/1.00.

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Example 13.4₃

Solution

(a) In applying Equation (13.4), we note that because k is given in units of s^{-1} , we must first convert 8.8 min to seconds:

$$8.8 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 528 \text{ s}$$

We write

$$\begin{aligned}\ln[A] &= -kt + \ln[A]_0 \\ &= -(6.7 \times 10^{-4} \text{ s}^{-1})(528 \text{ s}) + \ln(0.25) \\ &= -1.74\end{aligned}$$

Hence,

$$[A] = e^{-1.74} = 0.18 M$$

Note that in the $\ln[A]_0$ term, $[A]_0$ is expressed as a dimensionless quantity (0.25) because we cannot take the logarithm of units.

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Example 13.4 ₄

b) Using Equation (13.3),

$$\ln \frac{0.15 M}{0.25 M} = - (6.7 \times 10^{-4} \text{ s}^{-1}) t$$

$$t = 7.6 \times 10^2 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}}$$

$$= 13 \text{ min}$$

c) From Equation (13.3),

$$\ln \frac{0.26}{1.00} = - (6.7 \times 10^{-4} \text{ s}^{-1}) t$$

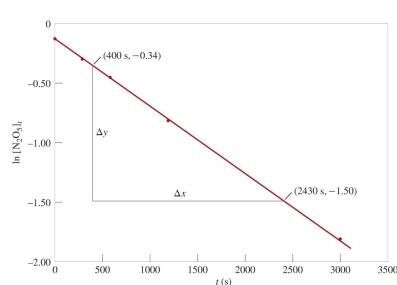
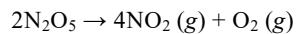
$$t = 2.0 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 33 \text{ min}$$

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Graphical Determination of k



$$\text{slope } (m) = \frac{\Delta y}{\Delta x}$$

$$= \frac{-1.50 - (-0.34)}{(2430 - 400) \text{ s}}$$

$$= -5.7 \times 10^{-4} \text{ s}^{-1}$$

$$m = -k$$

$$k = 5.7 \times 10^{-4} \text{ s}^{-1}$$

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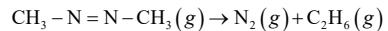
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Example 13.5₁

The rate of decomposition of azomethane ($\text{C}_2\text{H}_6\text{N}_2$) is studied by monitoring the partial pressure of the reactant as a function of time:



The data obtained at 300° C are shown in the following table:

Time (s)	Partial pressure of azomethane (mmHg)
0	284
100	220
150	193
200	170
250	150
300	132

Are these values consistent with first-order kinetics? If so, determine the rate constant.

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Example 13.5₂

Strategy

To test for first-order kinetics, we consider the integrated first-order rate law that has a linear form, which is Equation (13.4)

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

If the reaction is first order, then a plot of $\ln [A]$, versus t (y versus x) will produce a straight line with a slope equal to $-k$. Note that the partial pressure of azomethane at any time is directly proportional to its concentration in moles per liter ($PV = nRT$, so $P \propto n/V$).

Therefore, we substitute partial pressure for concentration [Equation (13.5)]:

$$\ln P_t = -kt + \ln P_0$$

where P_0 and P_t are the partial pressures of azomethane at $t = 0$ and $t = t$, respectively.

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Example 13.5₃

Solution

First we construct the following table of t versus $\ln P_t$.

t (s)	$\ln P_t$
0	5.649
100	5.394
150	5.263
200	5.136
250	5.011
300	4.883

Figure 13.11, which is based on the data given in the table, shows that a plot of $\ln P_t$ versus t yields a straight line, so the reaction is indeed first order. The slope of the line is given by

$$\text{slope} = \frac{5.05 - 5.56}{(233 - 33) \text{ s}} = -2.55 \times 10^{-3} \text{ s}^{-1}$$

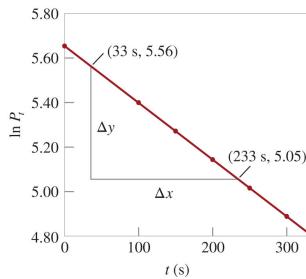
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Example 13.5₄

According to Equation (13.4), the slope is equal to $-k$, so $k = 2.55 \times 10^{-3} \text{ s}^{-1}$.



