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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*).

$$A \rightarrow B$$

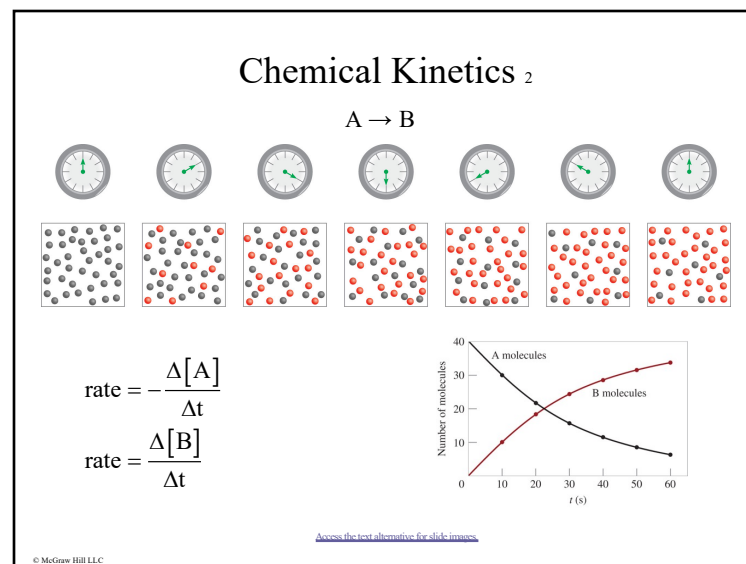
$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \Delta[A] = \begin{array}{l} \text{change in concentration of A over} \\ \text{time period } \Delta t \end{array}$$

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

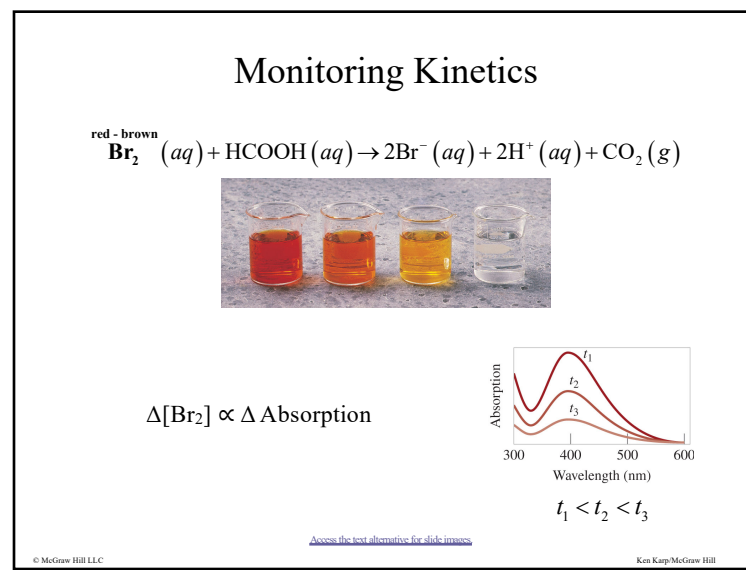
Because [A] decreases with time,  $\Delta[A]$  is **negative**.

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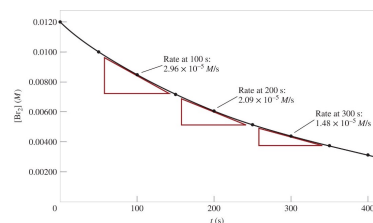


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## Kinetic Rates 1



Time (s)	$[\text{Br}_2]$ (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

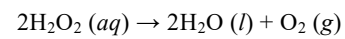
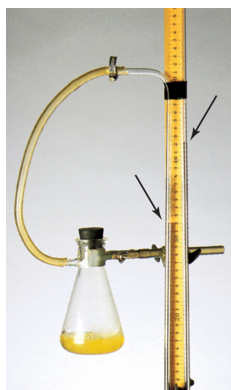
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## Kinetic Rates 2



