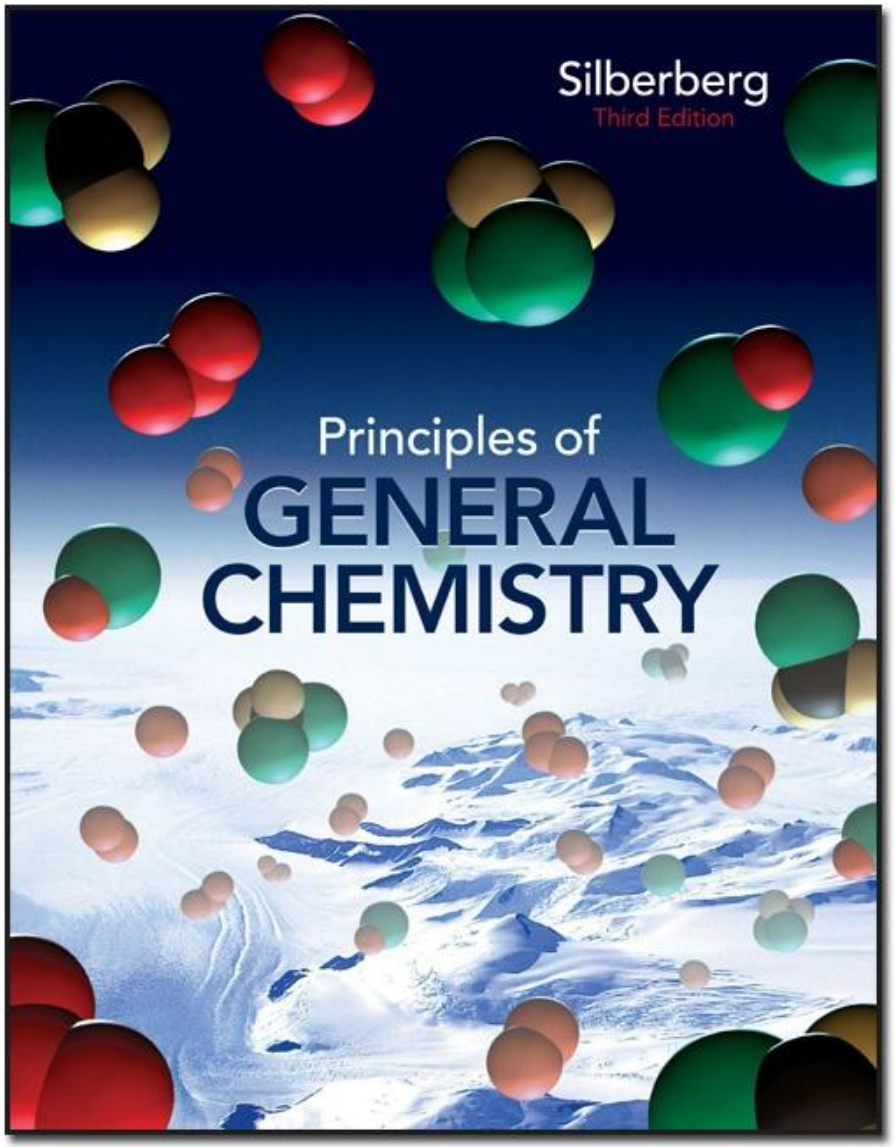


Chapter 16

Lecture Outline

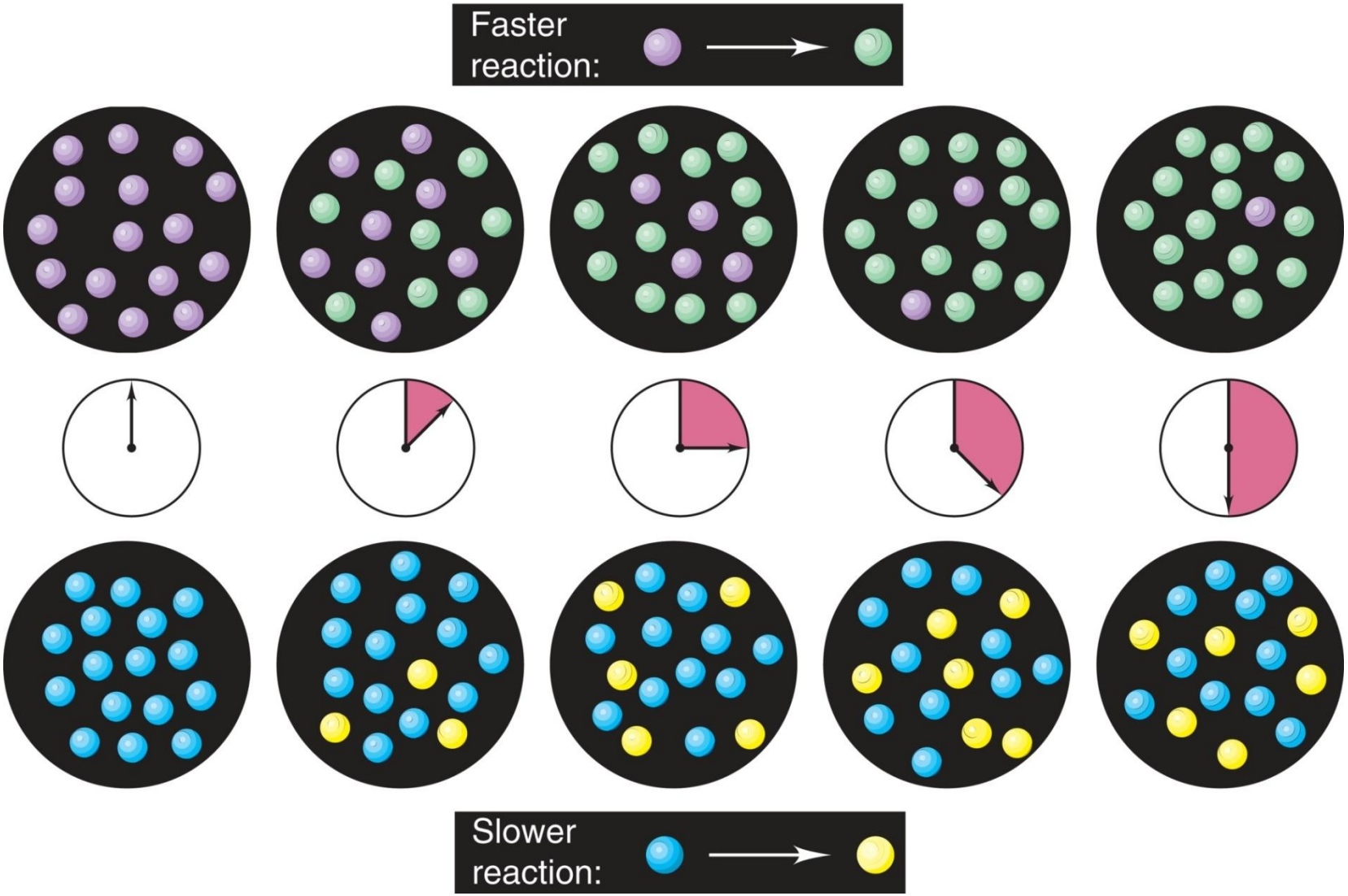
See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 16

Kinetics: Rates and Mechanisms of Chemical Reactions

Kinetics: Rates and Mechanisms of Chemical Reactions

Figure 16.1 **A faster reaction (*top*) and a slower reaction (*bottom*).**



Factors That Influence Reaction Rate

- Reaction rate: the change in the concentration of reactant or product as a function of time.(faster reaction: higher rate)

$H_2 + F_2 \longrightarrow 2HF_{(g)}$ very fast

$3H_2 + N_2 \longrightarrow 2NH_{3\ (g)}$ very slow

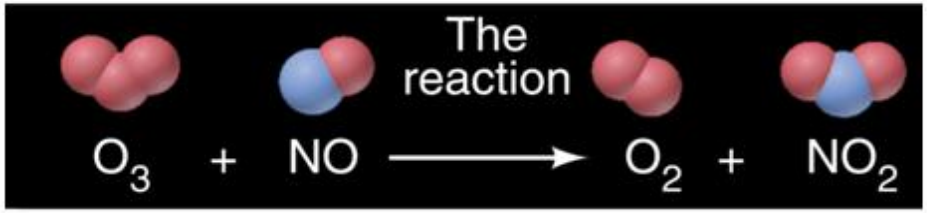
Particles must collide in order to react.

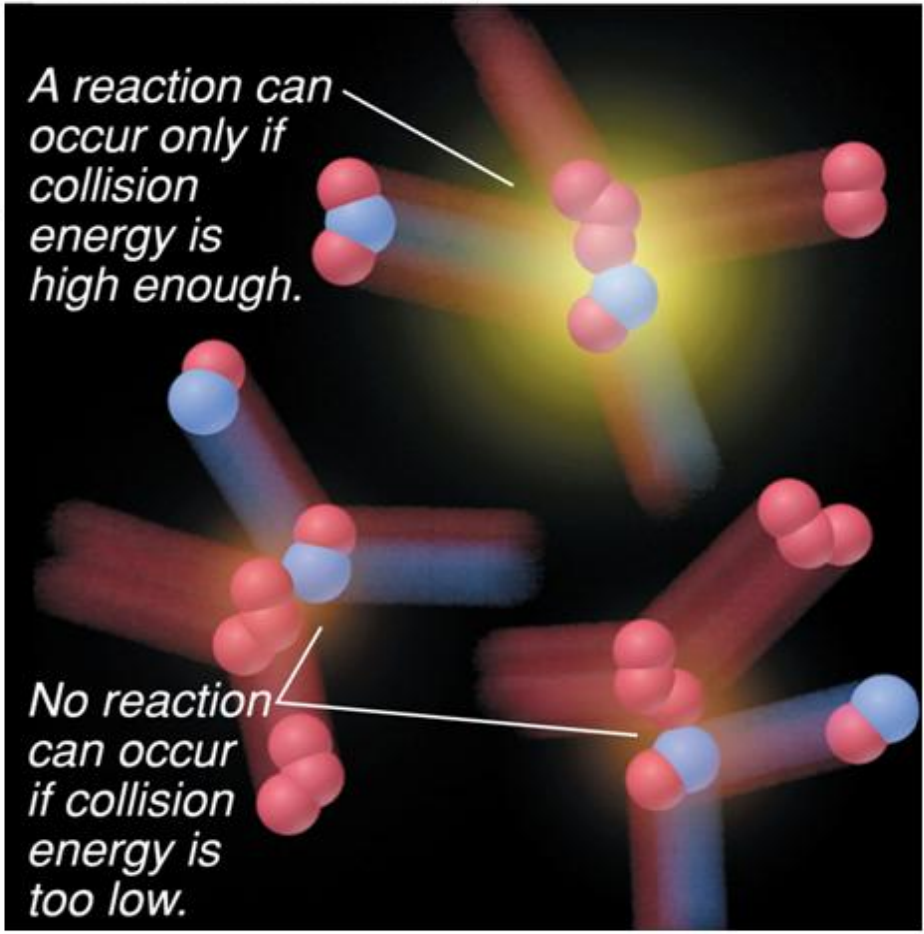
Four factors that affect rate

1- The higher the ***concentration*** of reactants, the greater the reaction rate. A higher concentration of reactant particles allows a greater number of collisions.(Rate ά collision freq. ά **concentration**)

2- The ***physical state*** of the reactants influences reaction rate. Substances must mix in order for particles to collide. More contact(larger surface area) between the reactant, faster reaction occurs.

Figure 16.2 **Sufficient collision energy is required for a reaction to occur.**





3- The higher the ***temperature***, the greater the reaction rate.

At higher temperatures particles have more energy and therefore collide more often and more effectively.

Temperature affects reaction rate by increasing the frequency and energy of collision.

(Rate ά collision freq. ά **tempreature**)

(Rate ά collision energy ά **concentration**)

4- catalyst…… section 16.7

Expressing the Reaction Rate

Reaction rate is measured in terms of the changes in concentrations of reactants or products per unit time.

For the general reaction A $\rightarrow$ B, we measure the concentration of A at t_1 and at t_2:

$$\text{Rate} = -\frac{\text{change in concentration of A}}{\text{change in time}} = -\frac{\text{conc A}_2 - \text{conc A}_1}{t_2 - t_1} = -\frac{\Delta[\text{A}]}{\Delta t} = \frac{\Delta[\text{B}]}{\Delta t}$$

Square brackets indicate a concentration in moles per liter.

