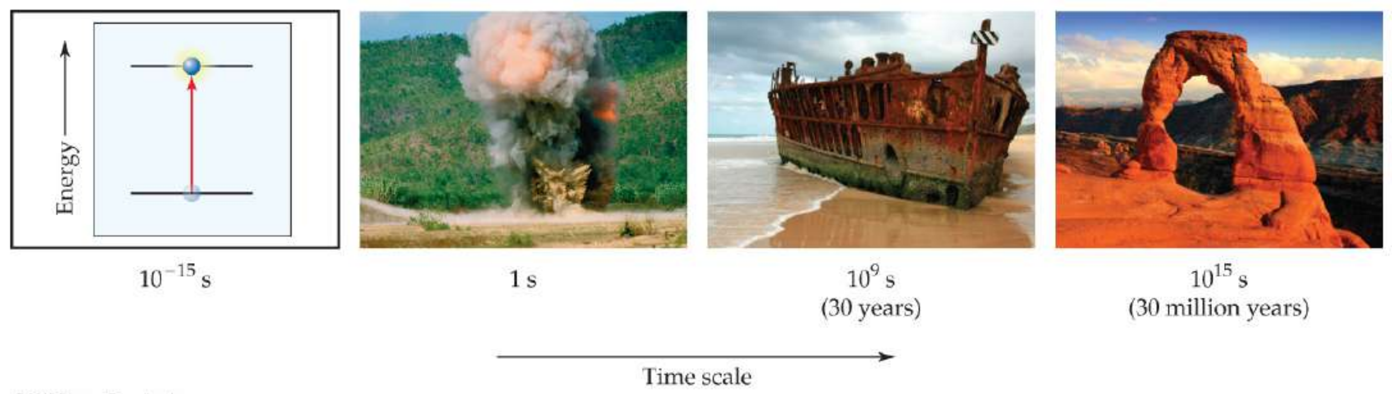
CHAPTER 14
CHEMICAL KINETICS

14.1 FACTORS THAT AFFECT REACTION RATES

CHEMICAL KINETICS

- In chemical kinetics we study the rate (or speed) at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism**, a molecular-level view of the path from reactants to products.



FACTORS THAT AFFECT REACTION RATES

1) Physical state of the reactants
2) Reactant concentrations
3) Reaction temperature
4) Presence of a catalyst

PHYSICAL STATE OF THE REACTANTS

- The more readily the reactants collide, the more rapidly they react.
- Homogeneous reactions are often faster.
- Heterogeneous reactions that involve solids are faster if the surface area is increased; i.e., a fine powder reacts faster than a pellet or tablet.

REACTANT CONCENTRATIONS

- Increasing reactant concentration generally increases reaction rate.
- Since there are more molecules, more collisions occur.

Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly

Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly

If a heated steel nail were placed in pure O_2, would you expect it to burn as readily as the steel wool does?

a. Yes, the nail and steel wool should have the same composition.

b. Yes, the O_2 is the major contributor to the reaction.

c. No, the surface area of the nail is not as great as that of the wool.

Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly

Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly

TEMPERATURE

- Reaction rate generally increases with increased temperature.
- Kinetic energy of molecules is related to temperature.
- At higher temperatures, molecules move more quickly, increasing numbers of collisions and the energy the molecules possess during the collisions.

PRESENCE OF A CATALYST

- Catalysts affect rate without being in the overall balanced equation.
- Catalysts affect the kinds of collisions, changing the mechanism (individual reactions that are part of the pathway from reactants to products).
- Catalysts are critical in many biological reactions.

In a reaction involving reactants in the gas state, how does increasing the partial pressures of the gases affect the reaction rate?

a. The effect of increasing the partial pressures of the reactive components of a gaseous mixture depends on which side of the chemical equation has the most gas molecules.

b. Increasing the partial pressures of the reactive components of a gaseous mixture has no effect on the rate of reaction if each reactant pressure is increased by the same amount.

c. Increasing the partial pressures of the reactive components of a gaseous mixture increases the rate of reaction.

d. Increasing the partial pressures of the reactive components of a gaseous mixture decreases the rate of reaction.

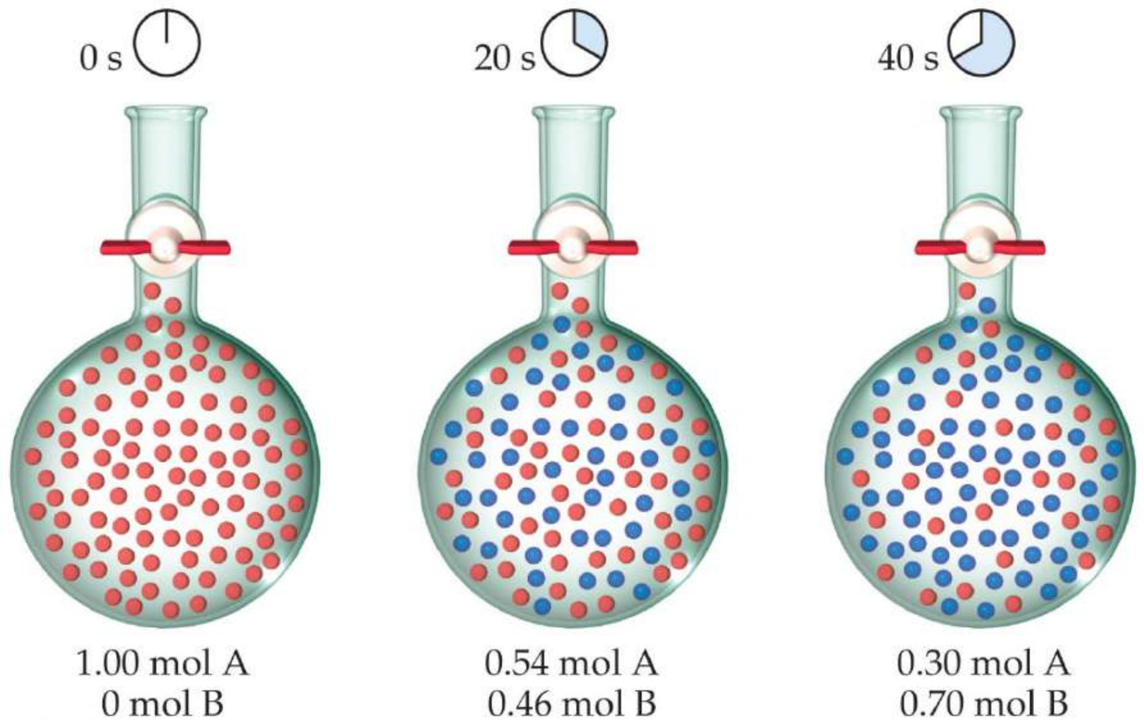
14.2 REACTION RATES

REACTION RATE

- **Rate** is a change in concentration over a time period: $\Delta[\ ]/\Delta t$.
- Δ means “change in.”
- [ ] means molar concentration.
- *t* represents time.
- Types of rate measured:
  - ➢average rate
  - ➢instantaneous rate
  - ➢initial rate

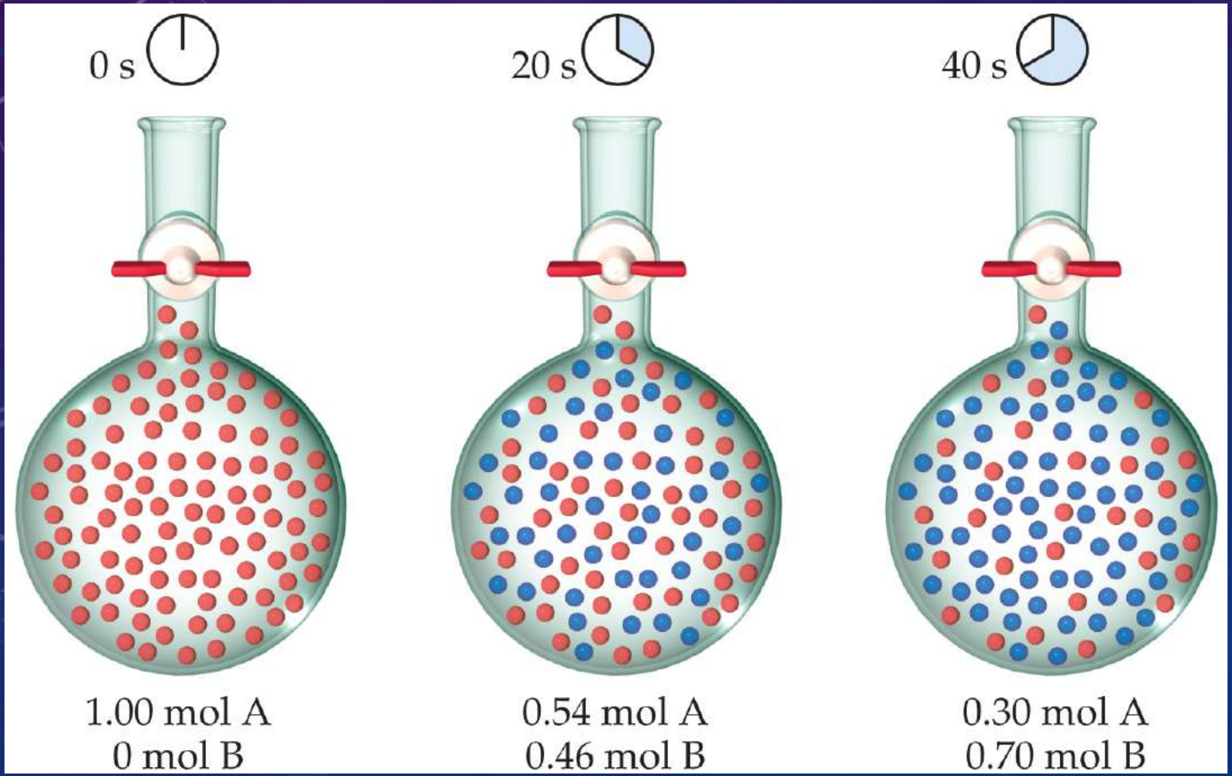
Estimate the number of moles of A in the mixture after 30 s.

a. ~0.6 mol A
b. ~0.4 mol A
c. < 0.4 mol A
d. > 0.3 mol A and < 0.4 mol A



Sample Exercise 14.1 Calculating an Average Rate of Reaction

From the data given in the caption of Figure 14.3, calculate the average rate at whichA disappears over the time interval from 20 s to 40 s.



Practice Exercise 1

If the experiment in Figure 14.3 is run for 60 s, 0.16 mol A remain. Which of the following statements is or are true?

(i)After 60 s there are 0.84 mol B in the flask.

(ii)The decrease in the number of moles of A from $t_1 = 0$ s to $t_2 = 20$ s is greater than that from $t_1 = 40$ to $t_2 = 60$ s.