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First-Order Reactions ₂

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

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

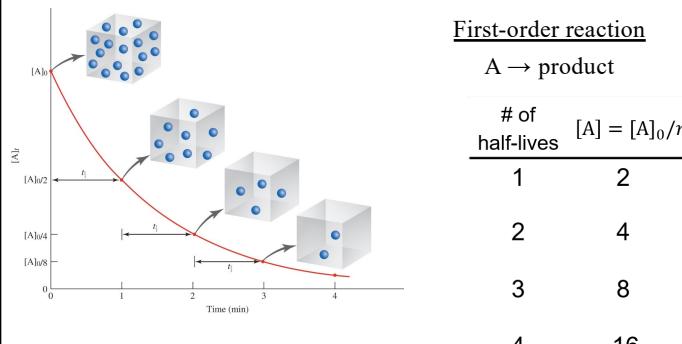
$$t_{\frac{1}{2}} = \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

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First-Order Reactions ₃



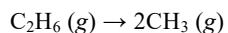
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Example 13.6₁

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4} s^{-1}$ at $700^\circ C$:



Calculate the half-life of the reaction in minutes.

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Example 13.6₂

Strategy

To calculate the half-life of a first-order reaction, we use Equation (13.6). A conversion is needed to express the half-life in minutes.

Solution

For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation (13.6)

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4} s^{-1}} \\ &= 1.29 \times 10^3 s \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 21.5 \text{ min} \end{aligned}$$

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Second-Order Reactions

$A \rightarrow \text{product}$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k[A]^2$$

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/\text{s}}{M^2} = 1/M \cdot \text{s}$$

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2$$

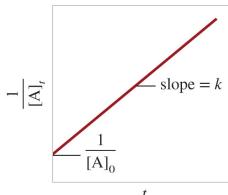
$[A]$ is the concentration of A at any time t

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

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

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

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



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Example 13.7₁

Iodine atoms combine to form molecular iodine in the gas phase



This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9 / M \cdot \text{s}$ at 23°C .

- If the initial concentration of I was $0.086 M$, calculate the concentration after 2.0 min.
- Calculate the half-life of the reaction if the initial concentration of I is $0.60 M$ and if it is $0.42 M$.

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Example 13.7₂

Strategy

- a) The relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction, we use Equation (13.7).
- b) We are asked to calculate the half-life. The half-life for a second-order reaction is given by Equation (13.8).

Solution

- (a) To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant. Applying Equation (13.7)

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

$$\frac{1}{[A]_t} = (7.0 \times 10^9 / M \cdot s) \left(2.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) + \frac{1}{0.086 M}$$

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Example 13.7₃

where $[A]$ is the concentration at $t = 2.0 \text{ min}$. Solving the equation, we get

$$[A]_t = 1.2 \times 10^{-12} M$$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that nearly all the I atoms combine after only 2.0 min of reaction time.

- b) We need Equation (13.8) for this part.

For $[I]_0 = 0.60 M$,

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

$$= \frac{1}{(7.0 \times 10^9 / M \cdot s)(0.60 M)}$$

$$= 2.4 \times 10^{-10} \text{ s}$$

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Example 13.7₄

For $[I]_0 = 0.42 \text{ M}$

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{1}{(7.0 \times 10^9 / \text{M} \cdot \text{s})(0.42 \text{ M})} \\ &= 3.4 \times 10^{-10} \text{ s} \end{aligned}$$

Check

These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant but depends on the initial concentration of the reactant(s).

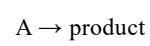
Does it make sense that a larger initial concentration should have a shorter half-life?

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Zero-Order Reactions



$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} \quad \text{rate} = k[\text{A}]^0 = k$$

$$k = \frac{\text{rate}}{[\text{A}]^0} = \text{M/s}$$

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

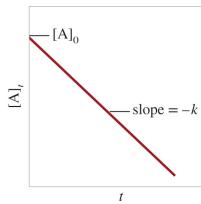
$[\text{A}]$ is the concentration of A at any time t

$[\text{A}]_0$ is the concentration of A at time $t = 0$

$$[\text{A}] = [\text{A}]_0 - kt$$

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

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



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

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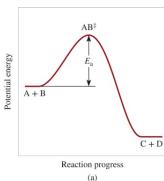
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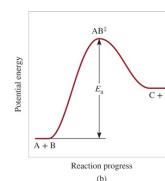
Exothermic and Endothermic Reactions