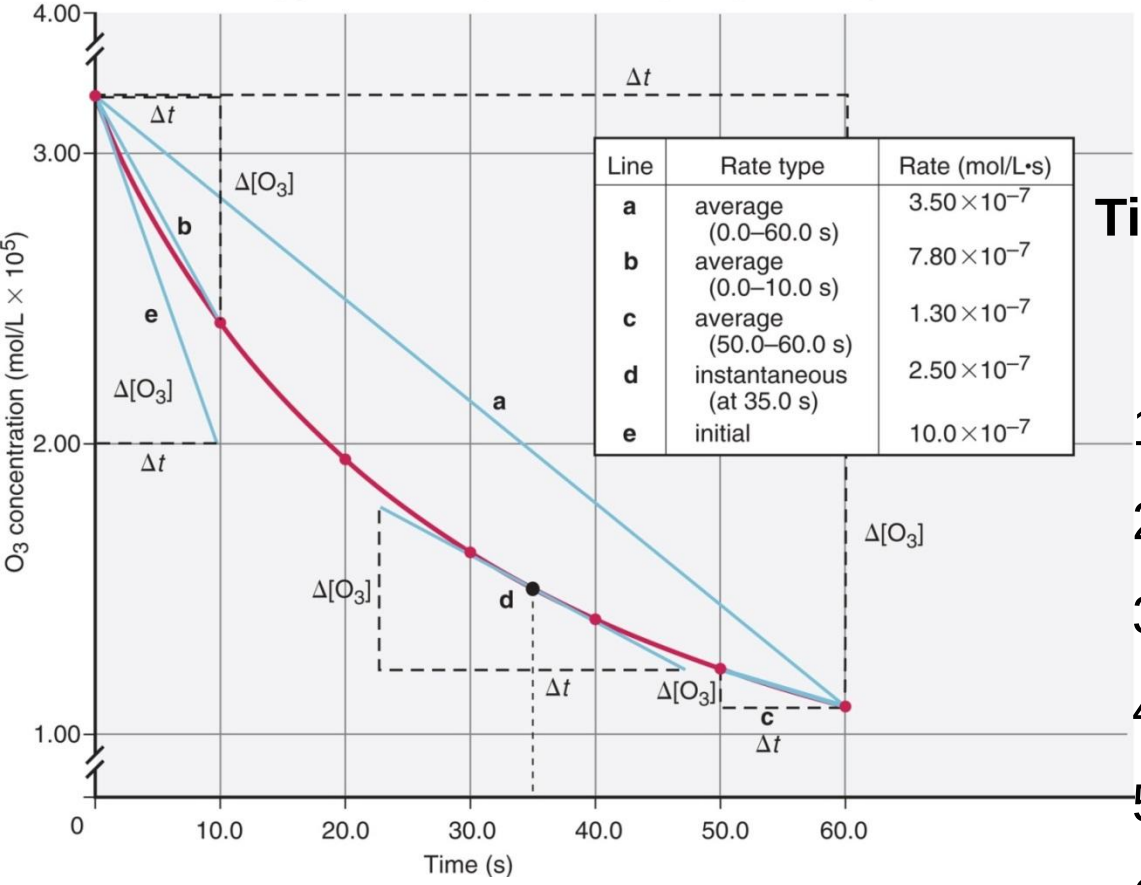
The ***negative*** sign is used because the concentration of A is ***decreasing***.

Rate is appositive number

Table 16.1 Concentration of O_3 at Various Times in its Reaction with C_2H_4 at 303 K

$$C_2H_4\,(g) + O_3\,(g) \rightleftharpoons C_2H_4O\,(g) + O_2\,(g)$$

$$\text{rate} = -\frac{\Delta[C_2H_4]}{\Delta t} = -\frac{\Delta[O_3]}{\Delta t}$$



Time (s)	Concentration of O_3 (mol/L)
0.0	3.20×10^{-5}
10.0	2.42×10^{-5}
20.0	1.95×10^{-5}
30.0	1.63×10^{-5}
40.0	1.40×10^{-5}
50.0	1.23×10^{-5}
60.0	1.10×10^{-5}

In Figure 16.3 Three types of reaction rates for the reaction of O_3 and C_2H_4.

1- Average rate: is the slope of the line joining two points along the curve. Line a Rate = $3.5*10^{-7}$ mole/L.s, line b Rate = $7.8*10^{-7}$ mole/L.s , line c Rate = $1.3*10^{-7}$ mole/L.s.

the decrease in [O3] over whole time period may not the same over any shorter time period.

2- **Instantaneous rate** :the rate at a particular instant during reaction (the slope of a line tangent to the curve at any point) Rate at 35.0 s is $2.5 * 10^{-7}$ mol/L.s (line d)

-In general we use the term reaction rate to mean instantaneous reaction rate.

3- **Initial rate** : the instantaneous rate at the moment the reactant are mixed (at t = 0 s) line e.in initial rate the product concentration and the reverse reaction are negligable.

In general, for the reaction

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

where *a*, *b*, *c*, and *d* are the coefficients for the balanced equation, the rate is expressed as:

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

Sample Problem 16.1 Expressing Rate in Terms of Changes in Concentration with Time

PROBLEM: Hydrogen gas has a nonpolluting combustion product (water vapor). It is used as a fuel abord the space shuttle and in earthbound cars with prototype engines:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

(a) Express the rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time.

(b) When $[O_2]$ is decreasing at 0.23 mol/L·s, at what rate is $[H_2O]$ increasing?

PLAN: We choose O_2 as the reference because its coefficient is 1. For every molecule of O_2 that disappears, two molecules of H_2 disappear, so the rate of $[O_2]$ decrease is ½ the rate of $[H_2]$ decrease. Similarly, the rate at which $[O_2]$ decreases is ½ the rate at which $[H_2O]$ increases.

Sample Problem 16.1

SOLUTION:

(a) $$\text{Rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

(b) Calculating the rate of change of $[H_2O]$:

$$\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = -(-0.23\ \text{mol/L·s})$$

$$\frac{\Delta[H_2O]}{\Delta t} = 2(0.23\ \text{mol/L·s}) \quad \boxed{= \mathbf{0.46\ mol/L·s}}$$

The Rate Law

For any general reaction occurring at a fixed temperature

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

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

-The rate depends only on reactant concentration and temperature.(initial rate)

-The term *k* is the ***rate constant***, which is specific for a given reaction at a given temperature.

-The exponents *m* and *n* are ***reaction orders*** and are determined ***by experiment***.

-The values of *m* and *n* are ***not*** necessarily related in any way to the coefficients *a* and *b*.

Some Lab methods for determining the initial rate

1- change in color : color papers when reaction start and increase with time.

$$2NO + O_2 \longrightarrow 2NO_2 \text{ (brown)}$$

2- change in pressure: the rate is proportional to the increase in gas pressure.

$$Zn + 2CH_3COOH \longrightarrow Zn^{2+} + 2CH_3CLOO^- + H_2 (g)$$

3- Change in conductivity: the conductivity of the reaction increases as the time proceeds.

$$(CH_3)_3C\text{-}Br + H2O \longrightarrow (CH_3)_3C\text{-}OH + H^+ + Br^- (g)$$

Reaction Orders

A reaction has an ***individual order*** "with respect to" or "in" each reactant.

For the simple reaction A → products:

If the rate doubles when [A] doubles, the rate depends on $[A]^1$ and the reaction is ***first order*** with respect to A.
Rate = $k[A]^1 = k[A]$

If the rate quadruples when [A] doubles, the rate depends on $[A]^2$ and the reaction is ***second order*** with respect to [A].
Rate = $k[A]^2$

If the rate does not change when [A] doubles, the rate does not depend on [A], and the reaction is ***zero order*** with respect to A. Rate = $k[A]^0 = k\ (1) = k$

Individual and Overall Reaction Orders

For the reaction $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$:

The rate law is rate = $k[NO]^2[H_2]$

The reaction is ***second order*** with respect to NO, ***first order*** with respect to H_2 and ***third order*** overall.

Note that the reaction is ***first order*** with respect to H_2 even though the coefficient for H_2 in the balanced equation is 2.

-Reaction orders *must* be determined *from experimental data* and cannot be deduced from the balanced equation.

-Reaction order are usually positive or zero but they can be fractional or negative.

$O_3 \Longleftrightarrow O_2$ rate = $k[O_3]^2[O_2]^{-1}$

Sample Problem 16.2 Determining Reaction Orders from Rate Laws

PROBLEM: For each of the following reactions, use the given rate law to determine the reaction order with respect to each reactant and the overall order.

(a) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; rate = $k[NO]^2[O_2]$
(b) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$; rate = $k[CH_3CHO]^{3/2}$
(c) $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$; rate = $k[H_2O_2][I^-]$

PLAN: We inspect the exponents in the rate law, *not* the coefficients of the balanced equation, to find the individual orders. We add the individual orders to get the overall reaction order.

SOLUTION:

(a) The exponent of [NO] is 2 and the exponent of $[O_2]$ is 1, so the reaction is **second order with respect to NO, first order with respect to O_2** and **third order overall**.

Sample Problem 16.2

(b) The reaction is $\frac{3}{2}$ **order in CH_3CHO** and $\frac{3}{2}$ **order overall**.

(c) The reaction is **first order in H_2O_2, first order in I^-,** and **second order overall**. The reactant H^+ does not appear in the rate law, so the reaction is **zero order with respect to H^+.**

Determining Reaction Orders

For the general reaction A + 2B → C + D,

the rate law will have the form

Rate = $k[A]^m[B]^n$

To determine the values of *m* and *n*, we run a series of experiments in which one reactant concentration changes while the other is kept constant, and we measure the effect on the initial rate in each case.

Table 16.2 Initial Rates for the Reaction Between A and B

Experiment	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)
1	1.75×10^{-3}	2.50×10^{-2}	3.00×10^{-2}
2	3.50×10^{-3}	5.00×10^{-2}	3.00×10^{-2}
3	3.50×10^{-3}	2.50×10^{-2}	6.00×10^{-2}
4	7.00×10^{-3}	5.00×10^{-2}	6.00×10^{-2}

[B] is kept constant for experiments 1 and 2, while [A] is doubled. Then [A] is kept constant while [B] is doubled.

Finding *m*, the order with respect to A:

We compare experiments 1 and 2, where [B] is kept constant but [A] doubles:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[A]_2^m \cancel{[B]_2^n}}{\cancel{k}[A]_1^m \cancel{[B]_1^n}} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

$$\frac{3.50\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{1.75\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{5.00\text{x}10^{-2}\ \text{mol/L}}{2.50\text{x}10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we get $2.00 = (2.00)^m$ so $m = 1$

Finding *n*, the order with respect to B:

We compare experiments 3 and 1, where [A] is kept constant but [B] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{\cancel{k}[\text{A}]_3^m [\text{B}]_3^n}{\cancel{k}[\text{A}]_1^m [\text{B}]_1^n} = \frac{[\text{B}]_3^n}{[\text{B}]_1^n} = \left(\frac{[\text{B}]_3}{[\text{B}]_1}\right)^n$$

$$\frac{3.50\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{1.75\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{6.00\text{x}10^{-2}\ \text{mol/L}}{3.00\text{x}10^{-2}\ \text{mol/L}}\right)^n$$

Dividing, we get $2.00 = (2.00)^n$ so $n = 1$

Table 16.3 Initial Rates for the Reaction Between O_2 and NO

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$ Rate = $k[O_2]^m[NO]^n$

Experiment	Initial Rate (mol/L·s)	Initial Reactant Concentrations (mol/L)	
		$[O_2]$	[NO]
1	3.21×10^{-3}	1.10×10^{-2}	1.30×10^{-2}
2	6.40×10^{-3}	2.20×10^{-2}	1.30×10^{-2}
3	12.48×10^{-3}	1.10×10^{-2}	2.60×10^{-2}
4	9.60×10^{-3}	3.30×10^{-2}	1.30×10^{-2}
5	28.8×10^{-3}	1.10×10^{-2}	3.90×10^{-2}

Finding *m*, the order with respect to O_2:

We compare experiments 1 and 2, where [NO] is kept constant but $[O_2]$ doubles:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[O_2]_2^m[\cancel{NO}]_2^n}{\cancel{k}[O_2]_1^m[\cancel{NO}]_1^n} = \frac{[O_2]_2^m}{[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

$$\frac{6.40\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{3.21\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{2.20\text{x}10^{-2}\ \text{mol/L}}{1.10\text{x}10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we get $1.99 = (2.00)^m$ or $2 = 2^m$, so $m = 1$

The reaction is first order with respect to O_2.

Sometimes the exponent is not easy to find by inspection. In those cases, we solve for m with an equation of the form $a = b^m$:

$$m = \frac{\log a}{\log b} = \frac{\log 1.99}{\log 2.00} = 0.993$$

This confirms that the reaction is first order with respect to O_2.

Reaction orders may be positive integers, zero, negative integers, or fractions.

Finding *n*, the order with respect to NO:

We compare experiments 1 and 3, where $[O_2]$ is kept constant but [NO] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \left(\frac{[NO]_3}{[NO]_1}\right)^n \qquad \frac{12.8\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{3.21\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{2.60\text{x}10^{-2}\ \text{mol/L}}{1.30\text{x}10^{-2}\ \text{mol/L}}\right)^n$$

Dividing, we get $3.99 = (2.00)^n$ or $4 = 2^n$, so $n = 2$.

Alternatively: $n = \dfrac{\log a}{\log b} = \dfrac{\log 3.99}{\log 2.00} = 2.00$

The reaction is second order with respect to NO.

The rate law is given by: rate = $k[O_2][NO]^2$

Sample Problem 16.3 Determining Reaction Orders from Rate Data

PROBLEM: Many gaseous reactions occur in a car engine and exhaust system. One of these is

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ rate = $k[NO_2]^m[CO]^n$

Use the following data to determine the individual and overall reaction orders:

Experiment	Initial Rate (mol/L·s)	Initial $[NO_2]$ (mol/L)	Initial [CO] (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

Sample Problem 16.3

PLAN: We need to solve the general rate law for *m* and for *n* and then add those orders to get the overall order. We proceed by taking the ratio of the rate laws for two experiments in which only the reactant in question changes concentration.

SOLUTION:

To calculate *m*, the order with respect to NO_2, we compare experiments 1 and 2:

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{k[NO_2]^m_2[CO]^n_2}{k[NO_2]^m_1[CO]^n_1} = \left(\frac{[NO_2]_2}{[NO_2]_1}\right)^m \qquad \frac{0.080}{0.0050} = \left(\frac{0.40}{0.10}\right)^m$$

$$16 = (4.0)^m \text{ so } m = 2$$

The reaction is second order in NO_2.