(iii)The average rate for the reaction from $t_1 = 40$ s to $t_2 = 60$ s is 7.0×10^{-3} *M*/s.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

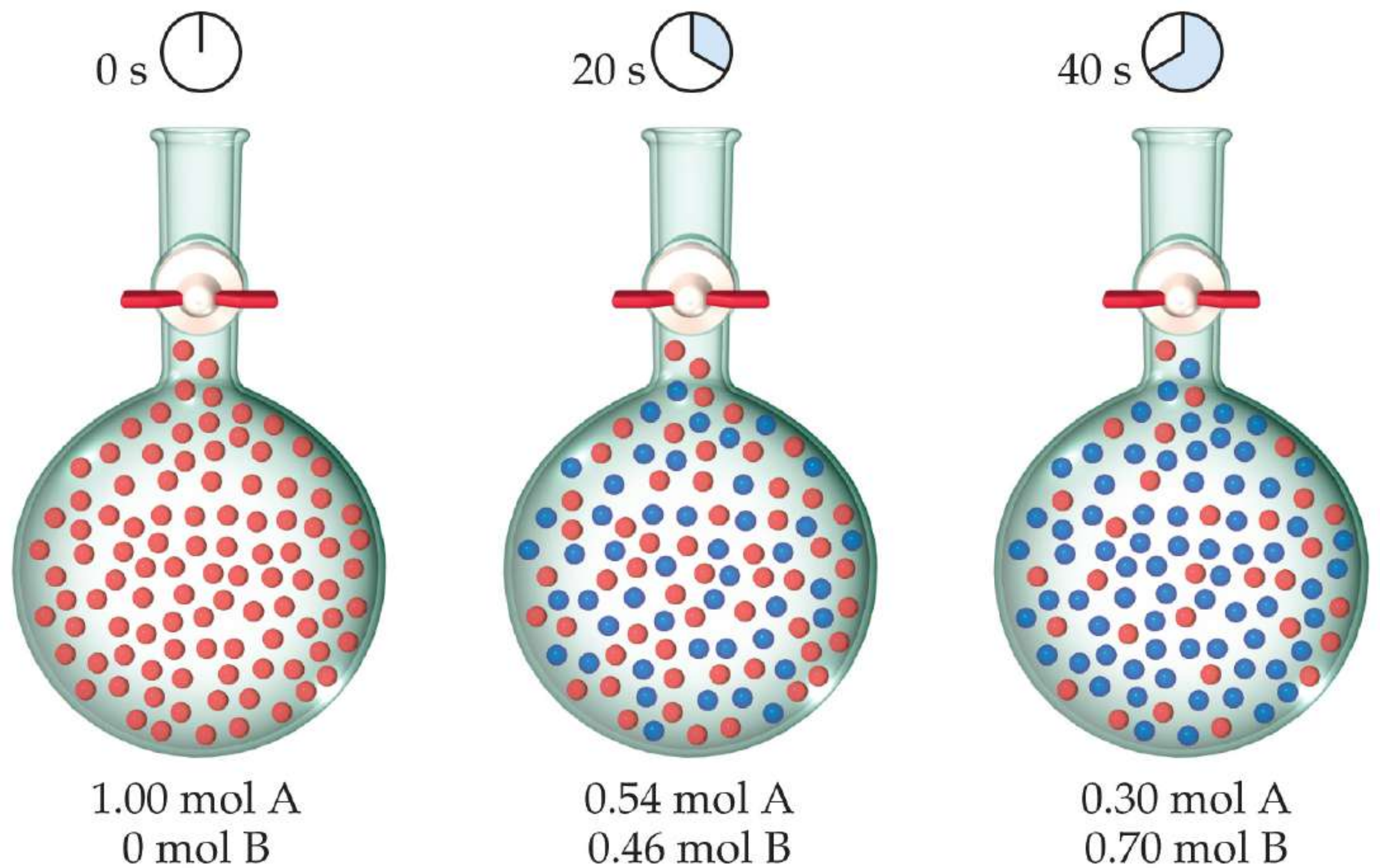
(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

(e) All three statements are true.

Practice Exercise 2

Use the data in Figure 14.3 to calculate the average rate of appearance of B over the time interval from 0 s to 40 s.



FOLLOWING REACTION RATES

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

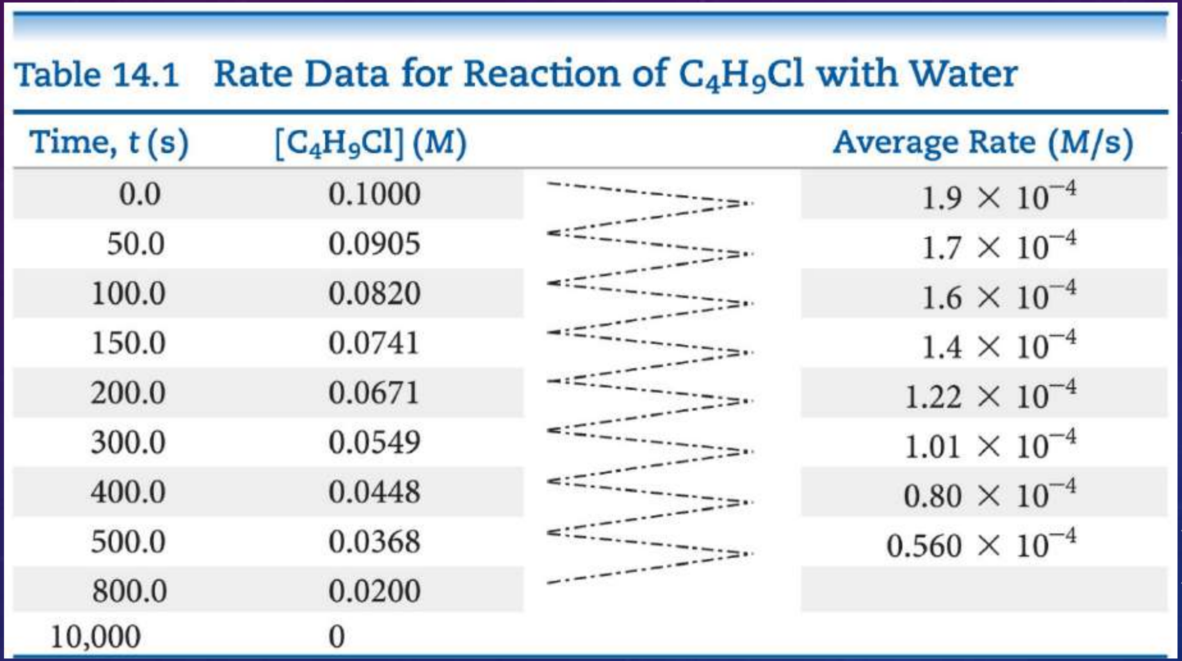


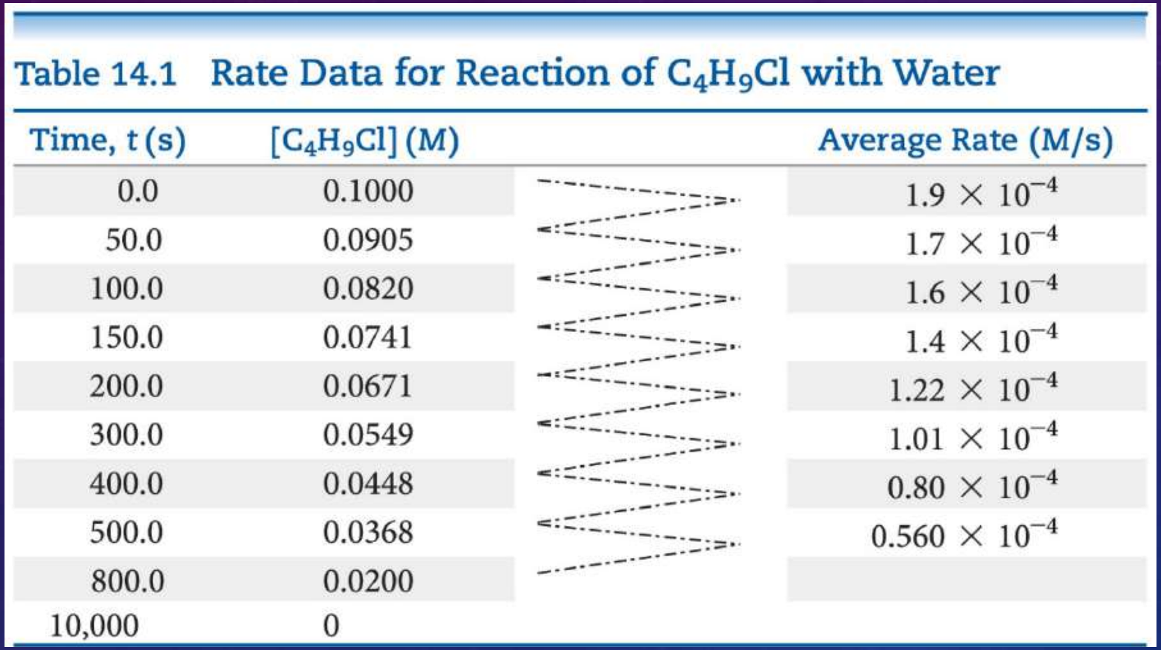
Table 14.1 Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- ➢ Rate of a reaction is measured using the concentration of a reactant or a product over time.
- ➢ In this example, $[C_4H_9Cl]$ is followed.

FOLLOWING REACTION RATES

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



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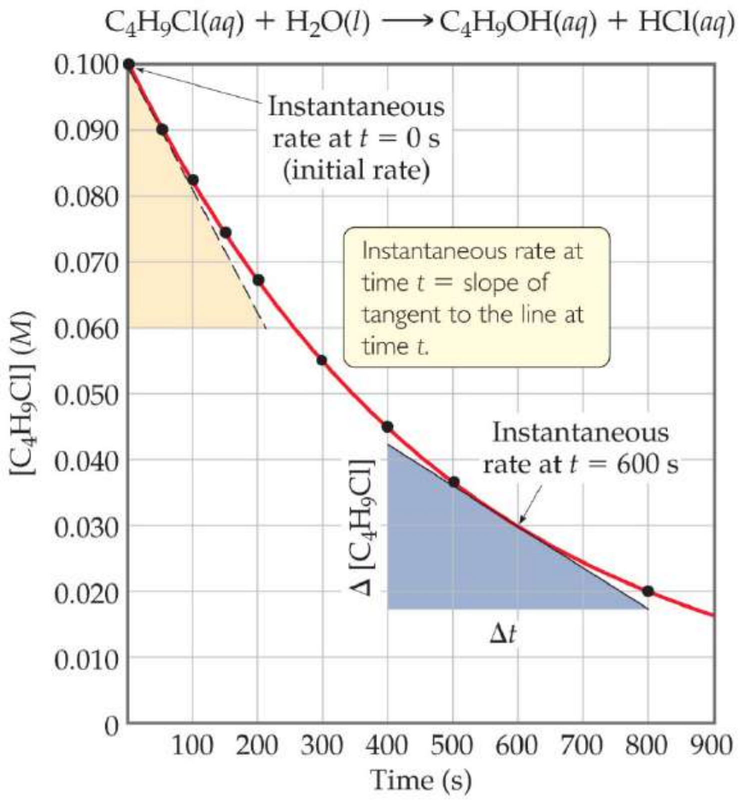
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- The average rate is calculated by the –(change in $[C_4H_9Cl]$) ÷ (change in time).
- The table shows the average rate for a variety of time intervals.

PLOTTING RATE DATA

- A plot of the data gives more information about rate.
- The slope of the curve at one point in time gives the **instantaneous rate**.
- The instantaneous rate at time zero is called the **initial rate**; this is often the rate of interest to chemists.
- This figure shows instantaneous and initial rate of the earlier example.