$$PV = nRT$$

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

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

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

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## Rates of Reaction

Table 13.1 Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

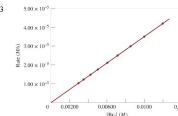
Time (s)	[Br <sub>2</sub> ] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]}$ (s <sup>-1</sup> )
00	0.0120	$4.20 \times 10^{-5}$	$3.50 \times 10^{-3}$
50.0	0.0101	$3.52 \times 10^{-5}$	$3.49 \times 10^{-3}$
100.0	0.00846	$2.96 \times 10^{-5}$	$3.50 \times 10^{-3}$
150.0	0.00710	$2.49 \times 10^{-5}$	$3.51 \times 10^{-3}$
200.0	0.00596	$2.09 \times 10^{-5}$	$3.51 \times 10^{-3}$
250.0	0.00500	$1.75 \times 10^{-5}$	$3.50 \times 10^{-3}$
300.0	0.00420	$1.48 \times 10^{-5}$	$3.52 \times 10^{-3}$
350.0	0.00353	$1.23 \times 10^{-5}$	$3.48 \times 10^{-3}$
400.0	0.00296	$1.04 \times 10^{-5}$	$3.51 \times 10^{-3}$

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

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

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

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



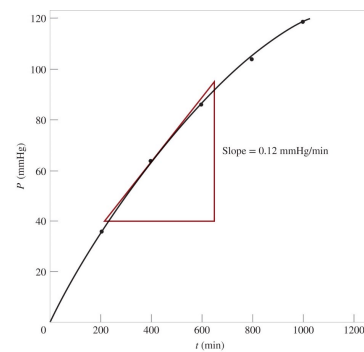
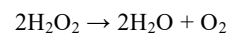
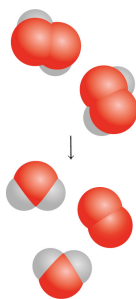
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## Decomposition of H<sub>2</sub>O<sub>2</sub>



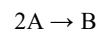
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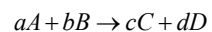
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## Reaction Rates and Stoichiometry



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

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



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

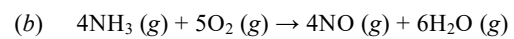
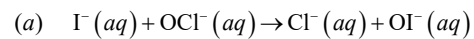
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## Example 13.1

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 13.1 <sub>2</sub>

**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,

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

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

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

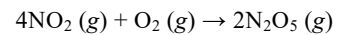
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### Example 13.2 <sub>1</sub>

Consider the reaction



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

- At what rate is  $\text{N}_2\text{O}_5$  being formed?
- At what rate is  $\text{NO}_2$  reacting?

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### Example 13.2<sub>2</sub>

**Strategy**

To calculate the rate of formation of  $\text{N}_2\text{O}_5$  and disappearance of  $\text{NO}_2$ , 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  $\text{O}_2$  is decreasing with time.

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### Example 13.2<sub>3</sub>

**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 <sub>4</sub>

b) Here we have

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

So

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

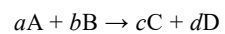
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### The Rate Law <sub>1</sub>

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<sup>th</sup> order** in A

Reaction is **y<sup>th</sup> order** in B

Reaction is **(x+y)<sup>th</sup> order overall**

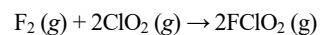
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## The Rate Law <sub>2</sub>



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

**Table 13.2** Rate data for reaction between  $\text{F}_2$  and  $\text{ClO}_2$

	$[\text{F}_2](\text{M})$	$[\text{ClO}_2](\text{M})$	Initial Rates (M/s)
	1.010	0.010	$1.2 \times 10^{-3}$
Double $[\text{F}_2]$ with $[\text{ClO}_2]$ constant	2.010	0.040	$4.8 \times 10^{-3}$
Rate Doubles	3.020	0.010	$2.4 \times 10^{-3}$

$x = 1$

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

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

Rate Quadruples

$y = 1$

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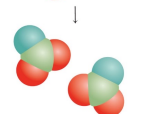
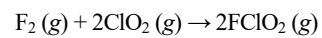
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## Rate Laws

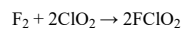
Rate laws are **always** determined experimentally.

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.