Sample Problem 16.3

To calculate *n*, the order with respect to CO, we compare experiments 1 and 3:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{k[NO_2]^m_3[CO]^n_3}{k[NO_2]^m_1[CO]^n_1} = \left(\frac{[CO]_3}{[CO]_1}\right)^n \qquad \frac{0.0050}{0.0050} = \left(\frac{0.20}{0.10}\right)^n$$

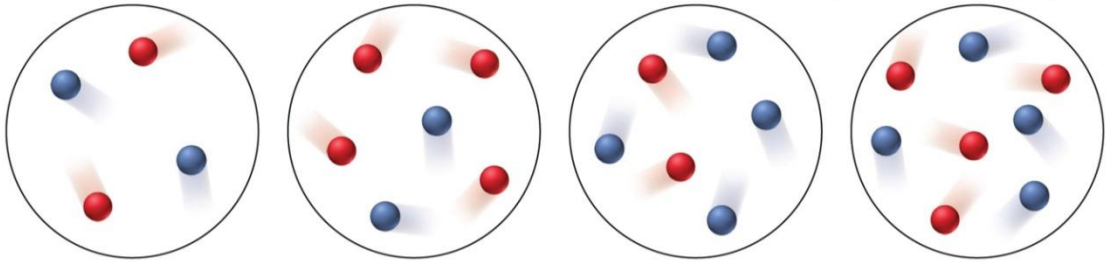
$1.0 = (2.0)^n$ so $n = 0$

The reaction is zero order in CO.

rate = $k[NO_2]^2[CO]^0$ or rate = $k[NO_2]^2$

Sample Problem 16.4 Determining Reaction Orders from Molecular Scenes

PROBLEM: At a particular temperature and volume, two gases, A (*red*) and B (*blue*), react. The following molecular scenes represent starting mixtures for four experiments:



Expt no:	1	2	3	4
Initial rate (mol/L·s)	0.50×10^{-4}	1.0×10^{-4}	2.0×10^{-4}	?

(a) What is the reaction order with respect to A? With respect to B? The overall order?

(b) Write the rate law for the reaction.

(c) Predict the initial rate of experiment 4.

PLAN: We find the individual reaction orders by seeing how a change in each reactant changes the rate. Instead of using concentrations we count the number of particles.

Sample Problem 16.4

SOLUTION:

(a) For reactant A (*red*):

Experiments 1 and 2 have the same number of particles of B, but the number of particles of A doubles. The rate doubles. **Thus the order with respect to A is 1.**

For reactant B (*blue*):

Experiments 1 and 3 show that when the number of particles of B doubles (while A remains constant), the rate quadruples. **The order with respect to B is 2**.

The overall order is 1 + 2 = 3.

(b) Rate = $k[A][B]^2$

(c) Between experiments 3 and 4, the number of particles of A doubles while the number of particles of B does not change. The rate should double, so rate = 2 x 2.0×10^{-4} = **4.0×10^{-4} mol/L·s**

Determining the rate constant

Table 16.4 Units of the Rate Constant *k* for Several Overall Reaction Orders

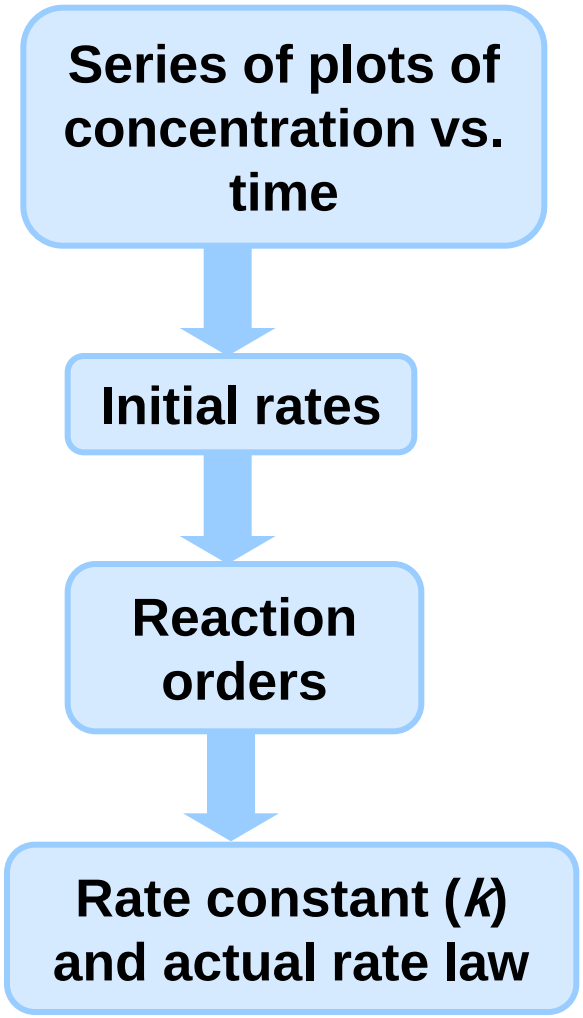
Overall Reaction Order	Units of *k* (*t* in seconds)
0	mol/L·s (or mol $L^{-1}s^{-1}$)
1	1/s (or s^{-1})
2	L/mol·s (or L $mol^{-1}s^{-1}$)
3	L^2/mol^2·s (or L^2 $mol^{-2}s^{-1}$)

General formula:

$$\text{Units of } k = \frac{\left(\frac{\text{L}}{\text{mol}}\right)^{\text{order}-1}}{\text{unit of } t}$$

The value of *k* is easily determined from experimental rate data. The ***units*** of *k* depend on the overall reaction order.

Figure 16.5 Information sequence to determine the kinetic parameters of a reaction.



Determine slope of tangent at t_0 *for each plot.*

Compare initial rates when [A] *changes and* [B] *is held constant (and vice versa).*

Substitute initial rates, orders, and concentrations into rate = $k[A]^m[B]^n$, *and solve for k.*

Integrated Rate Laws

An integrated rate law includes ***time*** as a variable.

First-order rate equation:

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

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

Second-order rate equation:

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

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

Zero-order rate equation:

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

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

Sample Problem 16.5 **Determining the Reactant Concentration after a Given Time**

PROBLEM: At 1000°C, cyclobutane (C_4H_8) decomposes in a first-order reaction, with the very high rate constant of 87 s^{-1}, to two molecules of ethylene (C_2H_4).

(a) If the initial C_4H_8 concentration is 2.00 M, what is the concentration after 0.010 s?

(b) What fraction of C_4H_8 has decomposed in this time?

PLAN: We must find the concentration of cyclobutane at time t, $[C_4H_8]_t$. The problem tells us the reaction is first-order, so we use the integrated first-order rate law:

$$\ln \frac{[C_4H_8]_0}{[C_4H_8]_t} = kt$$

Sample Problem 16.5

SOLUTION:

(a) $\ln \dfrac{[C_4H_8]_0}{[C_4H_8]_t} = kt$ $\quad \ln \dfrac{2.00\ \text{mol/L}}{[C_4H_8]_t} = (87\ \text{s}^{-1})(0.010\ \text{s}) = 0.87$

$$\frac{2.00\ \text{mol/L}}{[C_4H_8]_t} = e^{0.87} = 2.4$$

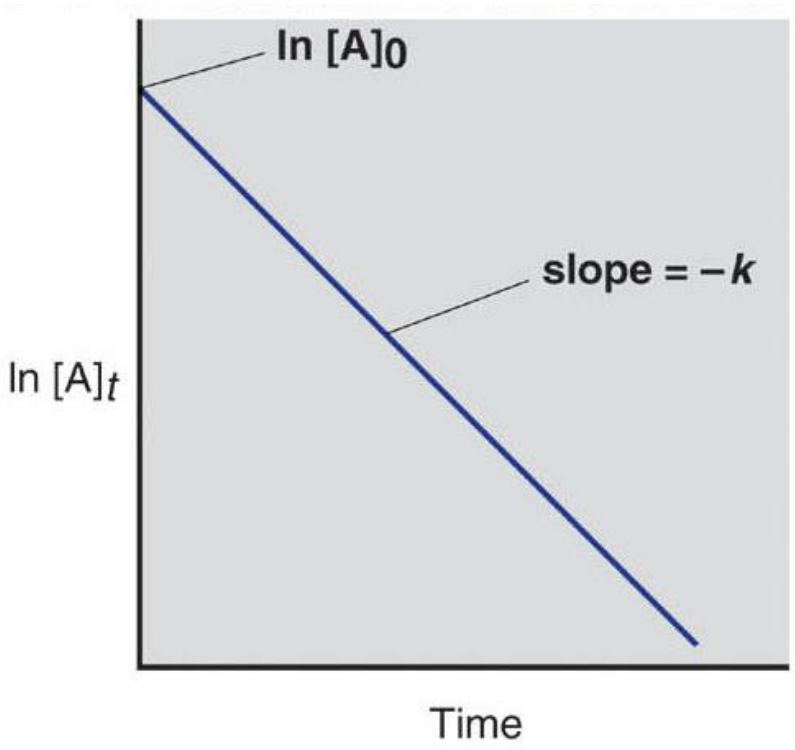
$$[C_2H_4] = \frac{2.00\ \text{mol/L}}{2.4} = \mathbf{0.83\ mol/L}$$

(b) Finding the fraction that has decomposed after 0.010 s:

$$\frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0} = \frac{2.00\ \text{M} - 0.83\ \text{M}}{2.00\ \text{M}} = \mathbf{0.58}$$

Figure 16.6A Graphical method for finding the reaction order from the integrated rate law.

First-order reaction



integrated rate law

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

straight-line form

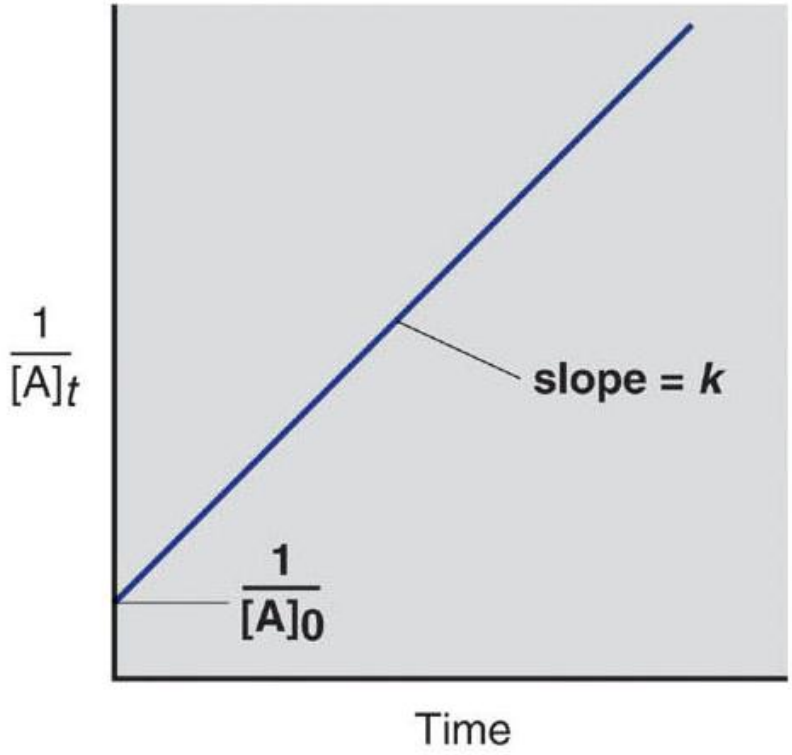
$$\ln[A]_t = -kt + \ln[A]_0$$

$$y = mx + b$$

A plot of ln [A] vs. time gives a straight line for a first-order reaction.

Figure 16.6B Graphical method for finding the reaction order from the integrated rate law.

Second-order reaction



integrated rate law

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

straight-line form

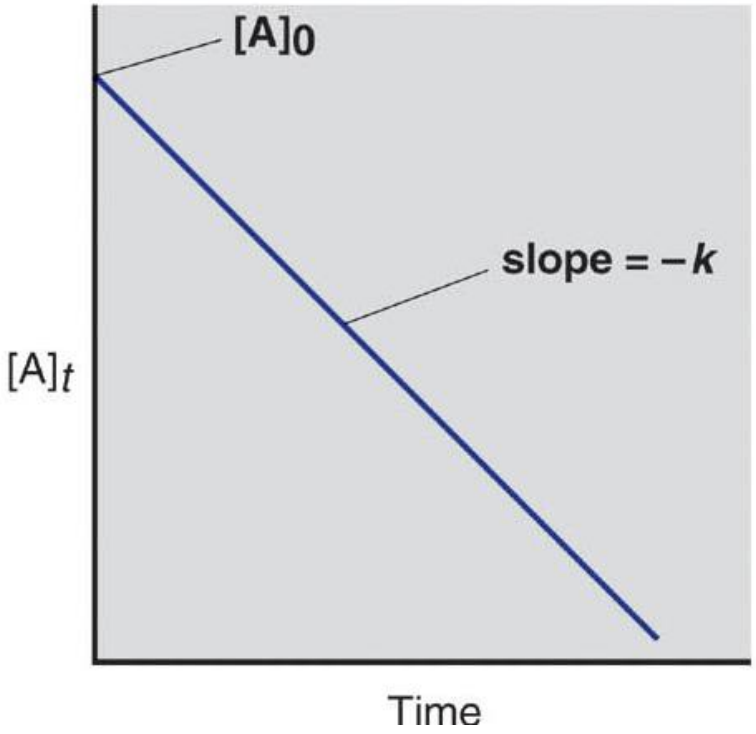
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

A plot of $\frac{1}{[A]}$ vs. time gives a straight line for a second-order reaction.

Figure 16.6C Graphical method for finding the reaction order from the integrated rate law.