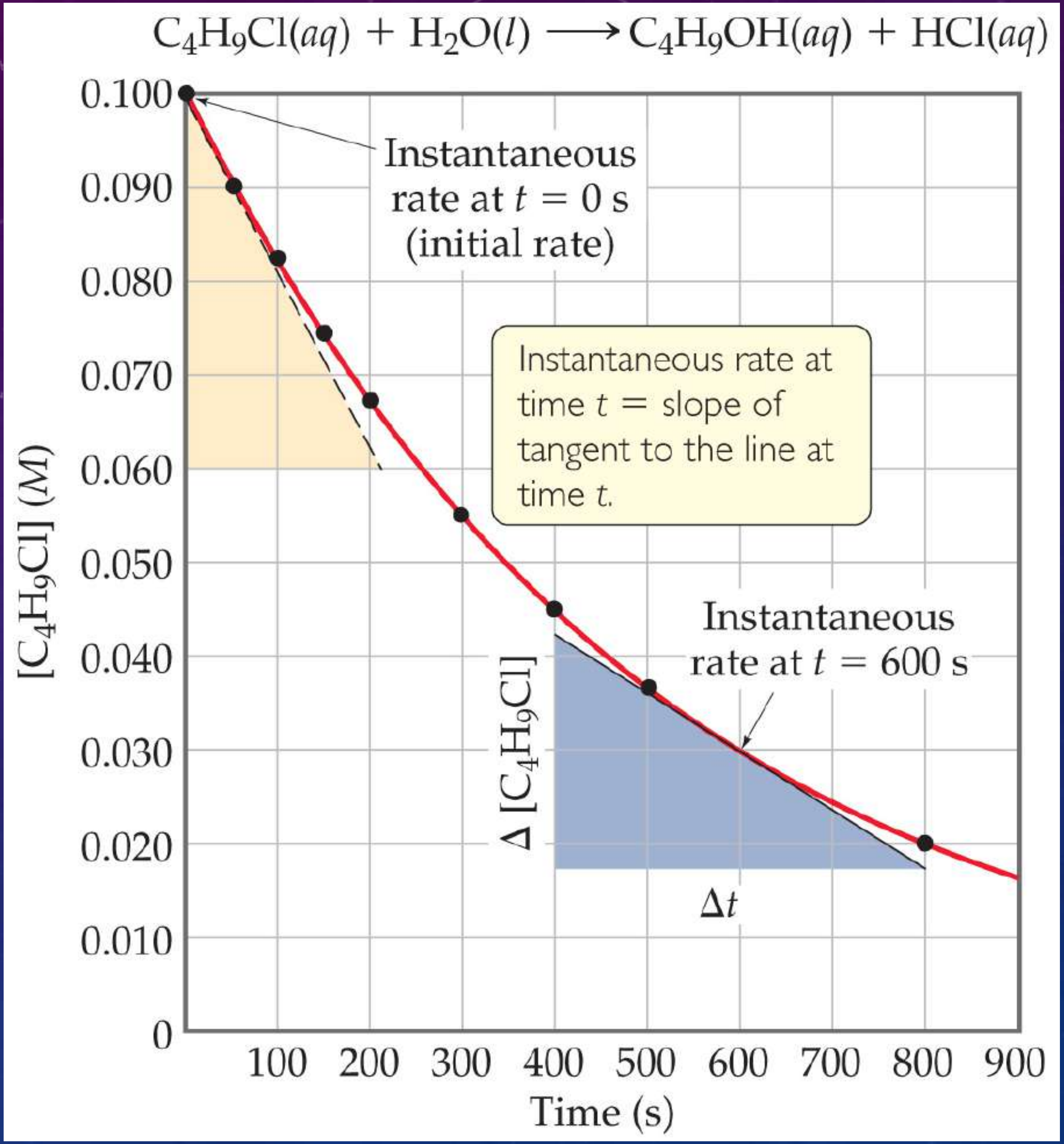


Instantaneous rate at time t = slope of tangent to the line at time t.

Note: Reactions typically slow down over time!

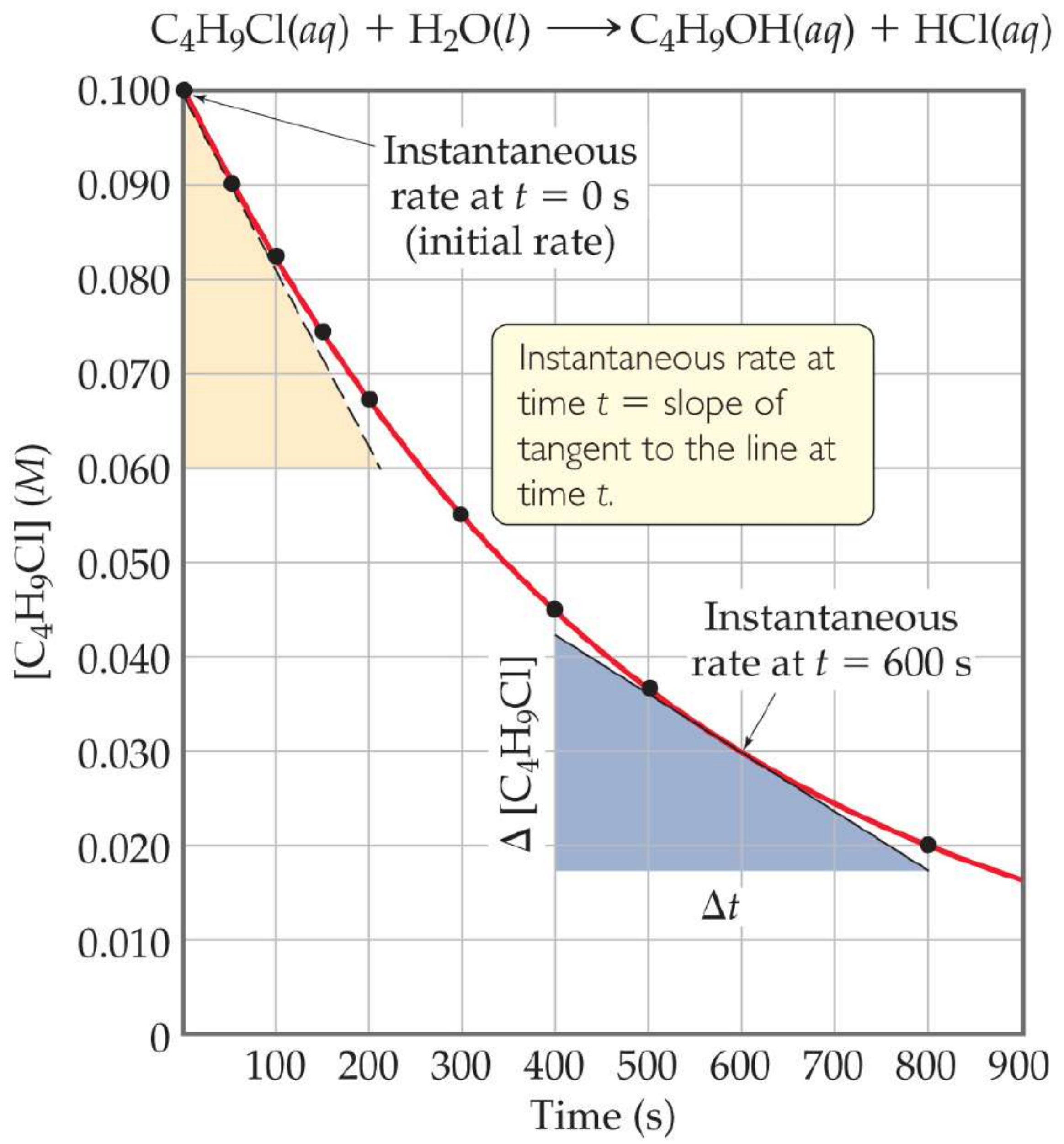
How does the instantaneous rate of reaction change as the reaction proceeds?

a. No change
b. Increases
c. Decreases



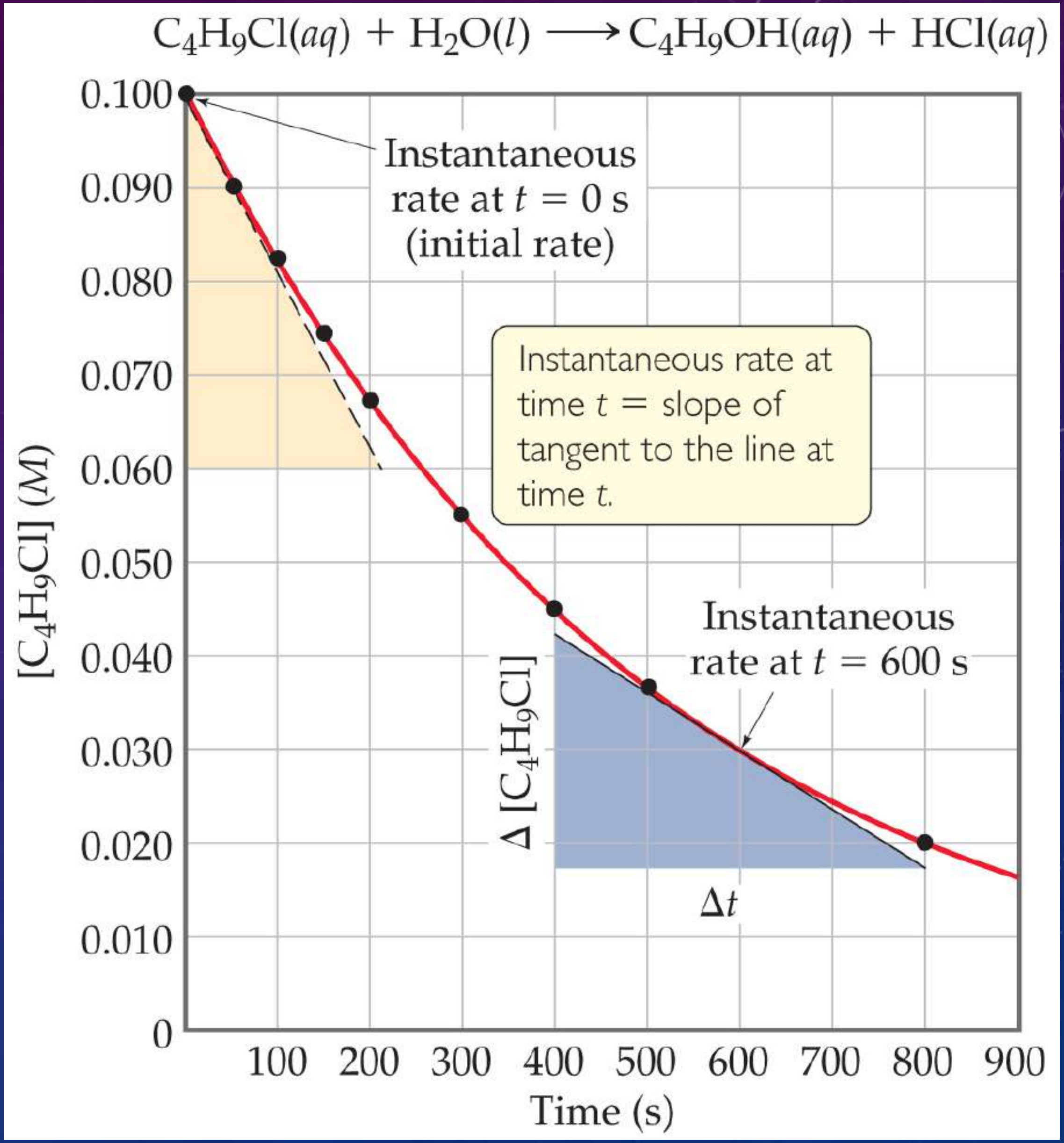
Sample Exercise 14.2

Using Figure 14.4, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ (the initial rate).



Practice Exercise 2

Using Figure 14.4, determine the instantaneous rate of disappearance of C_4H_9Cl at t = 300 s.