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



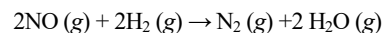
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### Example 13.3 <sub>1</sub>

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



From the following data collected at this temperature, determine

- the rate law
- the rate constant
- 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	$5.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	$1.3 \times 10^{-5}$
2	$10.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	$5.0 \times 10^{-5}$
3	$10.0 \times 10^{-3}$	$4.0 \times 10^{-3}$	$10.0 \times 10^{-5}$

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### Example 13.3 <sub>2</sub>

#### **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 H<sub>2</sub>.

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### Example 13.3 <sub>3</sub>

**Solution**

(a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H<sub>2</sub>, 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 13.3 <sub>4</sub>

Experiments 2 and 3 indicate that doubling [H<sub>2</sub>] 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 H<sub>2</sub>. 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<sub>5</sub>

- 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<sub>6</sub>

- c) Using the known rate constant and concentrations of NO and H<sub>2</sub>, 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***

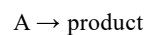
Note that the reaction is first order in H<sub>2</sub>, whereas the stoichiometric coefficient for H<sub>2</sub> in the balanced equation is 2. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

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## First-Order Reactions <sub>1</sub>



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

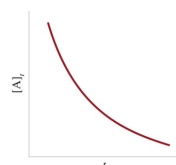
$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1}$$

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

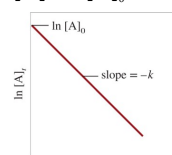
$[A]$  is the concentration of A at any time  $t$   
 $[A]_0$  is the concentration of A at time  $t = 0$

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

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



(a)



(b)

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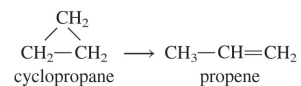
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## Example 13.4 <sub>1</sub>

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  $500^\circ \text{C}$ .



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

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## Example 13.4<sub>2</sub>

### 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  $[A]_t$  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,  $[A]_t/[A]_0 = 26\%/100\%$ , or 0.26/1.00.

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## Example 13.4<sub>3</sub>

### 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

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

Hence,

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

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

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),

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

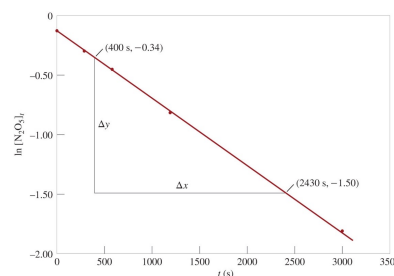
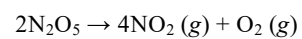
$$t = 2.0 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 33 \text{ min}$$

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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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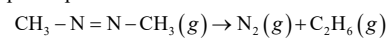
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### Example 13.5<sub>1</sub>

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 13.5<sub>2</sub>

#### **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  $\ln[A]_t$  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 13.5<sub>3</sub>

**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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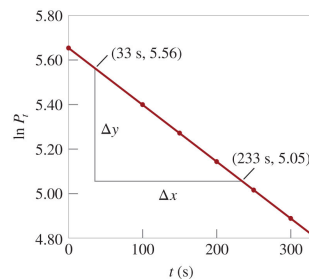
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### Example 13.5<sub>4</sub>

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 <sub>2</sub>

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

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

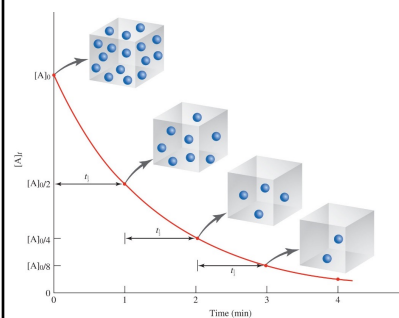
$$t_{1/2} = \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

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## First-Order Reactions <sub>3</sub>



### First-order reaction

$A \rightarrow \text{product}$

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

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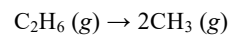
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### Example 13.6 <sub>1</sub>

The decomposition of ethane (C<sub>2</sub>H<sub>6</sub>) to methyl radicals is a first-order reaction with a rate constant of  $5.36 \times 10^{-4} \text{ s}^{-1}$  at 700°C:



Calculate the half-life of the reaction in minutes.