Zero-order reaction



integrated rate law

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

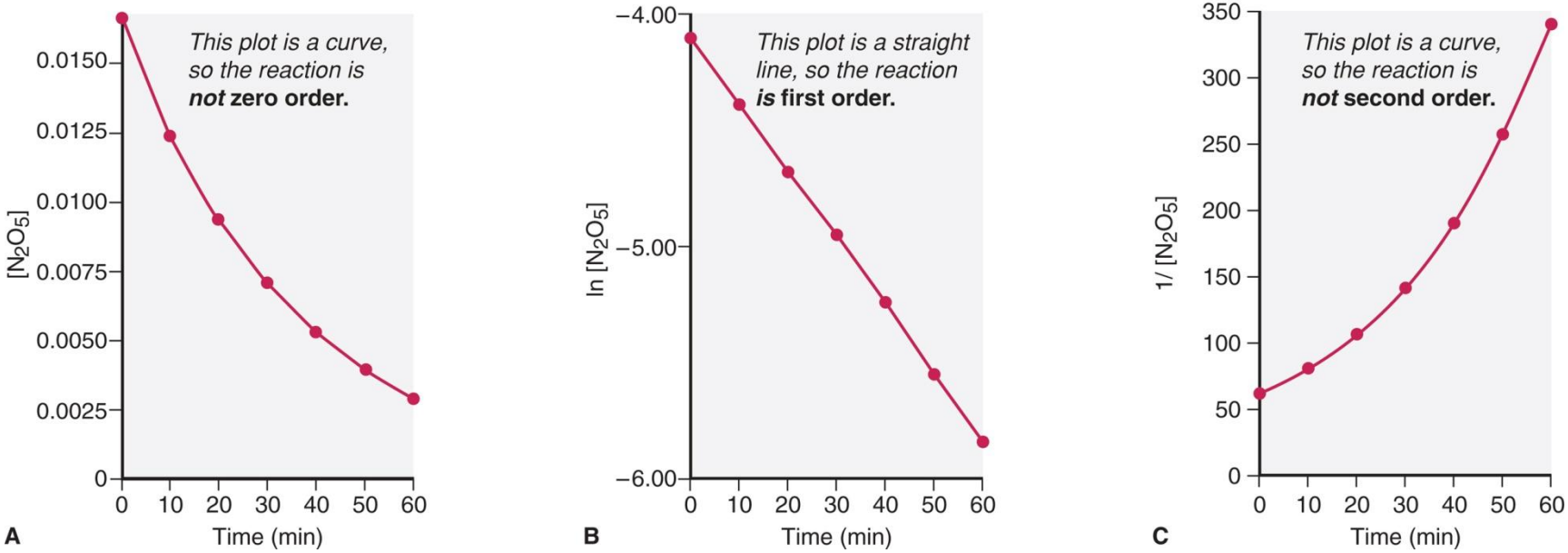
straight-line form

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

$$y = mx + b$$

A plot of [A] vs. time gives a straight line for zero -order reaction.

Figure 16.7 Graphical determination of the reaction order for the decomposition of N_2O_5.



Time (min)	$[N_2O_5]$	ln $[N_2O_5]$	$1/[N_2O_5]$
0	0.0165	−4.104	60.6
10	0.0124	−4.390	80.6
20	0.0093	−4.68	1.1×10^2
30	0.0071	−4.95	1.4×10^2
40	0.0053	−5.24	1.9×10^2
50	0.0039	−5.55	2.6×10^2
60	0.0029	−5.84	3.4×10^2

The concentration data is used to construct three different plots. Since the plot of ln $[N_2O_5]$ vs. time gives a straight line, the reaction is first order.

Reaction Half-life

The ***half-life*** ($t_{1/2}$) for a reaction is the time taken for the concentration of a reactant to drop to ***half its initial value***.

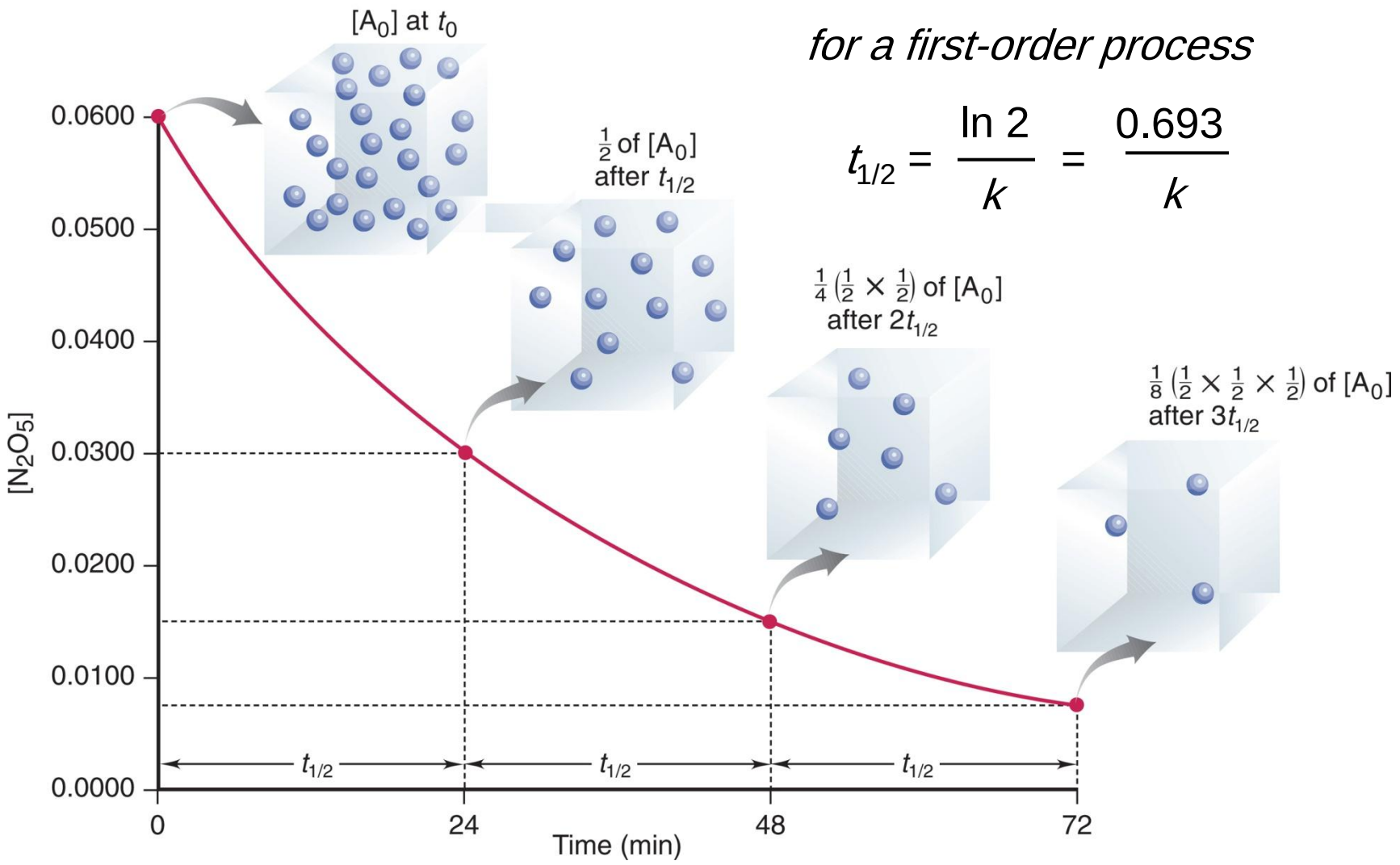
For a ***first-order*** reaction, $t_{1/2}$ does not depend on the starting concentration.

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

The half-life for a first-order reaction is a ***constant***.

Radioactive decay is a first-order process. The half-life for a radioactive nucleus is a useful indicator of its stability.

Figure 16.8 A plot of $[N_2O_5]$ vs. time for three reaction half-lives.

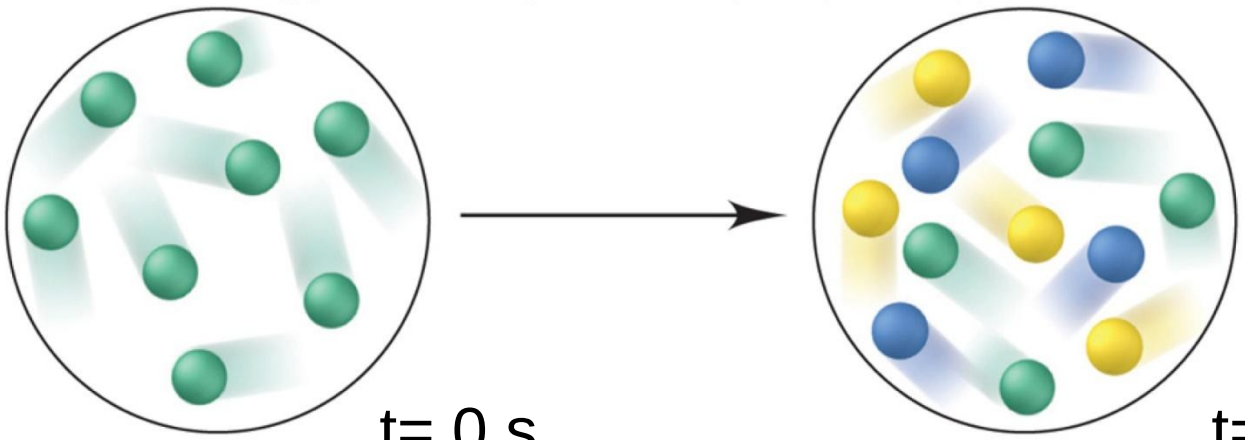


for a first-order process

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

Sample Problem 16.6 Using Molecular Scenes to Find Quantities at Various Times

PROBLEM: Substance A (*green*) decomposes to two other substances, B (*blue*) and C (*yellow*), in a first-order gaseous reaction. The molecular scenes below show a portion of the reaction mixture at two different times:



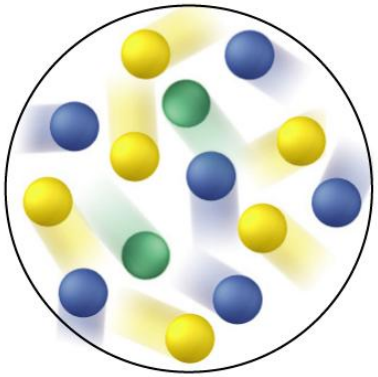
t= 0 s t= 30 s

(a) Draw a similar molecular scene of the reaction mixture at $t = 60.0$ s.
(b) Find the rate constant of the reaction.
(c) If the total pressure (P_{total}) of the mixture is 5.00 atm at 90.0 s, what is the partial pressure of substance B ($P_{B)?}$

Sample Problem 16.6

SOLUTION:

(a) After 30.0 s, the number of particles of A has decreased from 8 to 4; since [A] has halved in this time, 30.0 s is the half-life of the reaction. After 60.0 s another half-life will have passed, and the number of A particles will have halved again. Each A particle forms one B and one C particle.



$t = 60.0$ s

Sample Problem 16.6

(b) The rate constant k is determined using the formula for $t_{1/2}$ of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \quad \text{so} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30.0\ \text{s}}$$

$= 2.31 \times 10^{-2}\ \text{s}^{-1}$

(c) After 90.0 s, three half-lives will have passed. The number of A particles will have halved once again, and each A will have produced one B and one C. There will be 1 A, 7 B and 7 C particles.

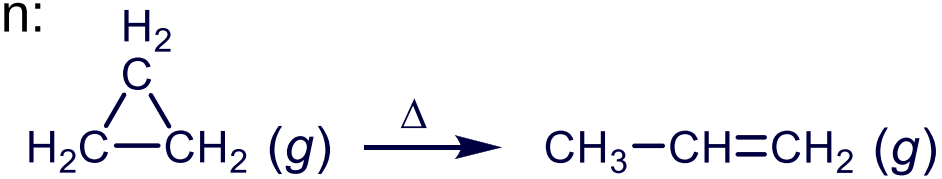
mole fraction of B, $X_B = \frac{7}{1 + 7 + 7} = 0.467$

$$P_B = X_B \times P_{total} = 0.467 \times 5.00\ \text{atm}$$

$= 2.33$ atm

Sample Problem 16.7 Determining the Half-Life of a First-Order Reaction

PROBLEM: Cyclopropane is the smallest cyclic hydrocarbon. Because its 60° bond angles allow poor orbital overlap, its bonds are weak. As a result, it is thermally unstable and rearranges to propene at 1000°C via the following first-order reaction:



The rate constant is 9.2 s^{-1}, **(a)** What is the half-life of the reaction? **(b)** How long does it take for the concentration of cyclopropane to reach one-quarter of the initial value?

PLAN: The reaction is first order, so we find $t_{1/2}$ using the half-life equation for a first order reaction. Once we know $t_{1/2}$ we can calculate the time taken for the concentration to drop to 0.25 of its initial value.

Sample Problem 16.7

SOLUTION:

(a) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{9.2\ s^{-1}}$ **= 0.075 s**

(b) For the initial concentration to drop to one-quarter of its value requires 2 half-lives to pass.

Time = 2(0.075 s) = 0.15 s

Half-life Equations

For a ***first-order*** reaction, $t_{1/2}$ does not depend on the initial concentration.