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

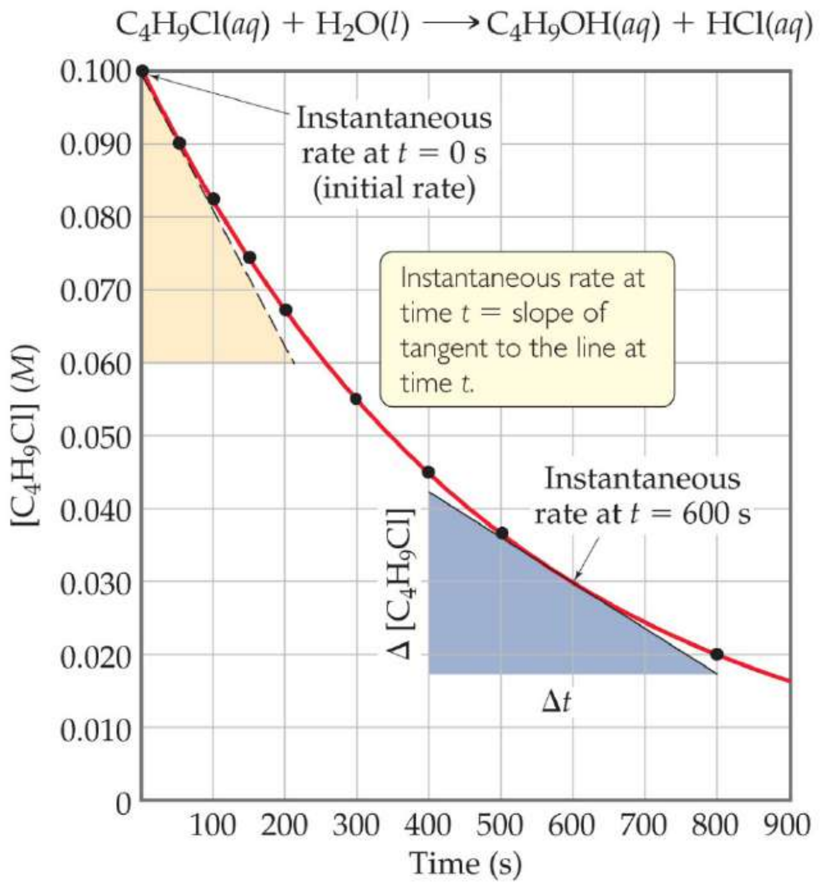
In Figure 14.4, order the rates from fastest to slowest: (i) The average rate of the reaction between 0 s and 600 s, (ii) the instantaneous rate at *t* = 0 s, and (iii) the instantaneous rate at *t* = 600 s. You should not have to do any calculations.

a. i > ii > iii

b. iii > ii > i

c. ii > i > iii

d. iii > i > ii


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

Instantaneous rate at $t = 0$ s (initial rate)

Instantaneous rate at time t = slope of tangent to the line at time t.

Instantaneous rate at $t = 600$ s

RELATIVE RATES

- As was said, rates are followed using a reactant *or* a product. Does this give the same rate for each reactant and product?
- Rate is dependent on stoichiometry.
- If we followed *use* of C_4H_9Cl and compared it to *production* of C_4H_9OH, the values would be the same. Note that the *change* would have opposite signs—one goes down in value, the other goes up.

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

RELATIVE RATES AND STOICHIOMETRY

What if the equation is *not* 1:1?

What will the relative rates be for:

$2\ O_3\ (g) \rightarrow 3\ O_2\ (g)$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

SAMPLE EXERCISE 14.3

a)How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction
$2\ O_3(g) \rightarrow 3O_2(g)$?
(b) If the rate at which O_2 appears, $\Delta[O_2]/\Delta t$, is 6.0×10^{-5} M/s at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[O_3]/\Delta t$?

Practice Exercise 1

At a certain time in a reaction, substance A is disappearing at a rate of 4.0×10^{-2} *M*/s, substance B is appearing at a rate of 2.0×10^{-2} *M*/s, and substance C is appearing at a rate of 6.0×10^{-2} *M*/s. Which of the following could be the stoichiometry for the reaction being studied?

(a) $2A + B \rightarrow 3C$ **(b)** $A \rightarrow 2B + 3C$

(c) $2A \rightarrow B + 3C$ **(d)** $4A \rightarrow 2B + 3C$

(e) $A + 2B \rightarrow 3C$

PRACTICE EXERCISE 2

If the rate of decomposition of N_2O_5 in the reaction

$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

at a particular instant is

$4.2 \times 10^{-7}\ M/s$, what is the rate of appearance of **(a)** NO_2 and **(b)** O_2 at that instant?

14.3 CONCENTRATION AND RATE LAWS

DETERMINING CONCENTRATION EFFECT ON RATE

- How do we determine what effect the concentration of each reactant has on the rate of the reaction?
- We keep every concentration constant *except* for one reactant and see what happens to the rate. *Then*, we change a different reactant. We do this until we have seen how *each* reactant has affected the rate.

AN EXAMPLE OF HOW CONCENTRATION AFFECTS RATE

- Experiments 1–3 show how $[NH_4^+]$ affects rate.
- Experiments 4–6 show how $[NO_2^-]$ affects rate.
- Result: The **rate law**, which shows the relationship between rate and concentration for all reactants:

Rate = k $[NH_4^+]$ $[NO_2^-]$

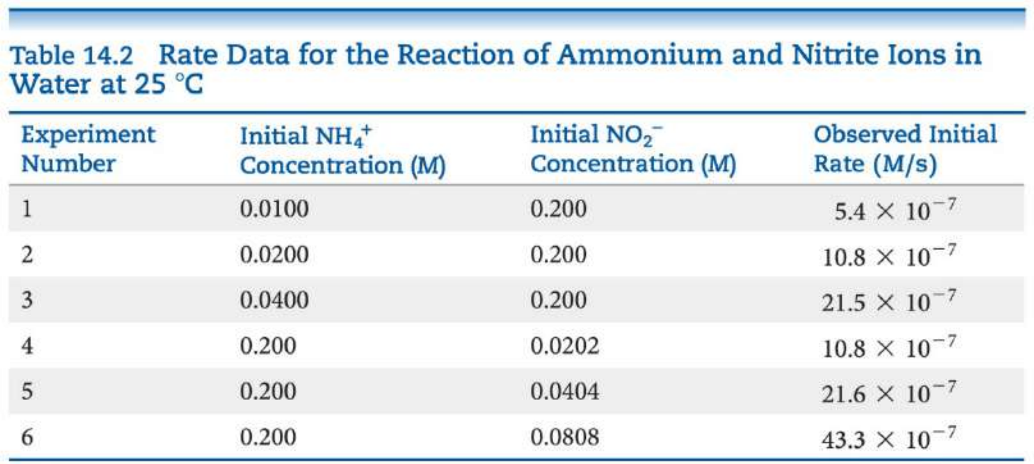


Table 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

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

MORE ABOUT RATE LAW

- The exponents tell the **order** of the reaction with respect to each reactant.
- In our example from the last slide:

Rate = k $[NH_4^+]$ $[NO_2^-]$

- The order with respect to each reactant is 1. (It is *first order* in NH_4^+ and NO_2^-.)
- The *reaction* is *second order* (1 + 1 = 2; we just add up all of the reactants' orders to get the reaction's order).
- What is k? It is the **rate constant**. It is a temperature-dependent quantity.

How do reaction rate, rate law, and rate constant differ?

(1)Reaction rate is experimentally measured as a reaction proceeds.
(2)Rate constant is calculated from a rate law.
(3)Rate law relates reaction rate to rate constant and concentrations.
(4)Rate law describes the mechanism of a reaction.
(5)Reaction rate depends on the stoichiometry of the reaction.

a. (1), (2), (4)
b. (2), (4), (4)
c. (2), (3), (5)
d. (1), (2), (3)

Does the rate constant have the same units as the rate?

a. Yes, the rate is directly proportional to the rate constant in a rate law.

b. Yes, only if the order of each concentration is one in the rate law.

c. No, as the order of each concentration changes in a rate law, the units of the rate constant change, but those of the rate are always concentration/time.

d. No, as the order of each concentration changes in a rate law, there are changes in the units of both.

The experimentally determined rate law for the reaction
$2\ NO(g) + 2\ H_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$ is
rate = $k[NO]^2[H_2]$.
What are the reaction orders in this rate law?

a. 2nd order in NO, 1st order in H_2, 2nd order overall

b. 2nd order in NO, 1st order in H_2, 3rd order overall

c. 1st order in NO, 1st order in H_2, 2nd order overall

d. 1st order in NO, 2nd order in H_2, 3rd order overall

The experimentally determined rate law for the reaction

$2\ NO(g) + 2\ H_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$ is

rate = $k[NO]^2[H_2]$.

Would the reaction rate increase more if we doubled the concentration of NO or the concentration of H_2?

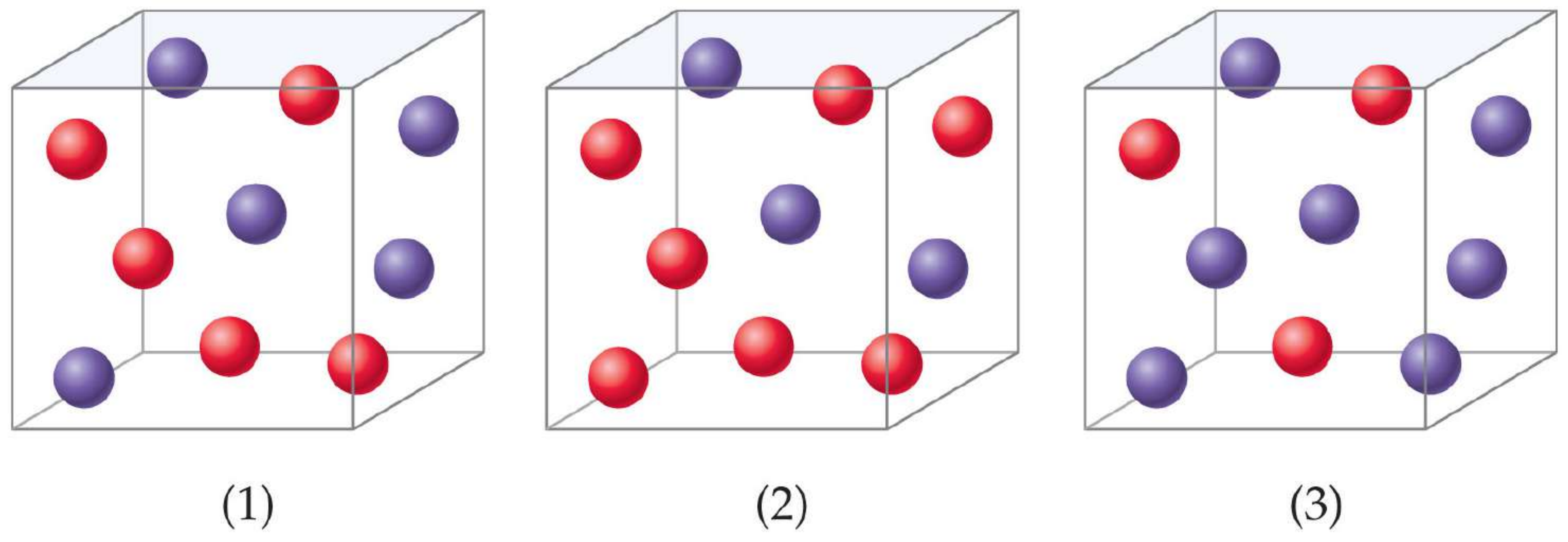
a. NO

b. H_2

c. Same effect from doubling NO or H_2

SAMPLE EXERCISE 14.4

Consider a reaction A + B → C for which rate = $k[A][B]^2$. Each of the boxes represent a reaction mixture (A is red, B is purple). Rank these mixtures in order of increasing rate of reaction.