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### Example 13.6 <sub>2</sub>

**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)

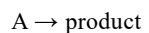
$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4} \text{ s}^{-1}} \\ &= 1.29 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 21.5 \text{ min} \end{aligned}$$

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## Second-Order Reactions



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

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

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

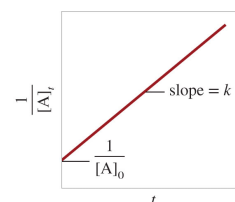
$$t_{1/2} = \frac{1}{k[A]_0}$$

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

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

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

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



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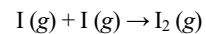
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## Example 13.7

Iodine atoms combine to form molecular iodine in the gas phase



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

- If the initial concentration of I was  $0.086 M$ , calculate the concentration after  $2.0 \text{ min}$ .
- 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 13.7<sub>2</sub>

### Strategy

- 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).
- 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 13.7<sub>3</sub>

where  $[A]_t$  is the concentration at  $t = 2.0$  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.

- We need Equation (13.8) for this part.

$$\text{For } [I]_0 = 0.60 M.$$

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

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

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

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### Example 13.7<sub>4</sub>

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

$$t_{\frac{1}{2}} = \frac{1}{(7.0 \times 10^9 / \text{M} \cdot \text{s})(0.42 \text{ M})}$$

$$= 3.4 \times 10^{-10} \text{ s}$$

#### 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

$A \rightarrow \text{product}$

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

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

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

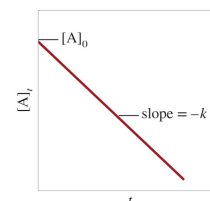
$[A]$  is the concentration of A at any time  $t$

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

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

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

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



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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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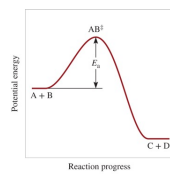
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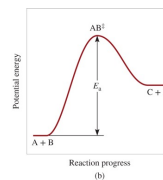
## Exothermic and Endothermic Reactions



Exothermic Reaction



Endothermic Reaction



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

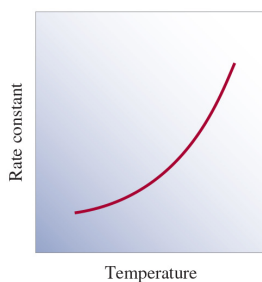
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## Temperature Dependence of the Rate Constant



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

(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:

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

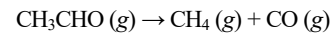
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## Example 13.8

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  $\text{CH}_3\text{CHO}$ , so  $k$  has the units of  $1/\text{M}^{1/2} \cdot \text{s}$ .

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

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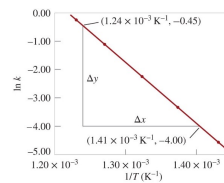
## Example 13.8<sub>2</sub>

### 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 13.8<sub>3</sub>

### Solution

First we convert the data to the following table

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

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 <sub>4</sub>

From the linear form of Equation (13.13)

$$\text{slope} = -\frac{E_a}{R} = -2.09 \times 10^4 \text{ K}$$

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

#### **Check**

It is important to note that although the rate constant itself has the units  $1/\text{M}^x \cdot \text{s}$ , 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 13.9<sub>1</sub>

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 13.9<sub>2</sub>

#### **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

$$k_1 = 3.46 \times 10^{-2} \text{ s}^{-1} \quad k_2 = ?$$

$$T_1 = 298 \text{ K} \quad T_2 = 350 \text{ K}$$

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 <sub>3</sub>

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

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

$$\frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = e^{-3.01} = 0.050$$

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

#### Check

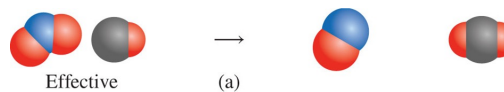
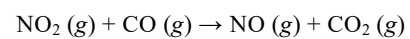
The rate constant is expected to be greater at a higher temperature. Therefore, the answer is reasonable.