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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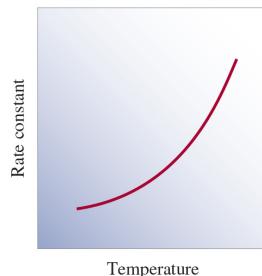
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Temperature Dependence of the Rate Constant

$$k = A \cdot e^{(-E_a/RT)}$$

(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

Alternate format:

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

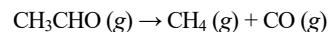
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Example 13.8

The rate constants for the decomposition of acetaldehyde



were measured at five different temperatures. The data are shown in the table. Plot $\ln k$ versus $1/T$, and determine the activation energy (in kJ/mol) for the reaction. Note that the reaction is "3/2" order in CH_3CHO , so k has the units of $1/M^{1/2} \cdot \text{s}$.

$k(1/\text{M}^{1/2} \cdot \text{s})$	$T(\text{K})$
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

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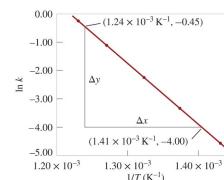
Example 13.8₂

Strategy

Consider the Arrhenius equation written as a linear equation

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

A plot of $\ln k$ versus $1/T$ (y versus x) will produce a straight line with a slope equal to $-E_a/R$. Thus, the activation energy can be determined from the slope of the plot.



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Example 13.8₃

Solution

First we convert the data to the following table

$\ln k$	$1/T (K^{-1})$
-4.51	1.43×10^{-3}
-3.35	1.37×10^{-3}
-2.254	1.32×10^{-3}
-1.070	1.27×10^{-3}
-0.237	1.23×10^{-3}

A plot of these data yields the graph in Figure 13.18. The slope of the line is calculated from two pairs of coordinates:

$$\text{slope} = \frac{-4.00 - (-0.45)}{(1.41 - 1.24) \times 10^{-3} \text{ K}^{-1}} = -2.09 \times 10^4 \text{ K}$$

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Example 13.8 4

From the linear form of Equation (13.13)

$$\begin{aligned}\text{slope} &= -\frac{E_a}{R} = -2.09 \times 10^4 \text{ K} \\ E_a &= (8.314 \text{ J/K} \cdot \text{mol})(2.09 \times 10^4 \text{ K}) \\ &= 1.74 \times 10^5 \text{ J/mol} \\ &= 1.74 \times 10^2 \text{ kJ/mol}\end{aligned}$$

Check

It is important to note that although the rate constant itself has the units $\text{M}^{-1} \cdot \text{s}^{-1}$, the quantity $\ln k$ has no units (we cannot take the logarithm of a unit).

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Alternate Form of the Arrhenius Equation

At two temperatures, T_1 and T_2

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

or

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

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Example 13.9₁

The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K.

What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

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Example 13.9₂

Strategy

A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (13.14)]. Make sure the units of R and E_a are consistent.

Solution

The data are

$$\begin{aligned}k_1 &= 3.46 \times 10^{-2} \text{ s}^{-1} & k_2 &=? \\T_1 &= 298 \text{ K} & T_2 &= 350 \text{ K}\end{aligned}$$

Substituting in Equation (13.14),

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = \frac{50.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[\frac{298 \text{ K} - 350 \text{ K}}{(298 \text{ K})(350 \text{ K})} \right]$$

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Example 13.9 ₃

We convert E_a to units of J/mol to match the units of R .
Solving the equation gives

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = -3.0$$

$$\frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = e^{-3.0} = 0.050$$

$$k_2 = 0.71 \text{ s}^{-1}$$

Check

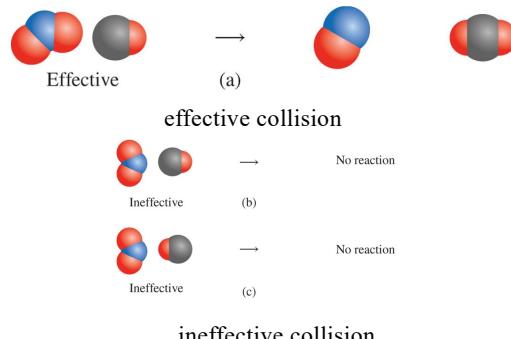
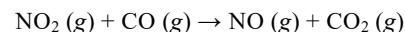
The rate constant is expected to be greater at a higher temperature. Therefore, the answer is reasonable.