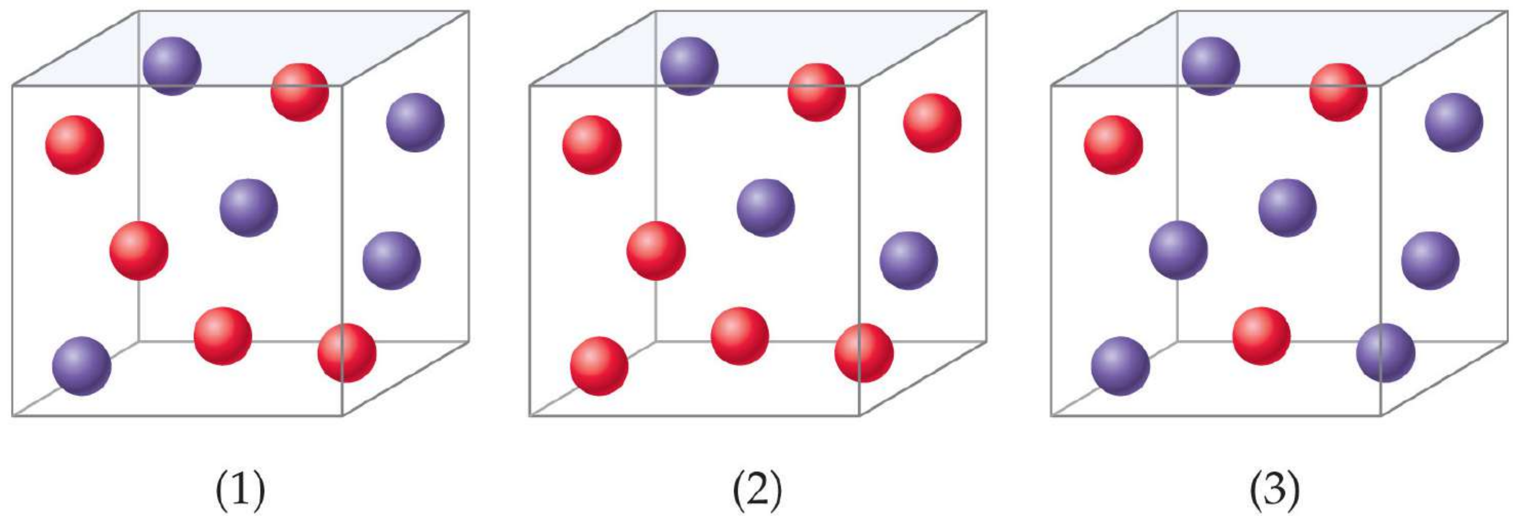


Practice Exercise 1

Suppose the rate law for the reaction in this Sample Exercise were rate = $k[A]^2[B]$. What would be the ordering of the rates for the three mixtures shown above, from slowest to fastest?

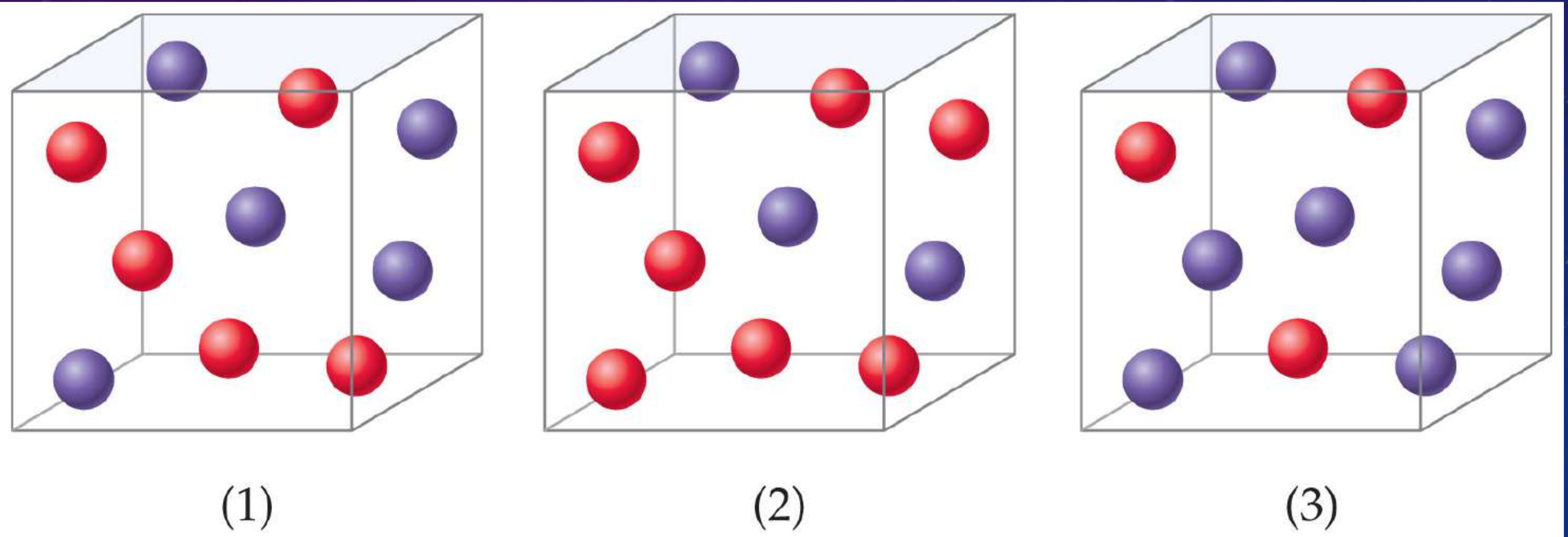
(a) 1 < 2 < 3 **(b)** 1 < 3 < 2 **(c)** 3 < 2 < 1

(d) 2 < 1 < 3 **(e)** 3 < 1 < 2



PRACTICE EXERCISE 2

Assuming the rate = *k*[A][B], rank the mixtures in order of increasing rate.



UNITS OF RATE CONSTANT

- Units of rate = (units of rate constant)(units of concentration)^x So,
- Units of rate constant = units of rate / (units of concentration)^x
- Units of *k* **MEMORIZE OR UNDERSTAND**
  - Zero order: M/s
  - First order: s^{-1}
  - Second order: $M^{-1}s^{-1}$
  - Third order: $M^{-2}s^{-1}$

Suppose the reactions A ⟶ B and X ⟶ Y have the same value of *k*. When [A] = [X], will the two reactions necessarily have the same rate?

a. Yes, the rate constant governs the rate.
b. No, the rate law can be different.

Sample Exercise 14.5

(a) What are the overall reaction orders for the reactions described in Equations 14.9 and 14.11? **(b)** What are the units of the rate constant for the rate law in Equation 14.9?

14.9 $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$

Rate = $k[N_2O_5]$

14.11 $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Rate = $k[CHCl_3][Cl_2]^{1/2}$

Practice Exercise 1

Which of the following are the units of the rate constant for Equation 14.11?

(a) $M^{-1/2}\ s^{-1}$

(b) $M^{-1/2}\ s^{-1/2}$

(c) $M^{1/2}\ s^{-1}$

(d) $M^{-3/2}\ s^{-1}$

(e) $M^{-3/2} s^{-1/2}$

14.11 $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Rate = $k[CHCl_3][Cl_2]^{1/2}$

Practice Exercise 2

(a) What is the reaction order of the reactant H_2 in Equation 14.10? **(b)** What are the units of the rate constant for Equation 14.10?

14.10 $H_2 + I_2 \rightarrow 2HI$

Rate = $k[H_2][I_2]$

METHOD OF INITIAL RATES

- **Used to find the form of the rate law**

1. Write the general form of the rate law, then determine order by doing the following.
2. Choose one reactant to start with
3. Find two experiments where the concentration of that reactant changes but all other reactants stay the same
4. Write the rate laws for both experiments
5. Divide the two rate laws
6. Use log rules to solve for the order
7. Follow the same technique for other reactants

EXAMPLE

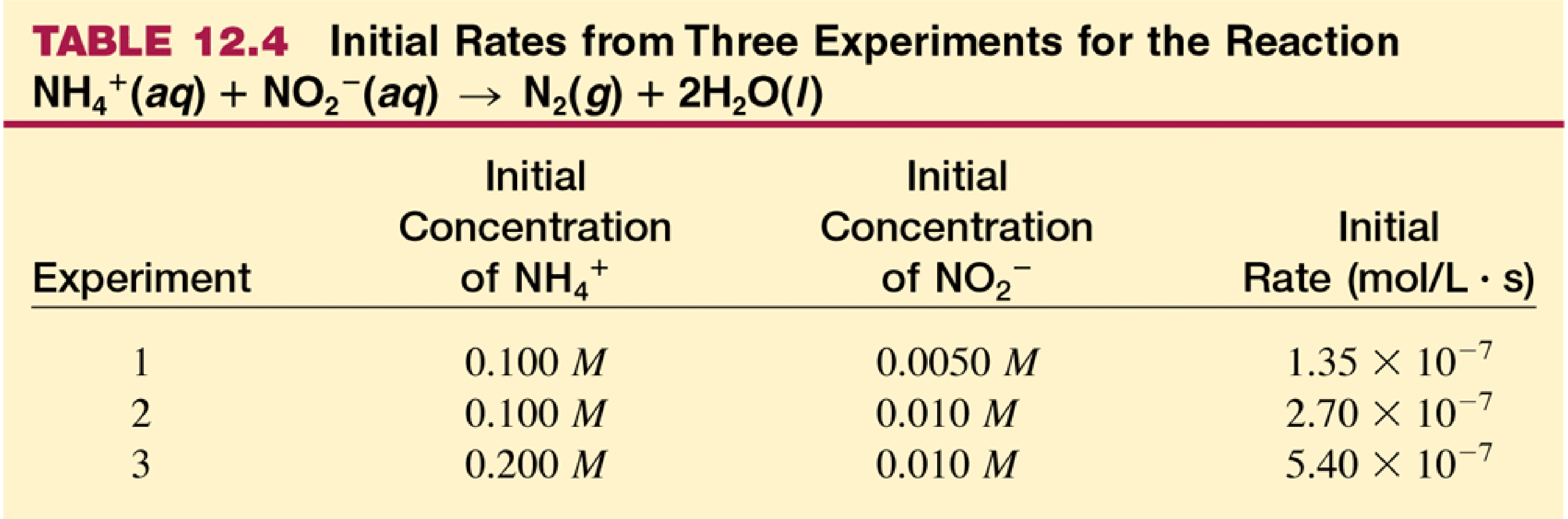


TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol/L · s)
1	0.100 *M*	0.0050 *M*	1.35×10^{-7}
2	0.100 *M*	0.010 *M*	2.70×10^{-7}
3	0.200 *M*	0.010 *M*	5.40×10^{-7}

- *Choose one reactant to start with*

NH_4^+

- *Find two experiments where the concentration of that reactant changes but all other reactants stay the same*