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### Importance of Molecular Orientation



effective collision



ineffective collision

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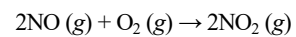
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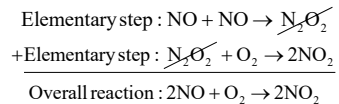
## Reaction Mechanisms 1

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*.



$\text{N}_2\text{O}_2$  is detected during the reaction!

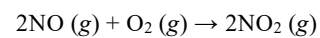


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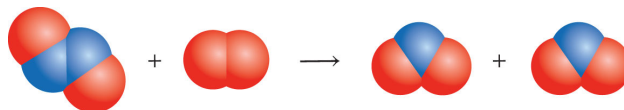
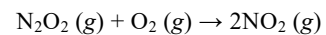
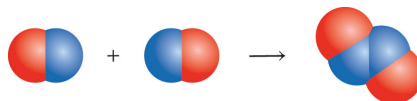
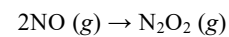
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## Reaction Mechanisms 2



Mechanism:



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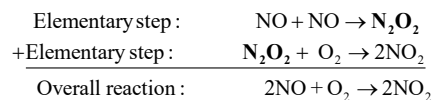
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## Reaction Mechanisms <sub>3</sub>

**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.

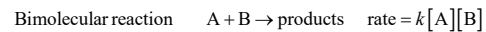
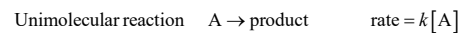
- **Unimolecular reaction** – elementary step with 1 molecule
- **Bimolecular reaction** – elementary step with 2 molecules
- **Termolecular reaction** – elementary step with 3 molecules

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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.

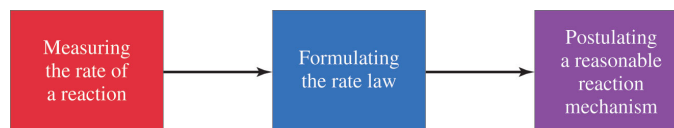
The **rate-determining step** is the **slowest** step in the sequence of steps leading to product formation.

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## Sequence of Steps in Studying a Reaction Mechanism



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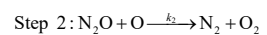
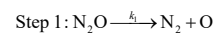
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## Example 13.10<sub>1</sub>

The gas-phase decomposition of nitrous oxide (N<sub>2</sub>O) 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 13.10<sub>2</sub>

**Strategy**

- Because the overall reaction can be broken down into elementary steps, knowing the elementary steps would enable us to write the overall reaction.
- What are the characteristics of an intermediate? Does it appear in the overall reaction?
- 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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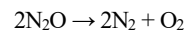
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### Example 13.10<sub>3</sub>

**Solution**

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



- 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.
- 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 13.10 <sub>4</sub>

### 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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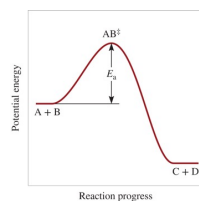
## Catalysts <sub>1</sub>

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

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

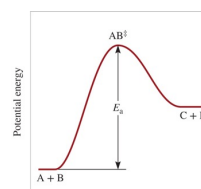
$$E_a \downarrow \quad k \uparrow$$

Uncatalyzed



(a)

Catalyzed



(b)

$$\text{rate}_{\text{catalysed}} > \text{rate}_{\text{uncatalysed}}$$

$$E'_a < E_a$$

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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.

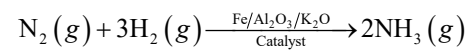
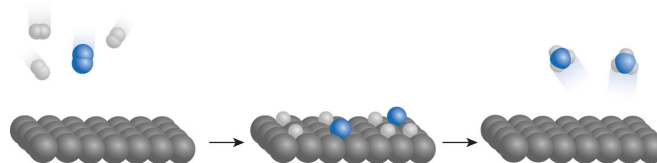
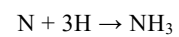
- Acid catalysis
- Base catalysis