For a ***second-order*** reaction, $t_{1/2}$ is ***inversely*** proportional to the initial concentration:

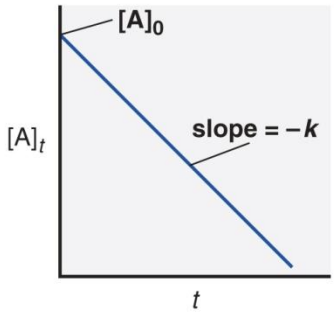
$$t_{1/2} = \frac{1}{k[A]^0} \qquad \text{(second order process; rate = } k[A]^2\text{)}$$

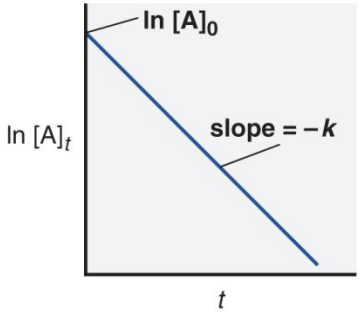
For a ***zero-order*** reaction, $t_{1/2}$ is ***directly*** proportional to the initial concentration:

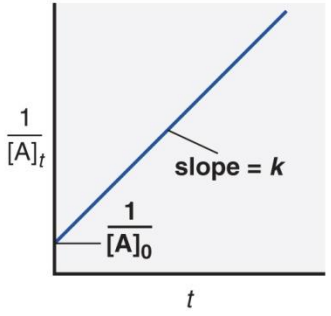
$$t_{1/2} = \frac{[A]_0}{2k^0} \qquad \text{(zero order process; rate = } k\text{)}$$

Table 16.5 An Overview of Zero-Order, First-Order, and Simple Second-Order Reactions

	Zero Order	First Order	Second Order
Rate law	rate = k	rate = k[A]	rate = k[A]^2
Units for k	mol/L·s	1/s	L/mol·s
Half-life	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Plot for straight line	$[A]_t$ vs. t	$\ln[A]_t$ vs. t	$\frac{1}{[A]_t}$ vs. t
Slope, y intercept	$-k$, $[A]_0$	$-k$, $\ln[A]_0$	k, $\frac{1}{[A]_0}$







Collision Theory and Concentration

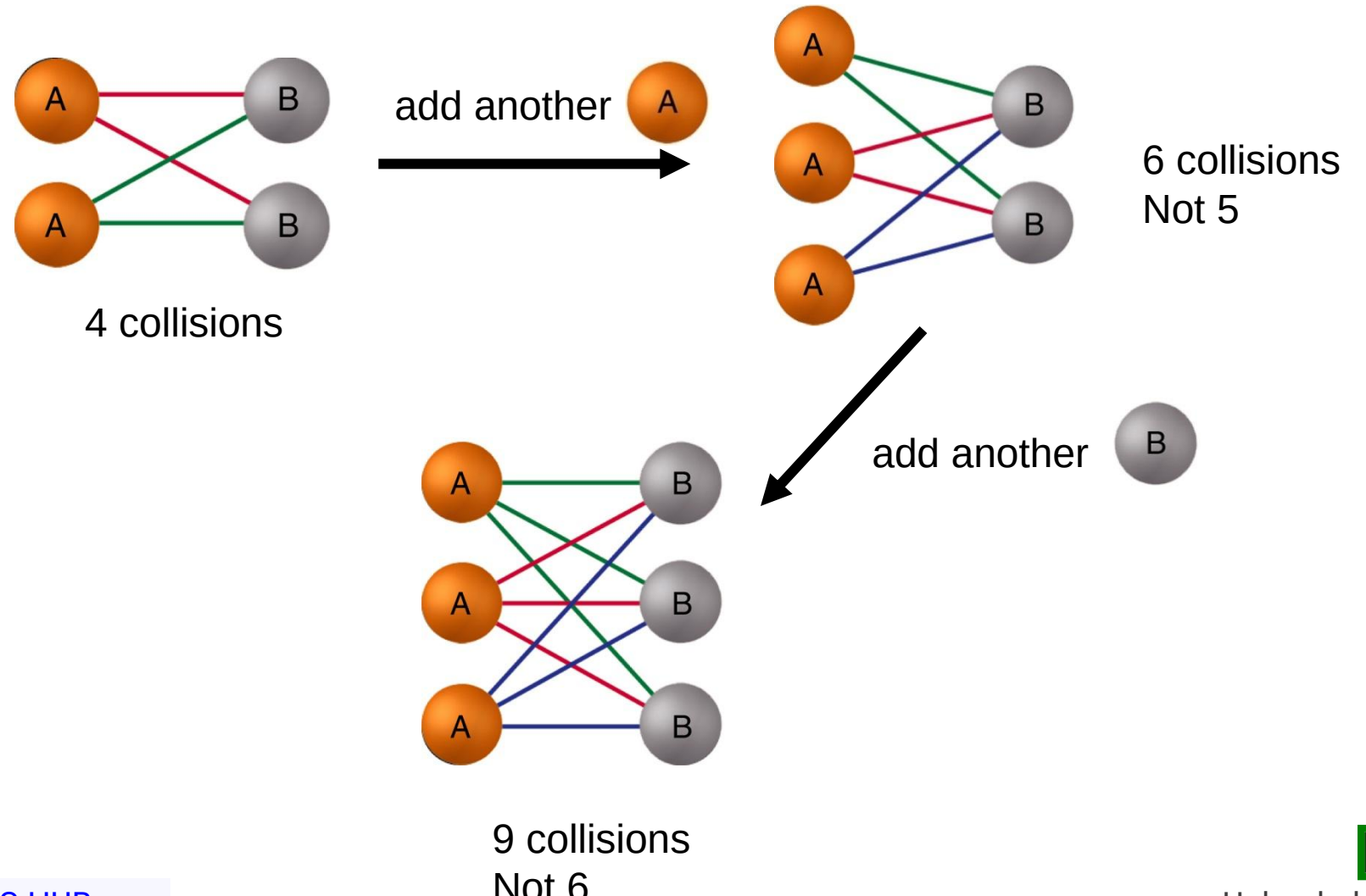
The basic principle of ***collision theory*** is that particles must collide in order to react.

An increase in the concentration of a reactant leads to a larger number of collisions, hence increasing reaction rate.

The number of collisions depends on the ***product*** (multiplication)of the numbers of reactant particles, not their sum.

Concentrations are multiplied in the rate law, not added.

Figure 16.9 The number of possible collisions is the product, not the sum, of reactant concentrations.



Temperature and the Rate Constant

Temperature has a dramatic effect on reaction rate.
For many reactions, an increase of 10°C will double or triple the rate.

Experimental data shows that ***k increases exponentially as T increases***. This is expressed in the ***Arrhenius equation***:

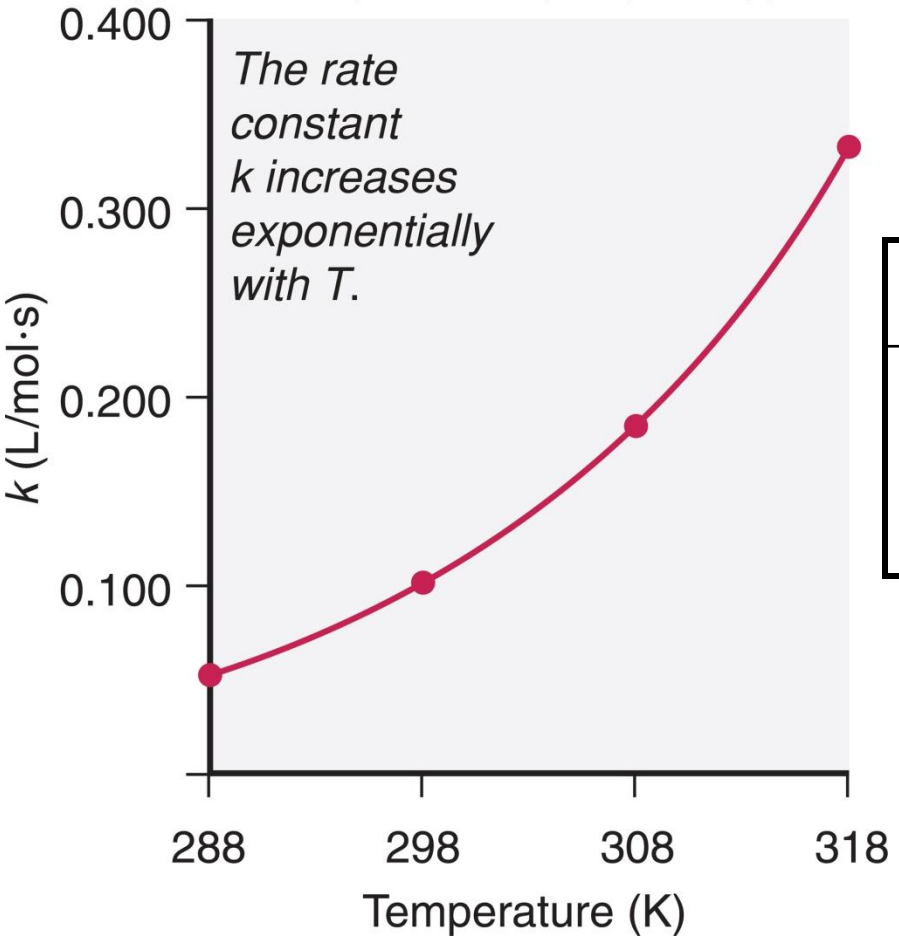
$$k = Ae^{-E_a/RT}$$

k = rate constant
A = frequency factor
E_a = activation energy

T : absolute temperature (K)

Higher T → larger k → increased rate

Figure 16.10 Increase of the rate constant with temperature for the hydrolysis of an ester.



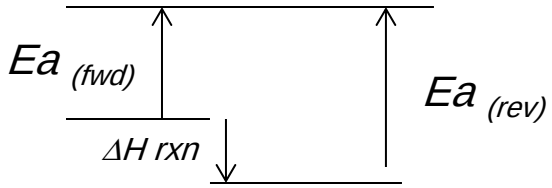
Expt	[Ester]	[H_2O]	T (K)	Rate (mol/L·s)	k (L/mol·s)
1	0.100	0.200	288	1.04×10^{-3}	0.0521
2	0.100	0.200	298	2.20×10^{-3}	0101
3	0.100	0.200	308	3.68×10^{-3}	0.184
4	0.100	0.200	318	6.64×10^{-3}	0.332

Reaction rate and k increase exponentially as T increases.

Activation Energy

In order to be ***effective***, collisions between particles must exceed a certain energy ***threshold***.

When particles collide effectively, they reach an ***activated state***. The energy difference between the reactants and the activated state is the ***activation energy*** (E_a) for the reaction.



The ***lower*** the activation energy, the ***faster*** the reaction.

$\Delta H_{rxn} = Ea_{(fwd)} - Ea_{(rev)}$, ΔH_{rxn} : > 0 endo , < 0 exo

Temperature and Collision Energy

An increase in temperature causes an increase in the kinetic energy of the particles. This leads to ***more frequent*** collisions and reaction rate increases.

- The effect of temperature on **collision frequency** is only a minor factor. not too much affect on rate.

At a higher temperature, the ***fraction*** of collisions with sufficient energy equal to or greater than E_a increases. Reaction rate therefore increases.

-Effect of temperature on **collision energy** is a major factor.

The fraction (f)of collision with energy equal to or grater than Ea is

$$f = e^{-E_a/RT}$$

Figure 16.12 **The effect of temperature on the distribution of collision energies.**

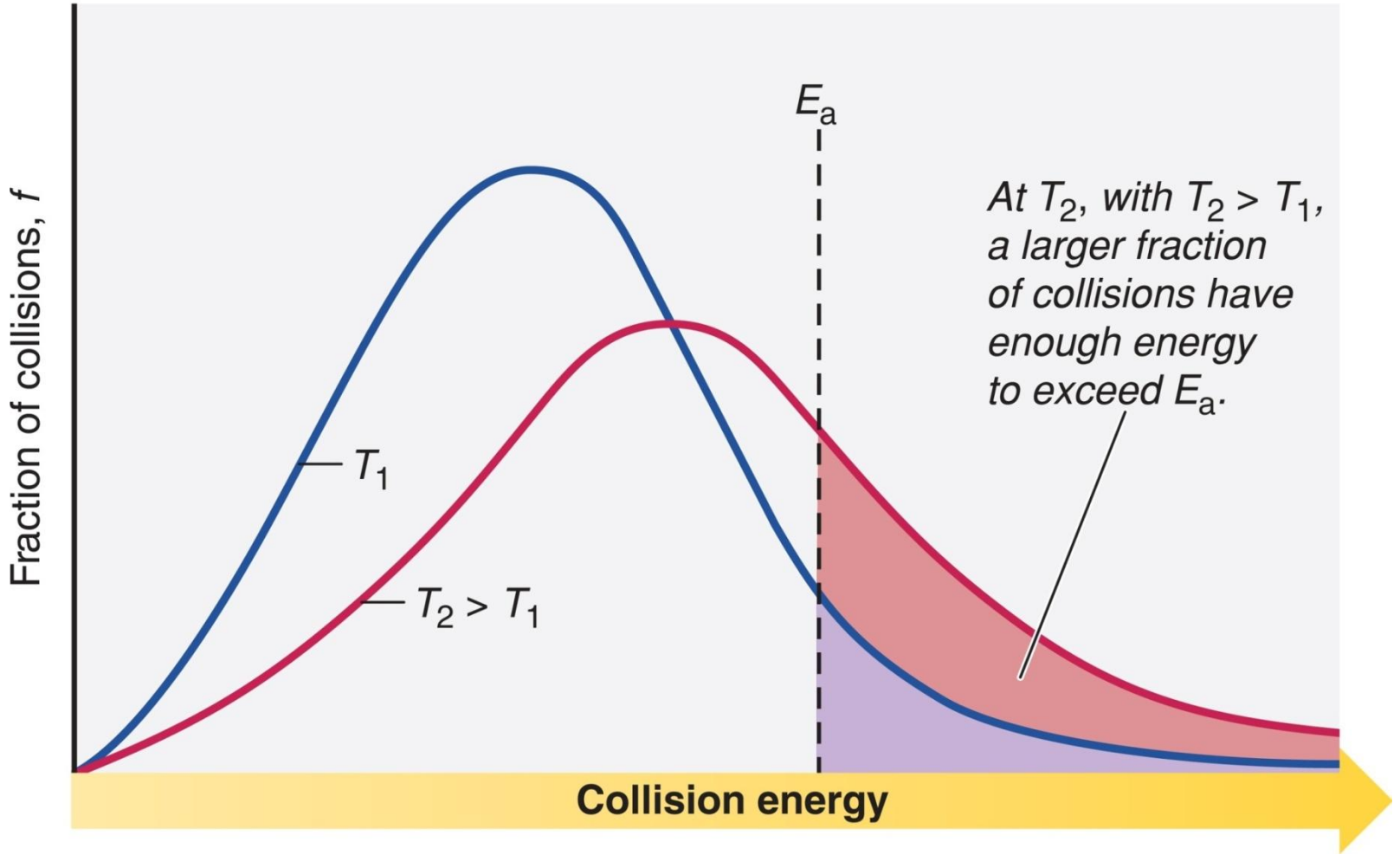


Table 16.6 The Effect of E_a and T on the Fraction (f) of Collisions with Sufficient Energy to Allow Reaction