Exp 2 & 3

EXAMPLE

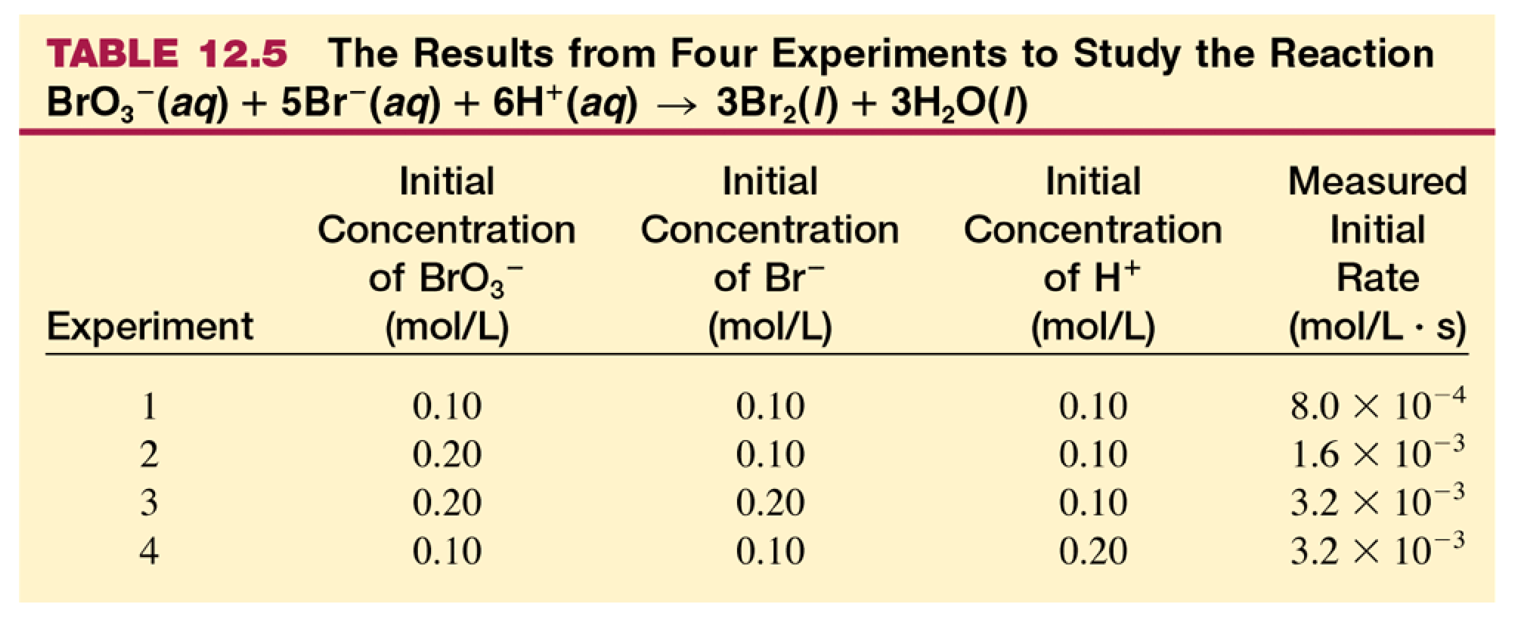


TABLE 12.5 The Results from Four Experiments to Study the Reaction $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

- BrO_3^- : Exp 1 & 2

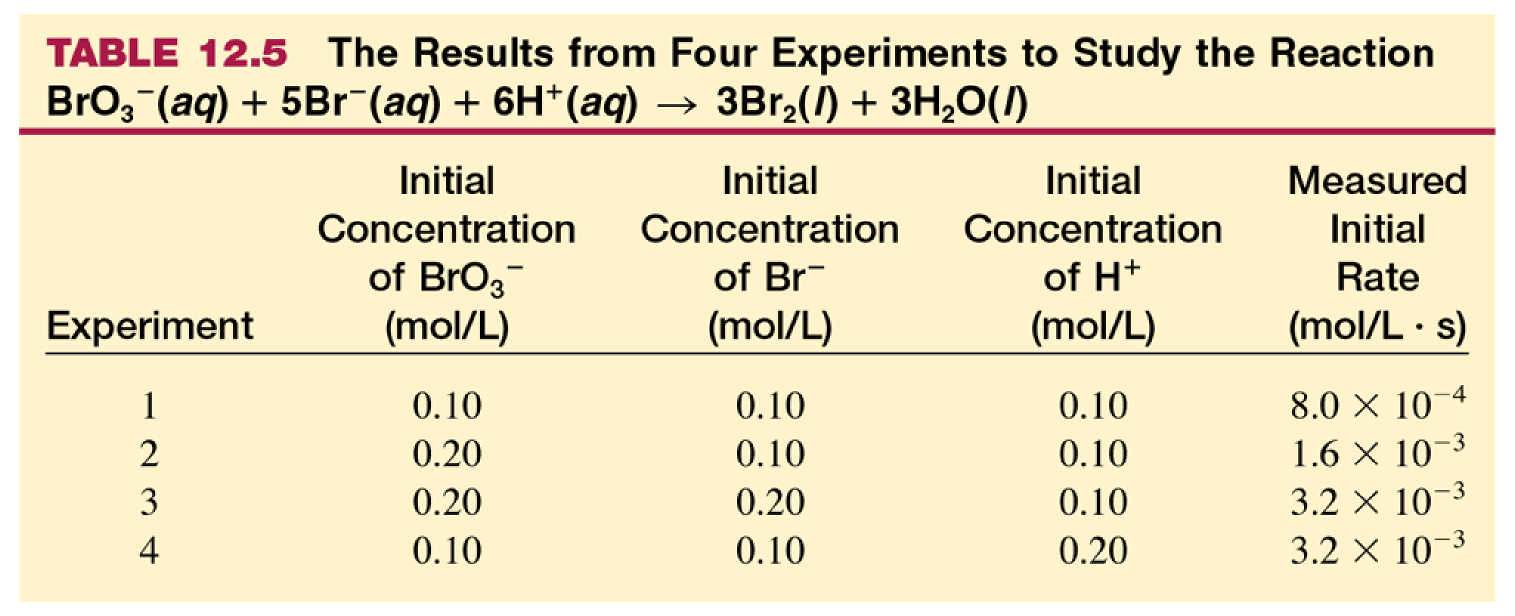
Exp 1: $\text{Rate} = \underline{8.0\text{x}10^{-4} = k(\cancel{0}.10)^x(\cancel{0.10})^y(\cancel{0.10})^z}$

Exp 2: $\text{Rate} = 1.6\text{x}10^{-3} = k(\cancel{0}.20)^x(\cancel{0.10})^y(\cancel{0.10})^z$

$0.50 = 0.50^x$

$x = 1$

EXAMPLE



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1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

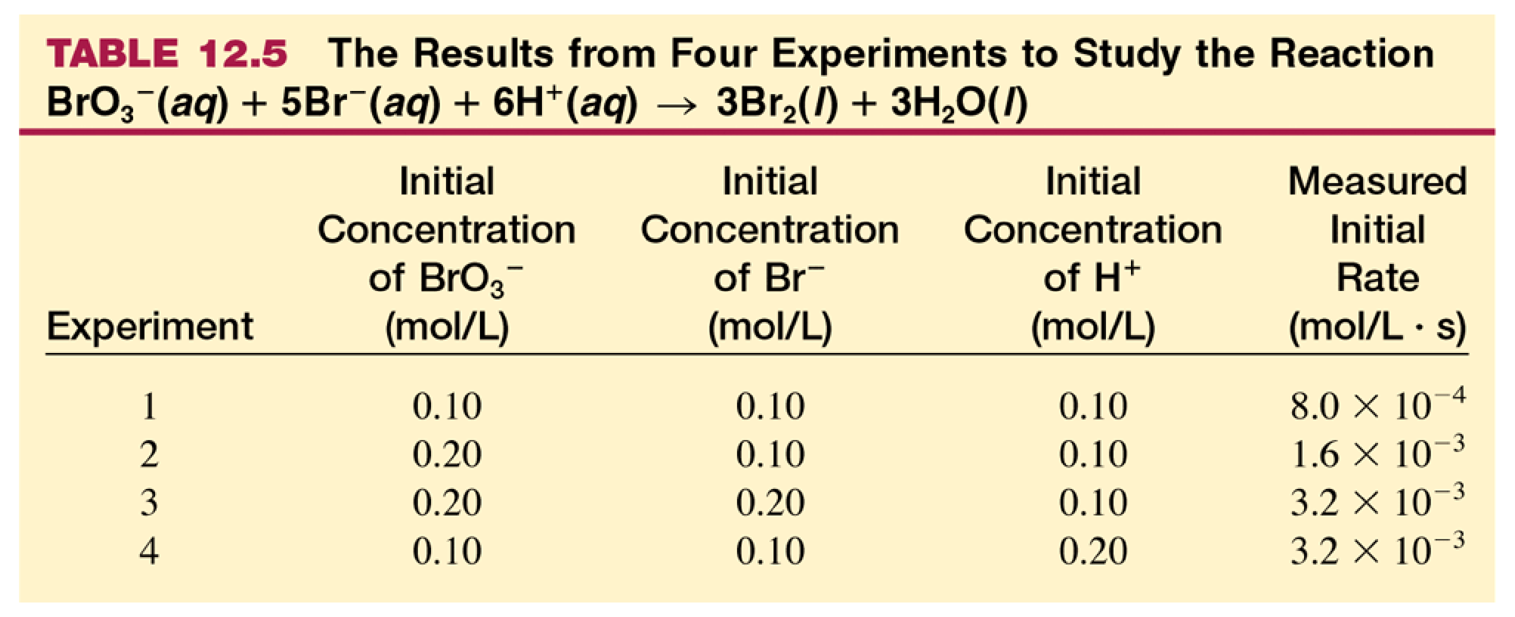
- Br^- : Exp 2 & 3

$$\frac{\text{Exp 2: Rate} = 1.6\text{x}10^{-3} = \cancel{k}\cancel{(0.20)^1}(0.10)^y\cancel{(0.10)^z}}{\text{Exp 3: Rate} = 3.2\text{x}10^{-3} = \cancel{k}\cancel{(0.20)^1}(0.20)^y\cancel{(0.10)^z}}$$

$0.50 = 0.50^y$

$y = 1$

EXAMPLE



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1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

- H^+ : Exp 1 & 4

Exp 1: Rate = $8.0\text{x}10^{-4} = k\cancel{(0.10)^1}\cancel{(0.10)^1}(0.10)^z$

Exp 4: Rate = $3.2\text{x}10^{-3} = k\cancel{(0.10)^1}\cancel{(0.10)^1}(0.20)^z$

$0.25 = 0.50^z$ OR $¼ = (½)^z$

$z = 2$

EXAMPLE

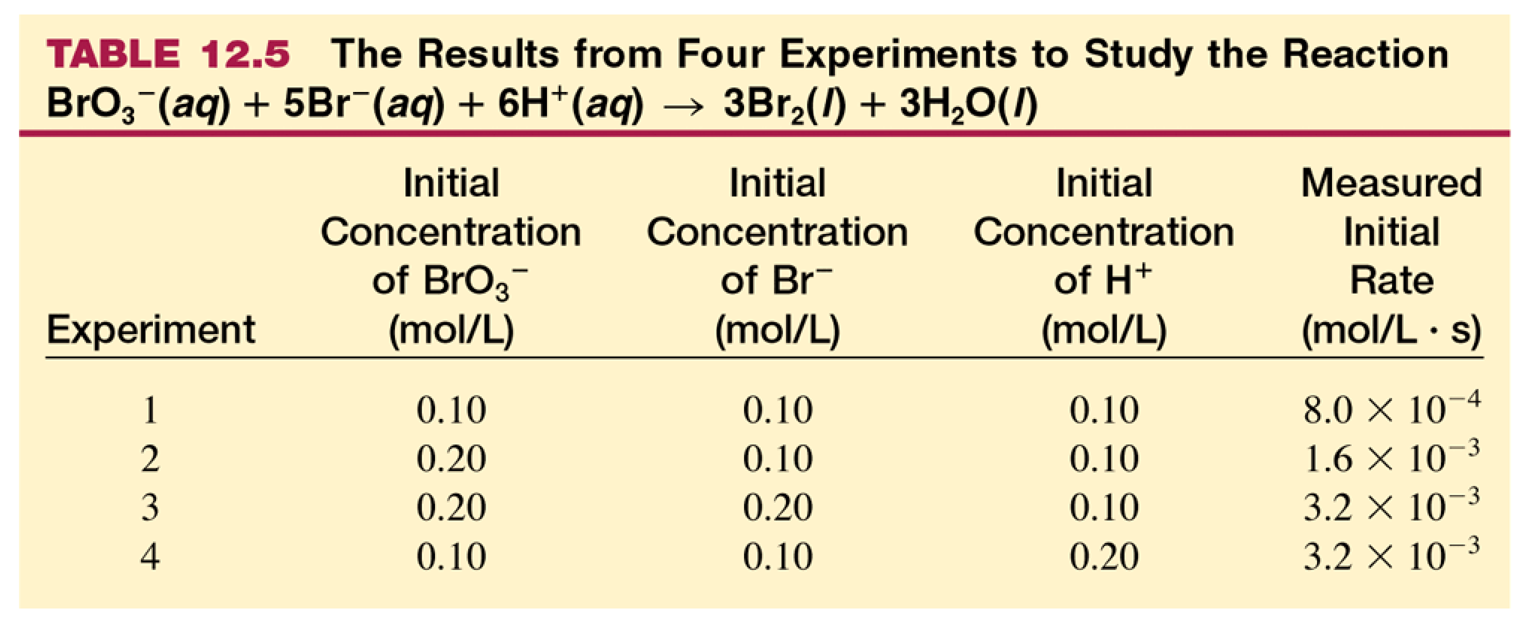


TABLE 12.5 **The Results from Four Experiments to Study the Reaction**
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