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## Haber Process



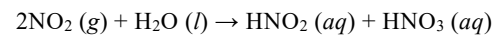
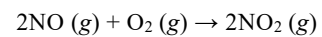
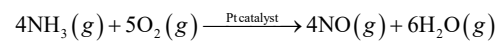
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## Ostwald Process

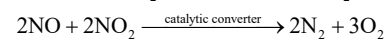
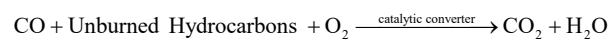
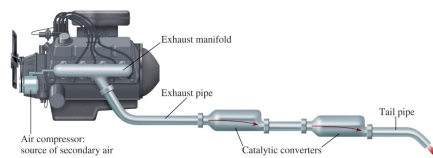


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## Catalytic Converters

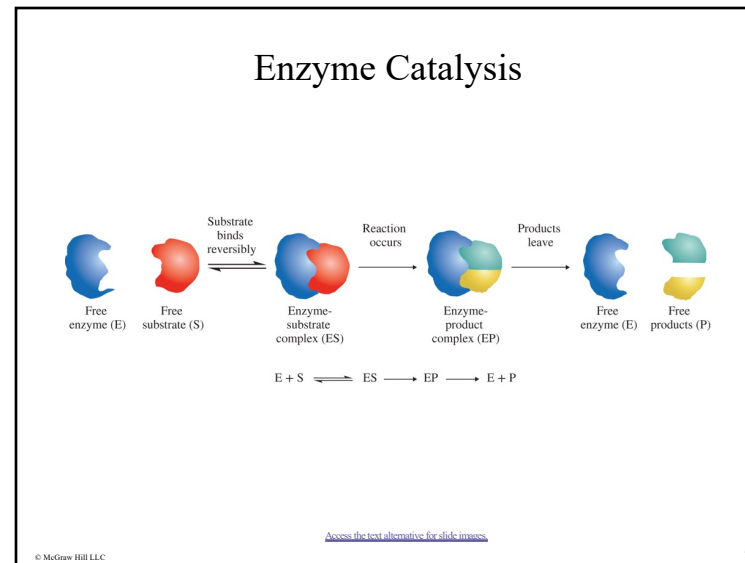


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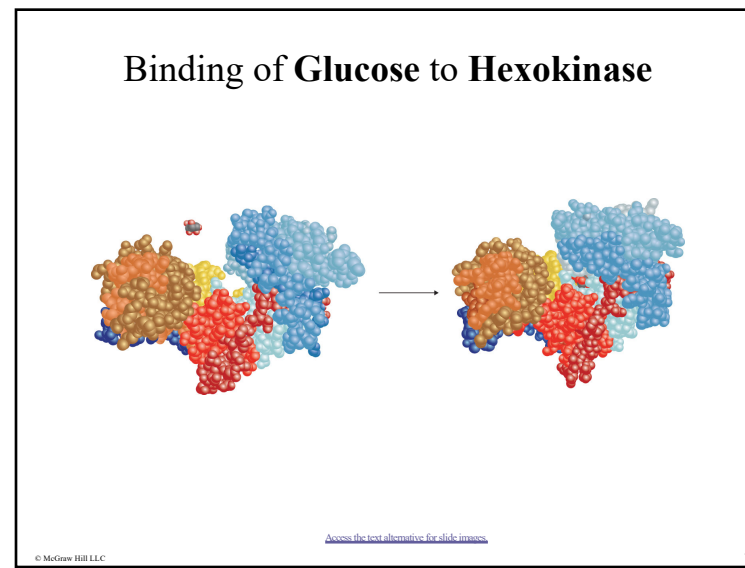
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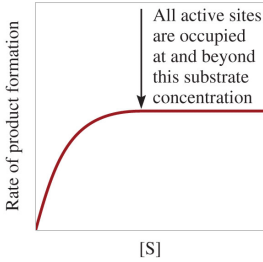
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## Enzyme Kinetics

$$E + S \xrightleftharpoons[k_{-1}]{k_1} ES$$

$$ES \xrightarrow{k_2} E + P$$

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

$$\text{rate} = k[ES]$$


[S]

All active sites are occupied at and beyond this substrate concentration

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