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Importance of Molecular Orientation

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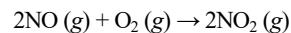
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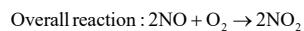
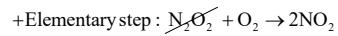
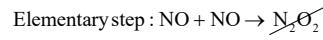
Reaction Mechanisms 1

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***.

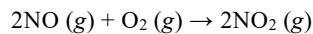


N_2O_2 is detected during the reaction!

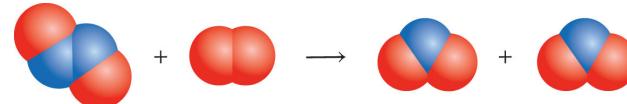
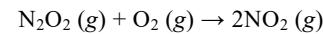
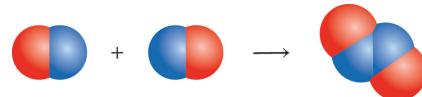
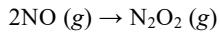

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Reaction Mechanisms 2



Mechanism:


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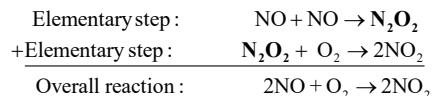
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Reaction Mechanisms 3

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.

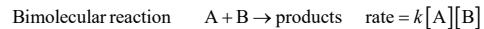
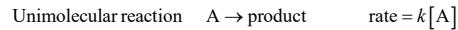


The **molecularity of a reaction** is the number of molecules reacting in an elementary step.

- **Unimolecular reaction** – elementary step with 1 molecule
- **Bimolecular reaction** – elementary step with 2 molecules
- **Termolecular reaction** – elementary step with 3 molecules

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Rate Laws and Elementary 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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Sequence of Steps in Studying a Reaction Mechanism



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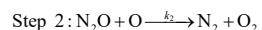
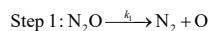
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Example 13.10₁

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:



Experimentally the rate law is found to be $\text{rate} = k[\text{N}_2\text{O}]$

- Write the equation for the overall reaction.
- Identify the intermediate.
- What can you say about the relative rates of steps 1 and 2?

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Example 13.10₂

Strategy

- a) Because the overall reaction can be broken down into elementary steps, knowing the elementary steps would enable us to write the overall reaction.
- b) What are the characteristics of an intermediate? Does it appear in the overall reaction?
- c) What determines which elementary step is rate determining? How does a knowledge of the rate-determining step help us write the rate law of a reaction?

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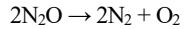
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Example 13.10₃

Solution

- a) Adding the equations for steps 1 and 2 gives the overall reaction



- b) Because the O atom is produced in the first elementary step and it does not appear in the overall balanced equation, it is an intermediate.
- c) If we assume that step 1 is the rate-determining step, then the rate of the overall reaction is given by

$$\text{rate} = k_1 [\text{N}_2\text{O}]$$

and $k = k_1$.

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Example 13.10₄

Check

There are two criteria that must be met for a proposed reaction mechanism to be plausible.

- 1) The individual steps (elementary steps) must sum to the corrected overall reaction.
- 2) The rate-determining step (the slow step) must have the same rate law as the experimentally determined rate law.

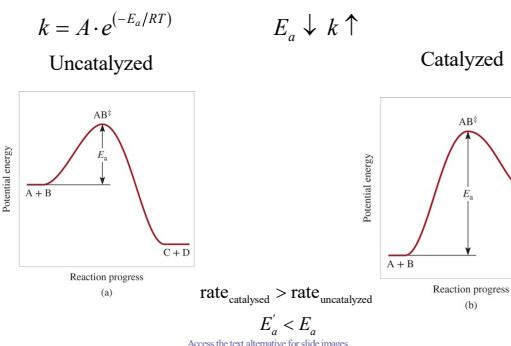
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Catalysts₁

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



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Catalysts 2

In **heterogeneous catalysis**, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In **homogeneous catalysis**, the reactants and the catalysts are dispersed in a single phase, usually liquid.