E_a (kJ/mol)	f (at T = 298 K)
50	1.70×10^{-9}
75	7.03×10^{-14}
100	2.90×10^{-18}

T	f (at E_a = 50 kJ/mol)
25°C (298 K)	1.70×10^{-9}
35°C (308 K)	3.29×10^{-9}
45°C (318 K)	6.12×10^{-9}

$$f = e^{-E_a/RT}$$

Smaller Ea → larger f → larger k → increased rate

(fraction of sufficiently energetic collision)

Calculating Activation Energy

E_a can be calculated from the Arrhenius equation:

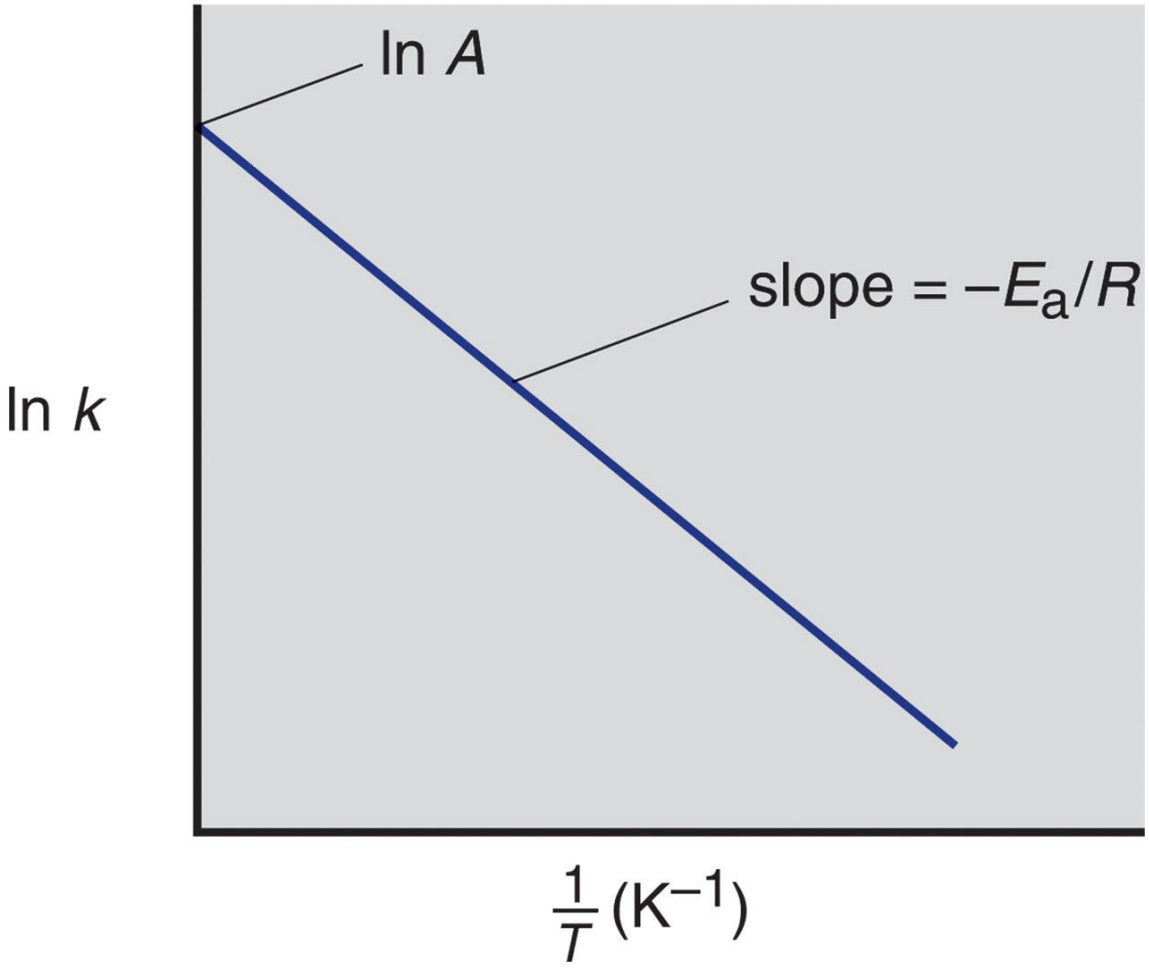
$$k = Ae^{-E_a/RT} \quad \text{so} \quad \ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

straight-line form

If data is available at two different temperatures:

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

Figure 16.13 Graphical determination of the activation energy.



$$\ln k = \ln A - \frac{E_a}{R}\left[\frac{1}{T}\right]$$

$$y = mx + b$$

Sample Problem 16.8 Determining the Energy of Activation

PROBLEM: The decomposition of hydrogen iodide, $2HI(g) \rightarrow H_2(g) + I_2(g)$, has rate constants of 9.51×10^{-9} L/mol·s at 500. K and 1.10×10^{-5} L/mol·s at 600. K. Find E_a.

PLAN: We are given two rate constants and two temperatures, so we can use the Arrhenius equation to solve for E_a.

SOLUTION:

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

$$E_a = -(8.314 \text{ J/mol·K})\left(\ln \frac{1.10 \times 10^{-5} \text{ L/mol·s}}{9.51 \times 10^{-9} \text{ L/mol·s}}\right)\left(\frac{1}{600.\text{K}} - \frac{1}{500.\text{ K}}\right)^{-1}$$

$$= 1.76 \times 10^5 \text{ J/mol} = 1.76 \times 10^2 \text{ kJ/mol}$$

Molecular Structure and Reaction Rate

For a collision between particles to be effective, it must have both sufficient ***energy*** and the appropriate ***relative orientation*** between the reacting particles.

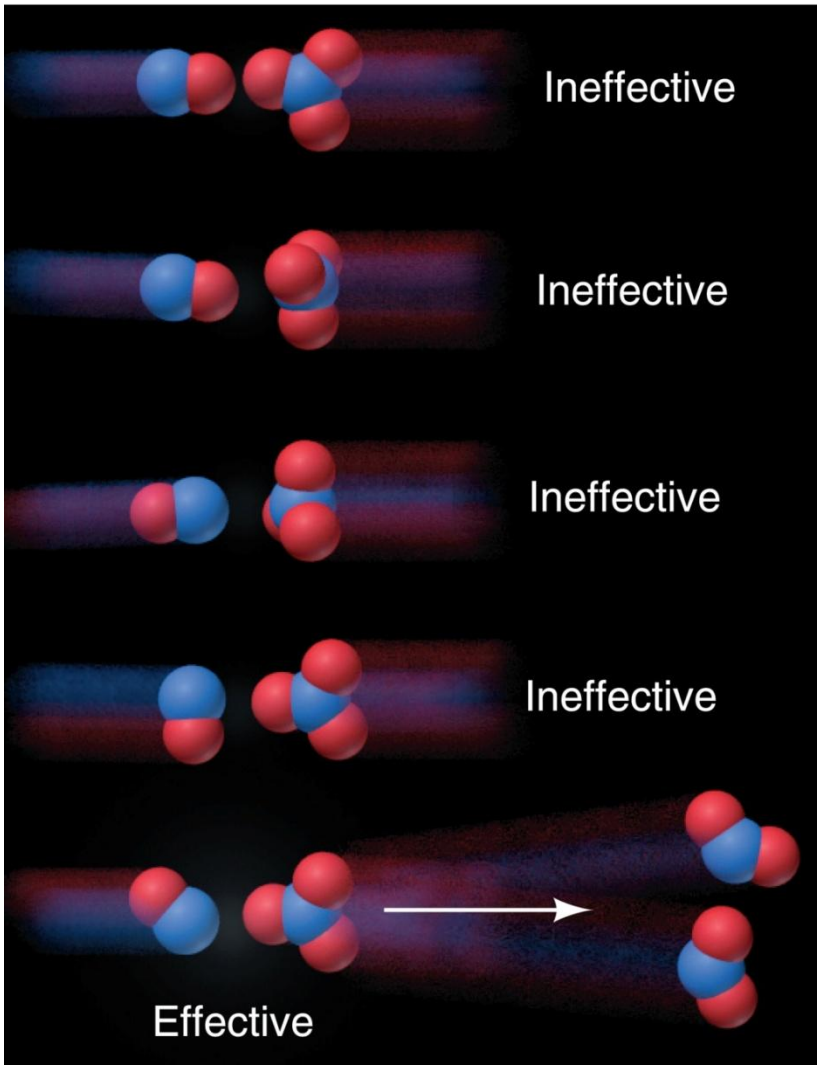
The term *A* in the Arrhenius equation is the ***frequency factor*** for the reaction.

$$k = Ae^{-E_a/RT} \qquad A = pZ$$

p = orientation probability factor
Z = collision frequency

The term *p* is specific for each reaction and is related to the structural complexity of the reactants.

Figure 16.14 The importance of molecular orientation to an effective collision.



$$NO(g) + NO_3(g) \rightarrow 2NO_2(g)$$

There is only one relative orientation of these two molecules that leads to an effective collision.

Transition State Theory

An effective collision between particles leads to the formation of a ***transition state*** or ***activated complex***.

The transition state is an unstable species that contains ***partial bonds***. It is a transitional species partway between reactants and products.

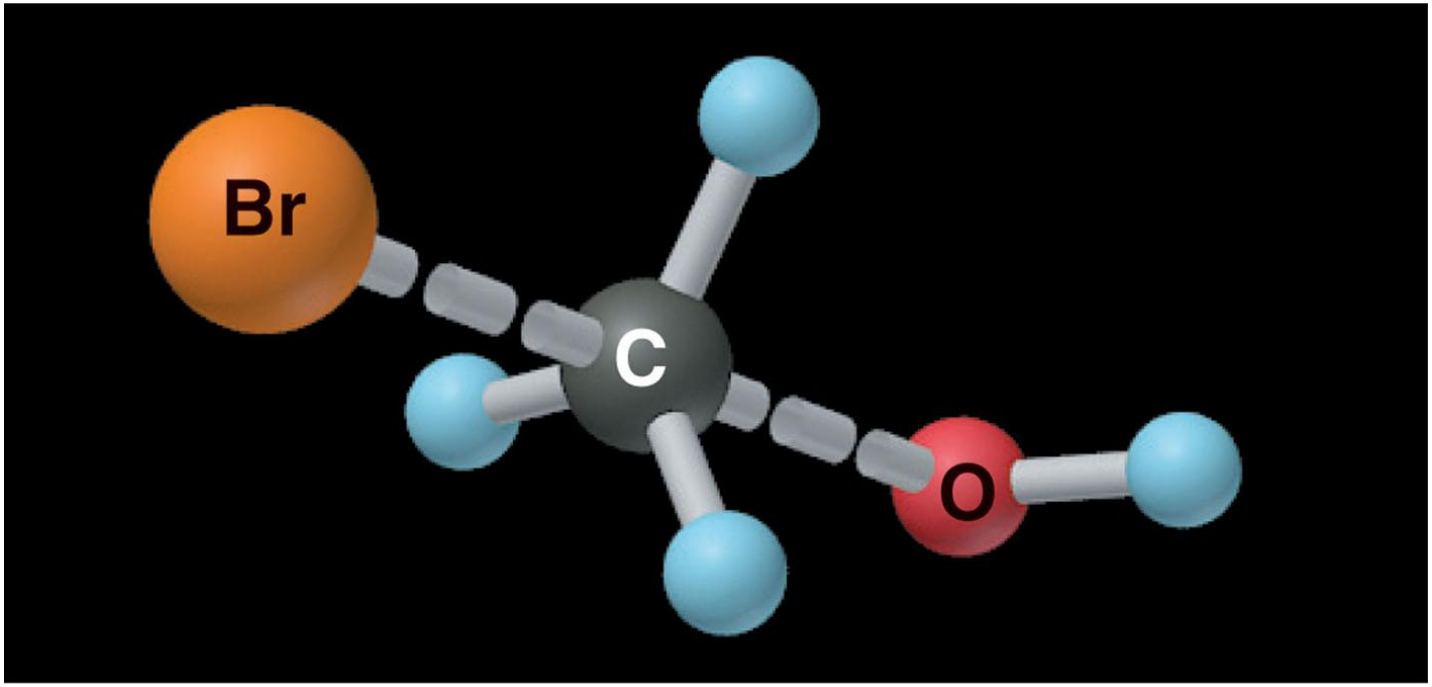
Transition states cannot be isolated.

The transition state exists at the point of maximum potential energy.

The energy required to form the transition state is the activation energy.

Figure 16.15 The transition state of the reaction between $BrCH_3$ and OH^-.

$$BrCH_3 + OH^- \rightarrow Br^- + CH_3OH$$



The transition state contains partial bonds (*dashed*) between C and Br and between C and O. It has a trigonal bypyramidal shape.

Figure 16.16 Depicting the reaction between $BrCH_3$ and OH^-.