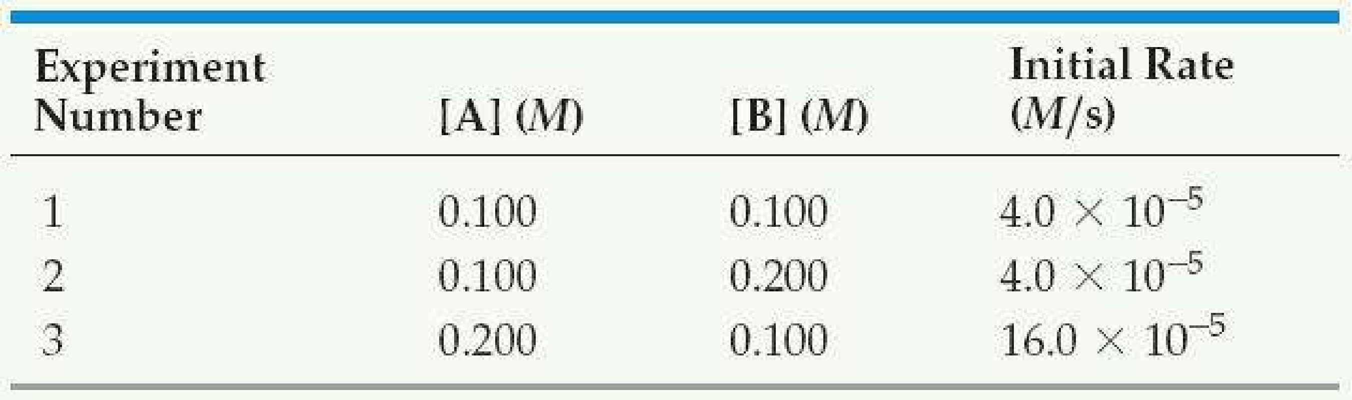
Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

- So Rate = $k[BrO_3^-]^1[Br^-]^1[H^+]^2$
  - Overall order of reaction = 4
- Solve for rate constant, k

$$k = \frac{8.0 \times 10^{-4}\,\frac{\cancel{mol}}{\cancel{L}\cdot s}}{(0.10\,\frac{\cancel{\mathrm{mol}}}{\cancel{\mathrm{L}}})^1(0.10\,\frac{\mathrm{mol}}{\mathrm{L}})^1(0.10\,\frac{\mathrm{mol}}{\mathrm{L}})^2} = 8.0\,\frac{L^3}{mol^3\cdot s}$$

Sample Exercise 14.6

The initial rate of a reaction A + B → C was measured for several different starting concentrations of A and B, and the results are as follows:



Experiment Number	[A] (*M*)	[B] (*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine **(a)** the rate law for the reaction, **(b)** the rate constant, **(c)** the rate of the reaction when [A] = 0.050 *M* and [B] = 0.100 *M*.

Practice Exercise 1

A certain reaction X + Y → Z is described as being first order in [X] and third order overall. Which of the following statements is or are true?:

(i) The rate law for the reaction is: Rate = $k[X][Y]^2$.

(ii) If the concentration of X is increased by a factor of 1.5, the rate will increase by a factor of 2.25.

(iii) If the concentration of Y is increased by a factor of 1.5, the rate will increase by a factor of 2.25.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

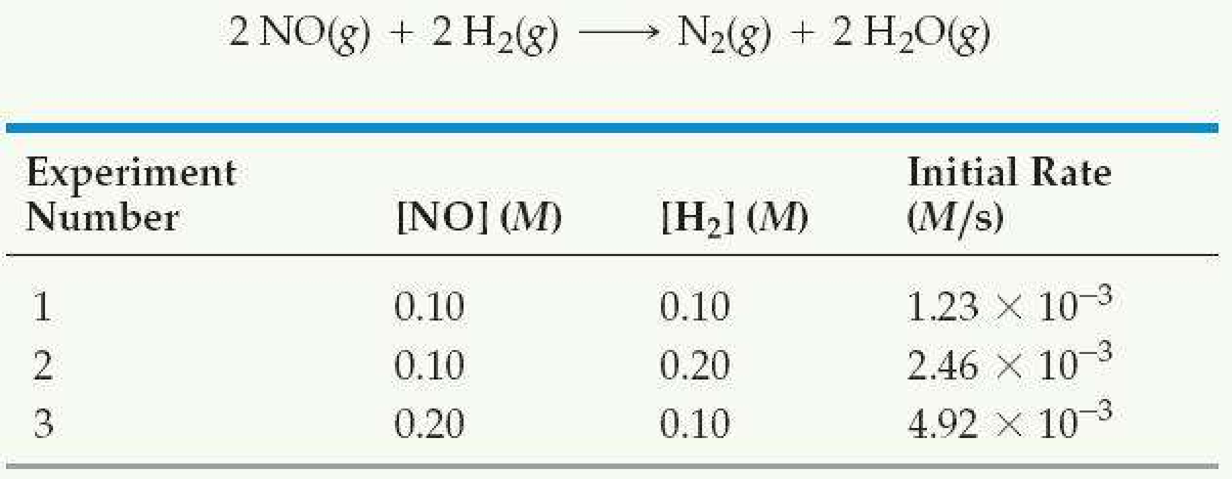
(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

(e) All three statements are true.

Practice Exercise 2

The following data were measured for the reaction of nitric oxide with hydrogen:



$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Experiment Number	[NO] (*M*)	$[H_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction.

(b) Calculate the rate constant.

(c) Calculate the rate when [NO] = 0.050 *M* and $[H_2]$ = 0.150 *M*

14.4 THE CHANGE OF CONCENTRATION WITH TIME

FIRST ORDER REACTIONS

Some rates depend *only* on one reactant to the first power.

These are *first order* reactions.

The rate law becomes:

Rate = k [A]

RELATING K TO [A] IN A FIRST ORDER REACTION

rate = $k\,[A]$

rate = $-\Delta\,[A]\,/\,\Delta t$

So: $k\,[A] = -\Delta\,[A]\,/\,\Delta t$

Rearrange to: $\Delta\,[A]\,/\,[A] = -\,k\,\Delta t$

Integrate: $\ln\,([A]\,/\,[A]_o) = -\,k\,t$

Rearrange: $\ln\,[A] = -\,\mathrm{k}\,\mathrm{t} + \ln\,[A]_o$

Note: this follows the equation of a line: $y = m\,x + b$

So, a plot of $\ln\,[A]$ vs. t is linear.

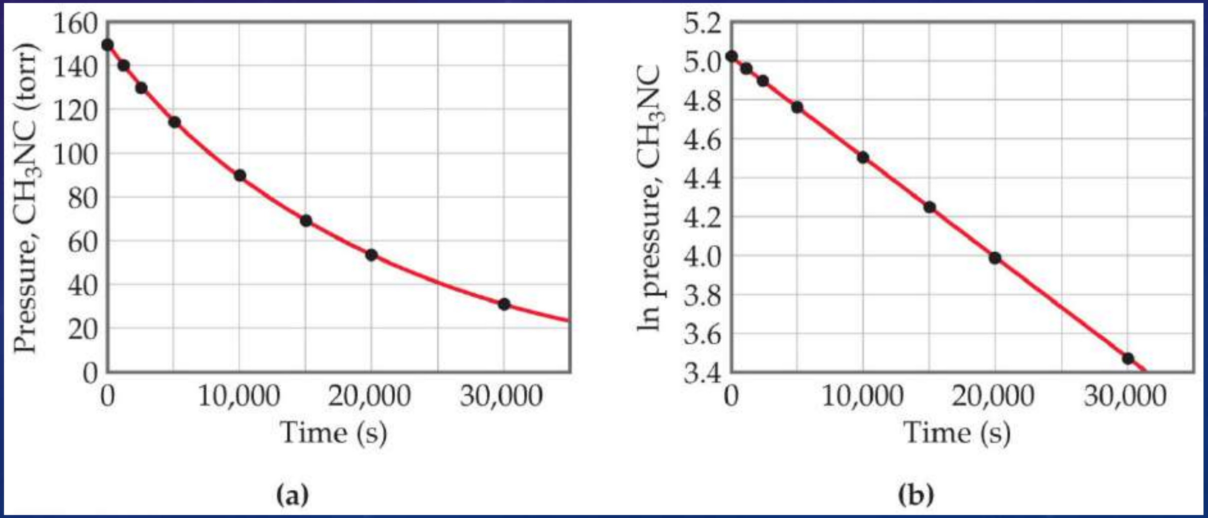
AN EXAMPLE: CONVERSION OF METHYL ISONITRILE TO ACETONITRILE

The equation for the reaction:

$CH_3NC \longrightarrow CH_3CN$

It is first order.

Rate = $k\,[CH_3NC]$



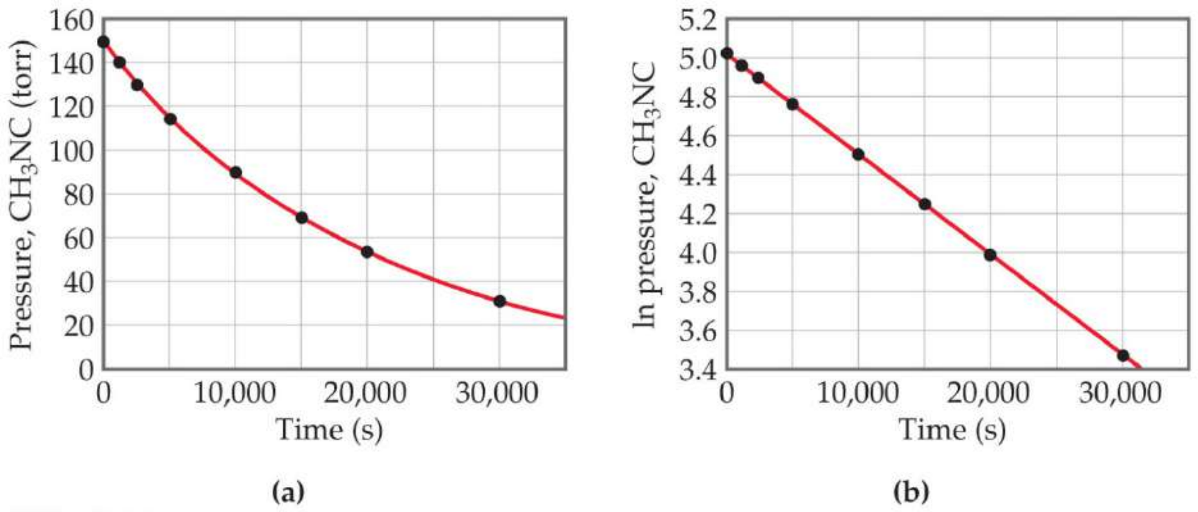
What can you conclude from the fact that the plot of ln *P* versus *t* is linear?

a. The reaction is zero order in CH_3NC.

b. The reaction is first order in CH_3NC.

c. The reaction is second order in CH_3NC.

d. No conclusion can be made without further information about the specific rate law.