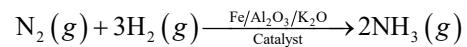
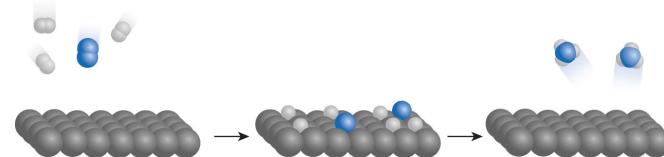
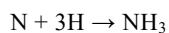
- Acid catalysis
- Base catalysis

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Haber Process



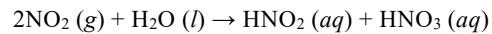
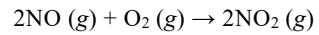
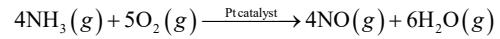
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Ostwald Process



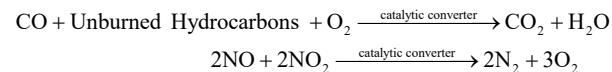
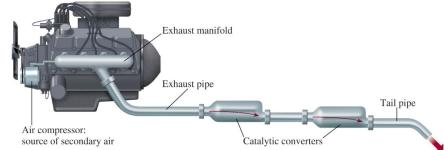
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Catalytic Converters

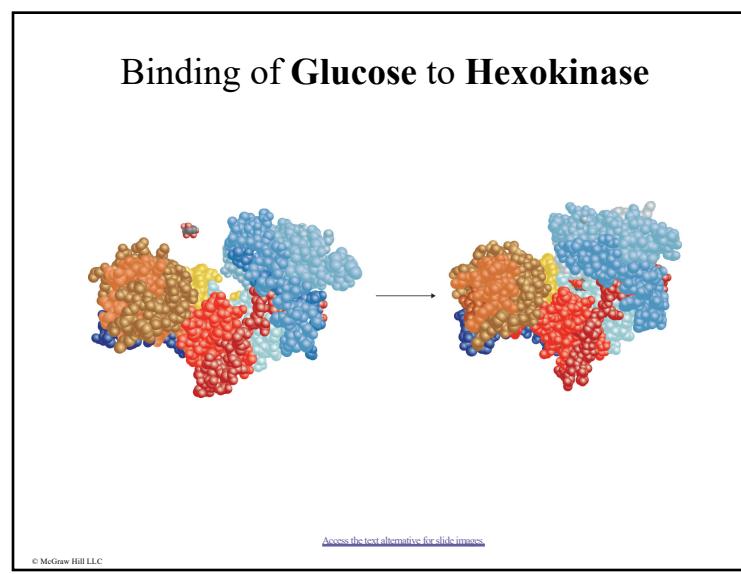
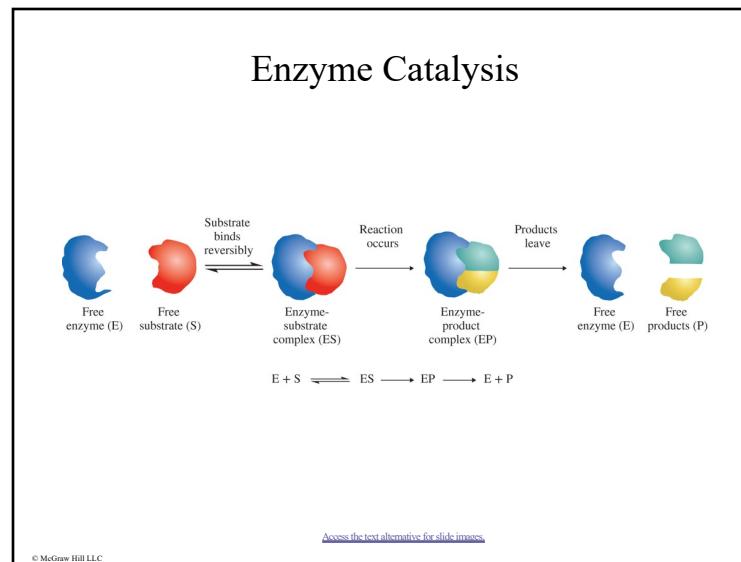
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Enzyme Kinetics

$$E + S \xrightleftharpoons[k_{-1}]{k_1} ES$$
$$ES \xrightarrow{k_2} E + P$$
$$\text{rate} = \frac{\Delta [P]}{\Delta t}$$
$$\text{rate} = k [ES]$$

Rate of product formation

[S]

All active sites are occupied at and beyond this substrate concentration

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