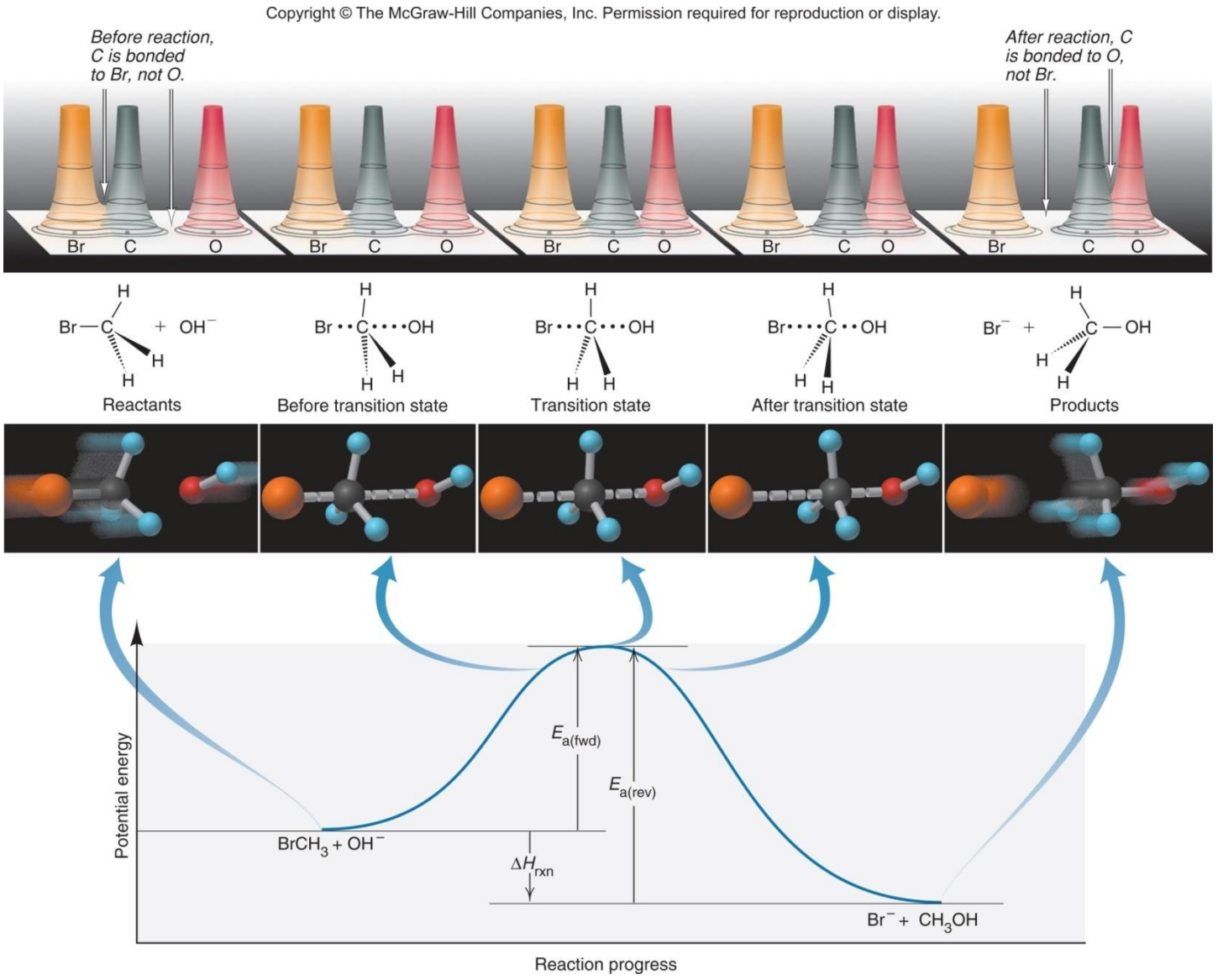
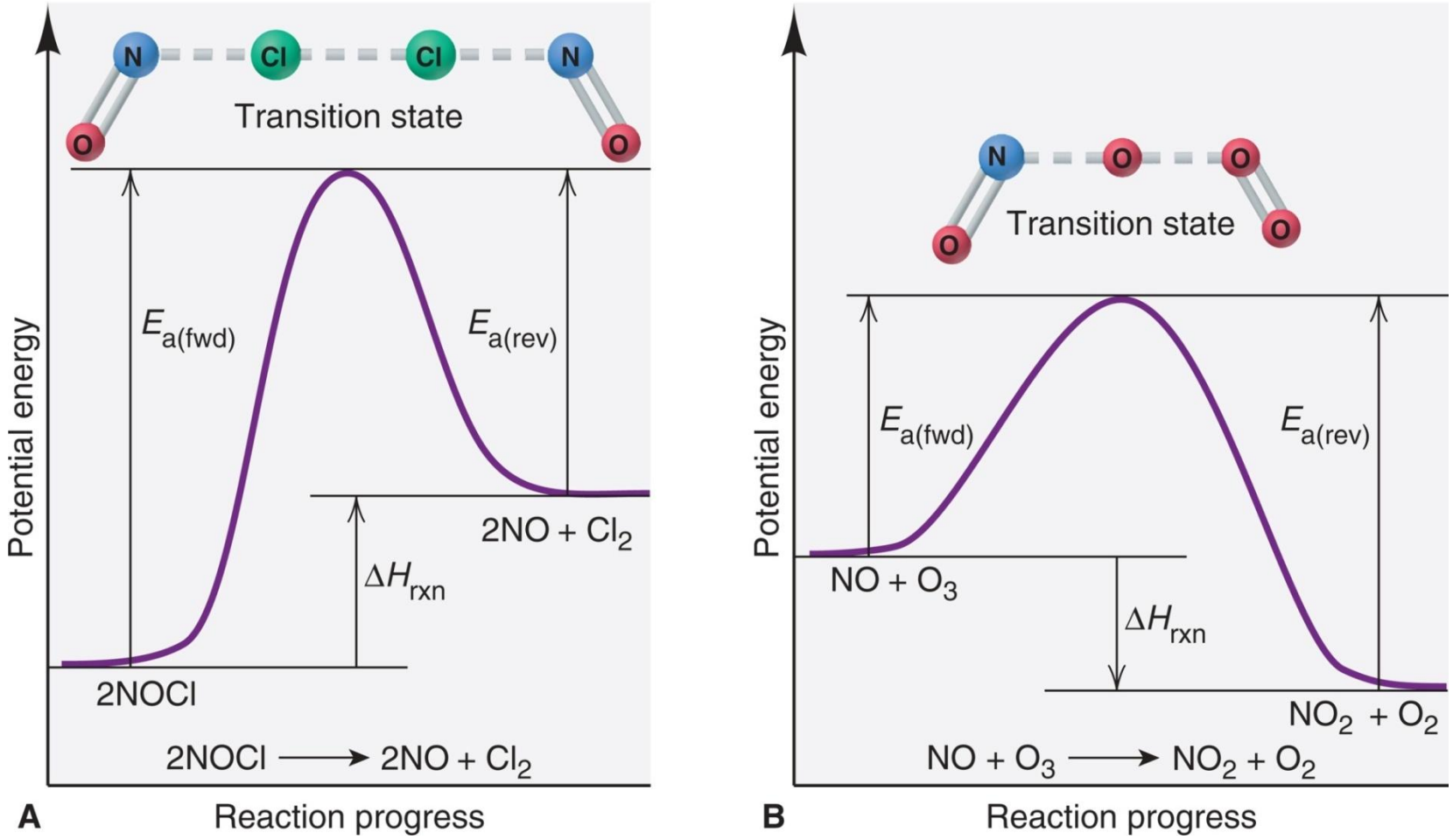


Figure 16.17 **Reaction energy diagrams and possible transition states for two reactions.**



Sample Problem 16.9 **Drawing Reaction Energy Diagrams and Transition States**

PROBLEM: A key reaction in the upper atmosphere is

$$O_3(g) + O(g) \rightarrow 2O_2(g)$$

The $E_{a(fwd)}$ is 19 kJ, and the ΔH_{rxn} for the reaction as written is -392 kJ. Draw a reaction energy diagram, predict a structure for the transition state, and calculate $E_{a(rev)}$.

PLAN: The reaction is highly exothermic (ΔH_{rxn} = -392 kJ), so the products are much lower in energy than the reactants. The small $E_{a(fwd)}$ (19 kJ) means that the energy of the reactants lies only slightly below that of the transition state. We calculate the value of $E_{a(rev)}$ from the value of ΔH and $E_{a(fwd)}$.

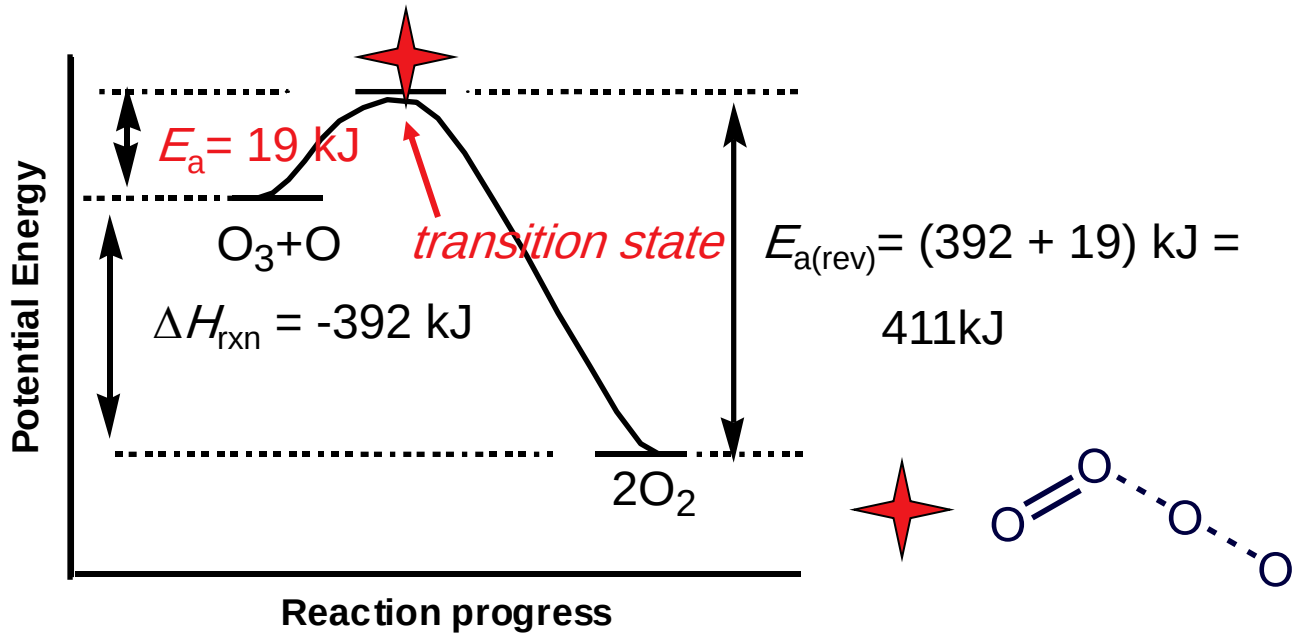
To predict the transition state structure, we note that one O-O bond of O_3 breaks and a new O-O bond forms.

Sample Problem 16.9

SOLUTION:

$\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$

So $E_{a(rev)} = + E_{a(fwd)} - \Delta H_{rxn}$ = 19 kJ – (-392 kJ) = **411 kJ**



Reaction Mechanisms

The ***mechanism*** of a reaction is the sequence of single reaction steps that make up the overall equation.

The individual steps of the reaction mechanism are called ***elementary steps*** because each one describes a ***single molecular event***.

Each elementary step is characterized by its ***molecularity***, the number of particles involved in the reaction.

The rate law for an elementary step ***can*** be deduced from the reaction stoichiometry – ***reaction order equals molecularity*** **for an elementary step only**.

Table 16.7 Rate Laws for General Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \longrightarrow$ product	Unimolecular	Rate = K [A]
$2A \longrightarrow$ product	Bimolecular	Rate = $k[A]^2$
$A + B \longrightarrow$ product	Bimolecular	Rate = $k[A][B]$
$2A + B \longrightarrow$ product	Termolecular	Rate = $k[A]^2[B]$

Sample Problem 16.10 Determining Molecularity and Rate Laws for Elementary Steps

PROBLEM: The following elementary steps are proposed for a reaction mechanism:

(1) $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$

(2) $NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$

(a) Write the overall balanced equation.
(b) Determine the molecularity of each step.
(c) Write the rate law for each step.

PLAN: We find the overall equation from the sum of the elementary steps. The molecularity of each step equals the total number of ***reactant*** particles. We write the rate law for each step using the molecularities as reaction orders.

Sample Problem 16.10

SOLUTION:

(a) Writing the overall balanced equation:

(1) $NO_2Cl(g) \rightarrow NO_2(g) + \cancel{Cl(g)}$

(2) $NO_2Cl(g) + \cancel{Cl(g)} \rightarrow NO_2(g) + Cl_2(g)$

$$\mathbf{2NO_2Cl(}g\mathbf{) \rightarrow 2NO_2(}g\mathbf{) + Cl_2(}g\mathbf{)}$$

(b) Step(1) is **unimolecular.**
Step(2) is **bimolecular.**

(c) $\mathbf{rate_1 = }k_1\mathbf{[NO_2Cl]}$

$\mathbf{rate_2 = }k_2\mathbf{[NO_2Cl][Cl]}$

The Rate-Determining Step of a Reaction

The ***slowest*** step in a reaction is the ***rate-determining*** or ***rate-limiting*** step.

The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$
has been proposed to occur by a two-step mechanism:

(1) $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ [slow; rate-determining]
(2) $NO_2(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ [fast]

Observed rate law: rate = $k[NO_2]^2$

The rate law for the rate-determining step becomes the rate law for the overall reaction.

Correlating Mechanism with the Rate Law

A valid mechanism must meet three criteria:

-The elementary steps must add up to the overall balanced equation.

- The elementary steps must be reasonable. Should generally involve one reactant particles or two (unimolecular or bimolecular

- The mechanism must correlate with the ***observed*** *rate law.*

A mechanism is a ***hypothesis*** –we cannot ***prove*** it is correct, but if it is consistent with the data, and can be used to predict results accurately, it is a useful ***model*** for the reaction.

Mechanisms with a Slow Initial Step

The overall reaction $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$ has an experimental rate law Rate = $k[NO_2][F_2]$.

The accepted mechanism is

(1) $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$ [slow; rate determining]

(2) $NO_2(g) + F(g) \rightarrow NO_2F(g)$ [fast]

$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$

The elementary steps sum to the overall balanced equation:

Both steps are bimolecular and are therefore reasonable.

$rate_1 = k_1[NO_2][F_2]$

$rate_2 = k_2[NO_2][F]$

Step 1 is the slow step, and $rate_1$ correlates with the ***observed*** rate law.

The mechanism is therefore reasonable.

Mechanisms with a Fast Initial Step

The overall reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ has an experimental rate law Rate = $k[NO]^2[O_2]$.

A proposed mechanism is

(1) $NO(g) + O_2(g) \leftrightarrows NO_3(g)$ [fast]

(2) $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$ [slow; rate determining]

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

The elementary steps sum to the overall balanced equation:

Both steps are bimolecular and are therefore reasonable.

$rate_{1(fwd)} = k_1[NO][O_2]$

$rate_{1(rev)} = k_{-1}[NO_3]$

$rate_2 = k_2[NO_3][NO]$

When equilibrium (1) has been established

$rate_{1(fwd)} = rate_{1(rev)}$

$k_1[NO][O_2] = k_{-1}[NO_3]$

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

$$\text{rate}_2 = k_2[NO_3][NO] = k_2\left(\frac{k_1}{k_{-1}}[NO][O_2]\right)[NO]$$

The ratio of rate constants is itself a constant, equal to the overall rate constant for the reaction, so
$\text{rate}_2 = k[NO]^2[O_2]$ which is consistent with the observed rate law.

For any mechanism, only reactants involved up to and including the slow (rate-determining) step appear in the overall rate law.

Catalysis: Speeding up a Reaction

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

In general, a catalyst provides an alternative reaction pathway that has a ***lower total activation energy*** than the uncatalyzed reaction.

A catalyst will speed up both the forward and the reverse reactions.

A catalyst does not affect either ΔH or the overall yield for a reaction.

catalyst → ***Lower E_a*** → ***larger k*** → ***higher rate***

Figure 16.19 Reaction energy diagram for a catalyzed (*green*) and uncatalyzed (*red*) process.

1) A + catalyst ⟶ C

2) C + B ⟶ product + catalyst

$[E_{a1(fwd)} + E_{a2(fwd)}] < E_{a(fwd)}$ uncatalyzed

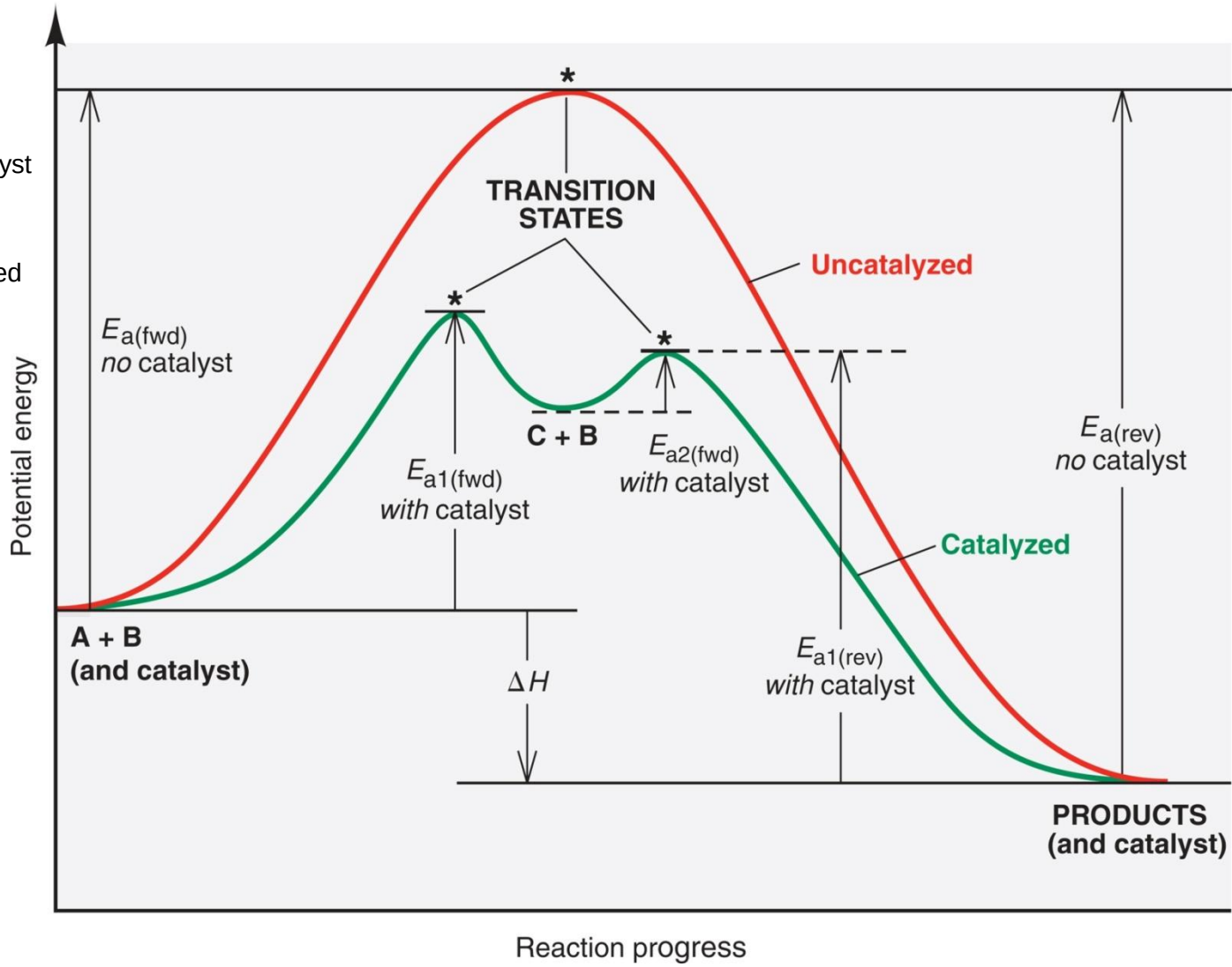
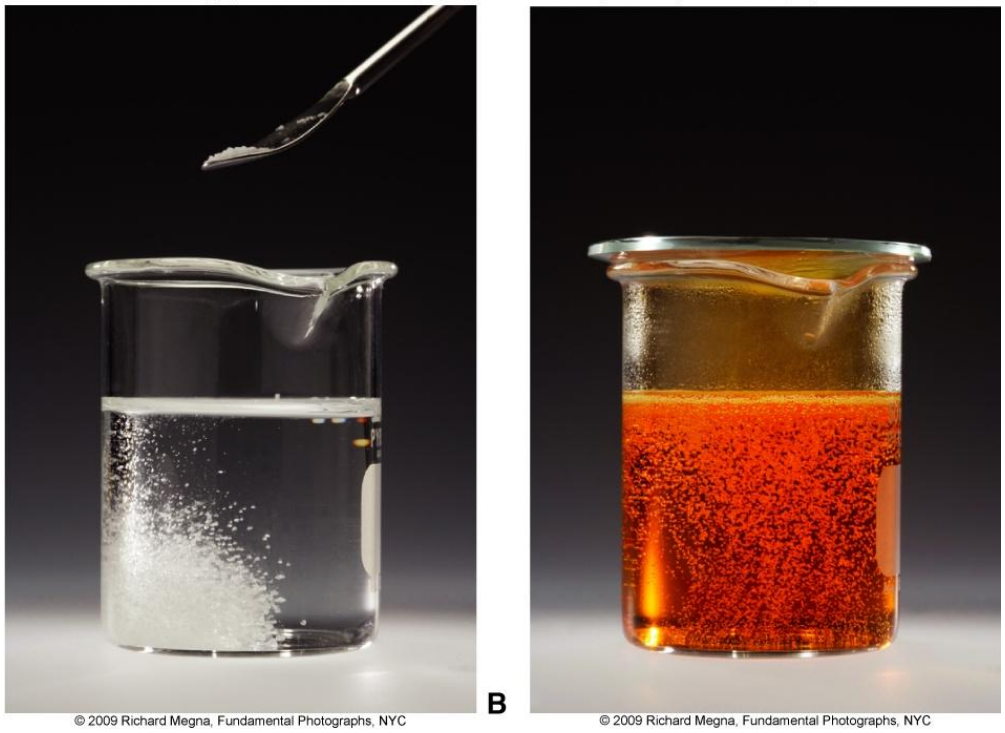


Figure 16.20 The catalyzed decomposition of H_2O_2.

A ***homogeneous*** catalyst is in the same phase as the reaction mixture.It must be a gas, liquid, solid.



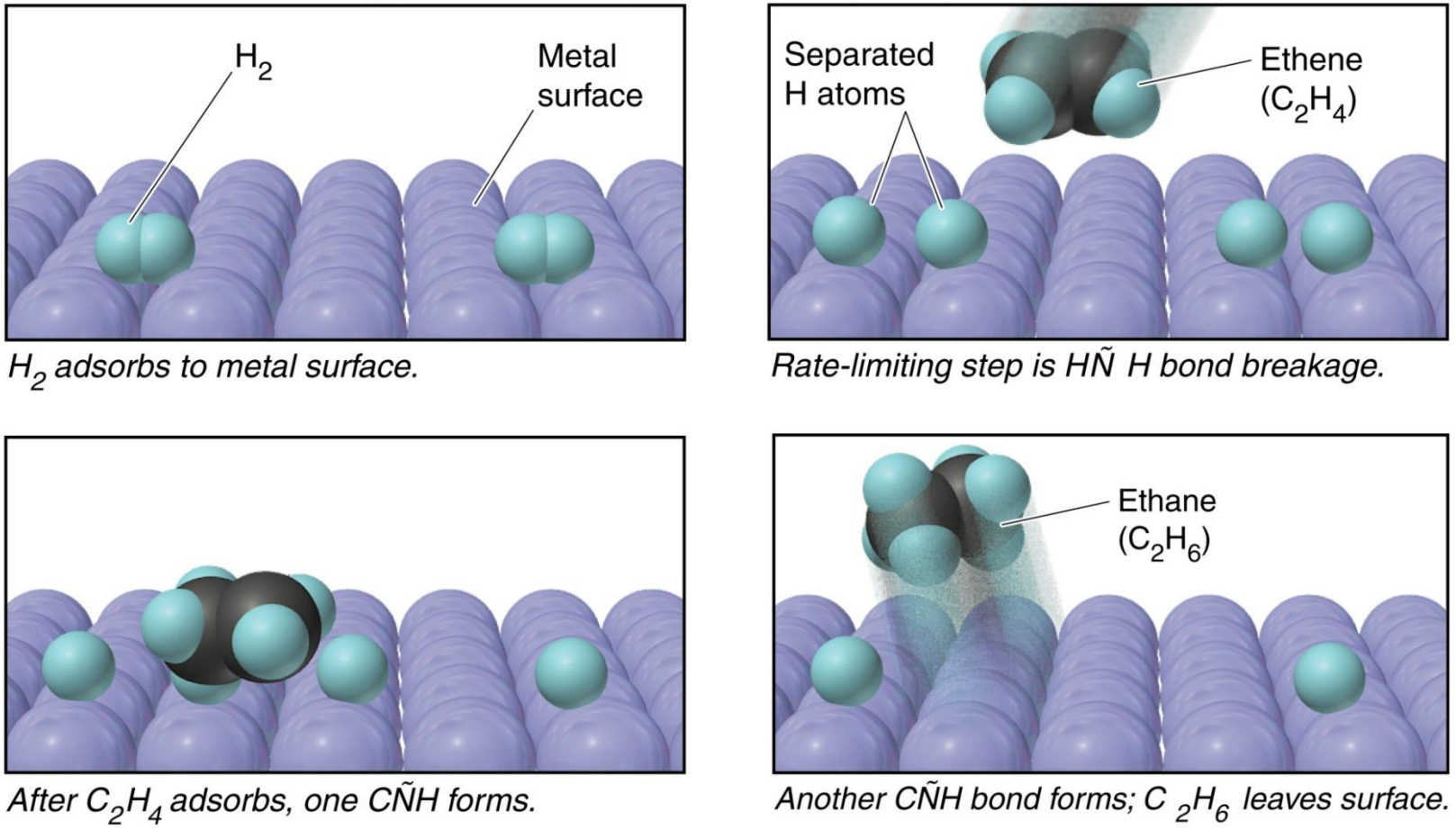
A

B

A small amount of NaBr is added to a solution of H_2O_2.

Oxygen gas forms quickly as $Br^-(aq)$ catalyzes the H_2O_2 decomposition; the intermediate Br_2 turns the solution orange.

Figure 16.21 The metal-catalyzed hydrogenation of ethene.



H_2 adsorbs to metal surface.

Rate-limiting step is HÑ H bond breakage.

After C_2H_4 adsorbs, one CÑH forms.

Another CÑH bond forms; C_2H_6 leaves surface.

A ***heterogeneous*** catalyst is in a different phase than the reaction mixture. most often solids interact with gaseous or liquid reactants. Ni, Pt.