FINDING THE RATE CONSTANT, *K*

- Besides using the rate law, we can find the rate constant from the plot of ln [*A*] vs. *t*.
- Remember the integrated rate law:

$$\ln [A] = -kt + \ln [A]_o$$

- The plot will give a line. Its slope will equal $-k$.

Sample Exercise 14.7 Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12 ° C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7}\ \text{g/cm}^3$. Assume that the average temperature of the lake is 12 ° C. **(a)** What is the concentration of the insecticide on June 1 of the following year? **(b)** How long will it take for the concentration of the insecticide to decrease to $3.0 \times 10^{-7}\ \text{g/cm}^3$?

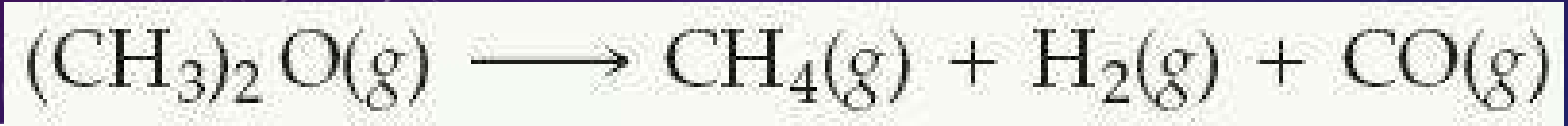
Practice Exercise 1

At 25 °C, the decomposition of dinitrogen pentoxide, $N_2O_5(g)$, into $NO_2(g)$ and $O_2(g)$ follows first-order kinetics with $k = 3.4 \times 10^{-5}\ s^{-1}$. A sample of N_2O_5 with an initial pressure of 760 torr decomposes at 25 °C until its partial pressure is 650 torr. How much time (in seconds) has elapsed?

(a) 5.3×10^{-6}
(b) 2000
(c) 4600
(d) 34,000
(e) 190,000

Practice Exercise 2

The decomposition of dimethyl ether, $(CH_3)_2O$, at 510 ° C is a first-order process with a rate constant of $6.8 \times 10^{-4}\ s^{-1}$:



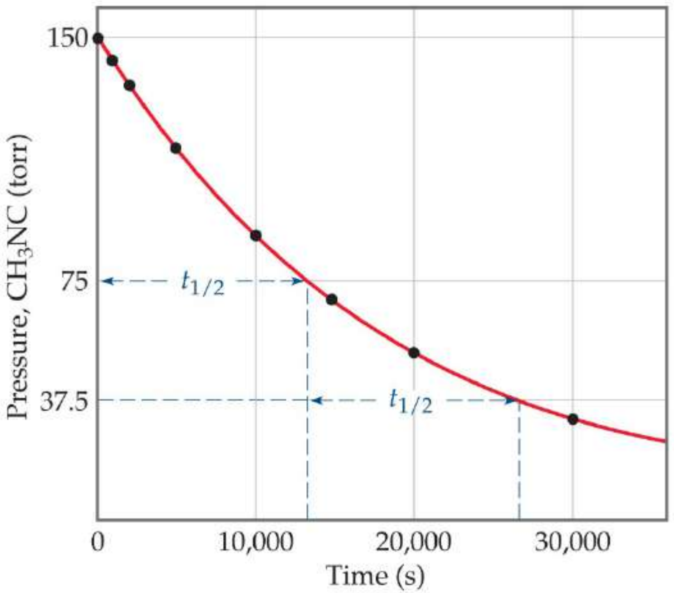
$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420 s?

HALF-LIFE

Definition: The amount of time it takes for one-half of a reactant to be used up in a chemical reaction.

- First Order Reaction:
  - $\ln [A] = -k t + \ln [A]_o$
  - $\ln ([A]_o/2) = -k t_{½} + \ln [A]_o$
  - $-\ln ([A]_o/2) + \ln [A]_o = k t_{½}$
  - $\ln ([A]_o / [A]_o/2) = k t_{½}$
  - $\ln 2 = k t_{½}$ or $t_{½} = 0.693/k$



SECOND ORDER REACTIONS

- Some rates depend *only* on a reactant to the second power.
- These are *second order* reactions.
- The rate law becomes:

Rate = $k\,[A]^2$

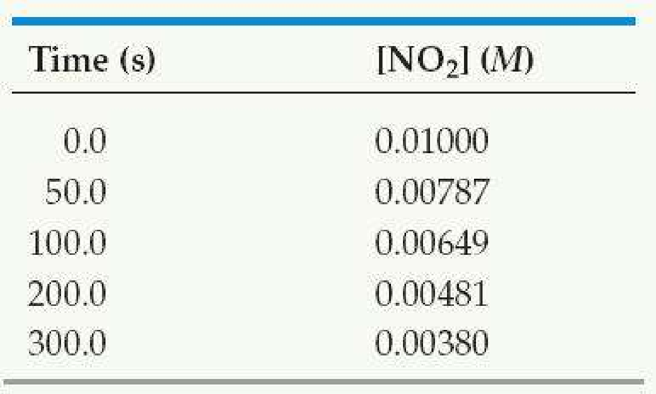
SOLVING THE SECOND ORDER REACTION FOR $A \rightarrow$ PRODUCTS

- rate = $k\,[A]^2$
- rate = $-\,\Delta\,[A]\,/\,\Delta\,t$
- So, $k\,[A]^2 = -\,\Delta\,[A]\,/\,\Delta\,t$
- Rearranging: $\Delta\,[A]\,/\,[A]^2 = -\,k\;\Delta\,t$
- Using calculus: $1/[A] = 1/[A]_o + k\,t$
- Notice: The linear relationships for first order and second order reactions differ!

Sample Exercise 14.8

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 ° C,

$$\mathrm{NO_2}(g) \longrightarrow \mathrm{NO}(g) + \tfrac{1}{2}\mathrm{O_2}(g):$$



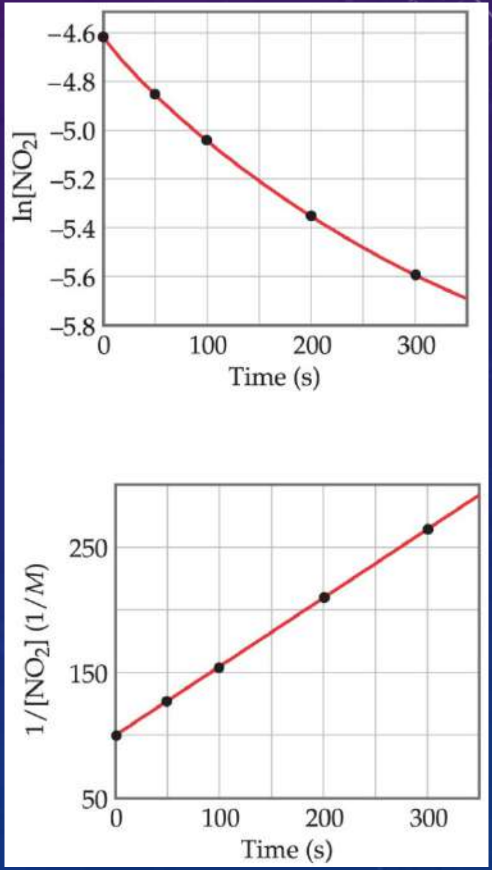
Time (s)	$[\mathrm{NO_2}]$ (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Is the reaction first or second order in $\mathrm{NO_2}$?

AN EXAMPLE OF A SECOND ORDER REACTION: DECOMPOSITION OF NO_2

- A plot following NO_2 decomposition shows that it must be second order because it is linear for $1/[NO_2]$, *not* linear for $\ln [NO_2]$.
- Equation:

$NO_2 \longrightarrow NO + \frac{1}{2} O_2$



Practice Exercise 1

For a certain reaction A → products, a plot of ln[A] versus time produces a straight line with a slope of -3.0×10^{-2} s^{-1}. Which of the following statements is or are true?:

(i) The reaction follows first-order kinetics.

(ii) The rate constant for the reaction is 3.0×10^{-2} s^{-1}.

(iii) The initial concentration of [A] was 1.0 *M*.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

(e) All three statements are true.

Practice Exercise 2

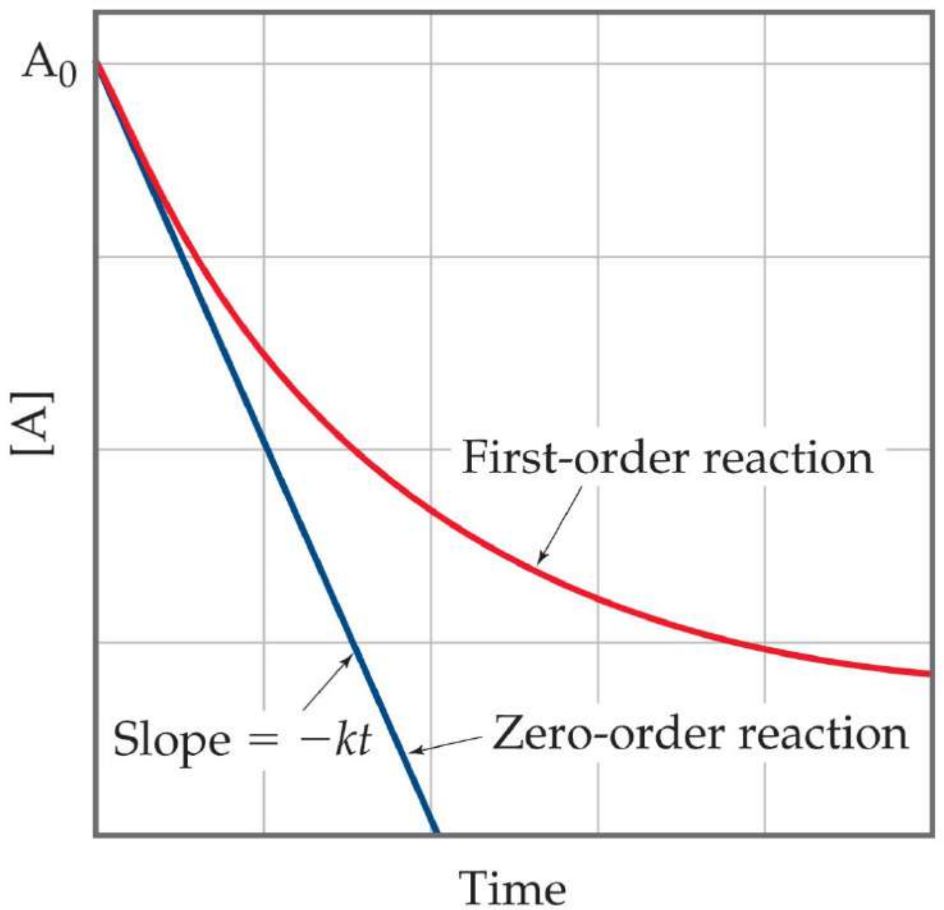
Consider again the decomposition of NO_2 discussed in the Sample Exercise. The reaction is second order in NO_2 with $k = 0.543\ M^{-1}\ s^{-1}$. If the initial concentration of NO_2 in a closed vessel is 0.0500 *M*, what is the remaining concentration after 0.500 h?

HALF-LIFE AND SECOND ORDER REACTIONS

- Using the integrated rate law, we can see how half-life is derived:
  - $1/[A] = 1/[A]_o + k\,t$
  - $1/([A]_o/2) = 1/[A]_o + k\,t_{½}$
  - $2/[A]_o - 1/[A]_o = k\,t_{½}$
  - $t_{½} = 1 / (k\,[A]_o)$
- So, half-life is a concentration dependent quantity for second order reactions!

ZERO ORDER REACTIONS

- Occasionally, rate is *independent* of the concentration of the reactant:
- Rate = *k*
- These are *zero order* reactions.
- These reactions are linear in concentration.



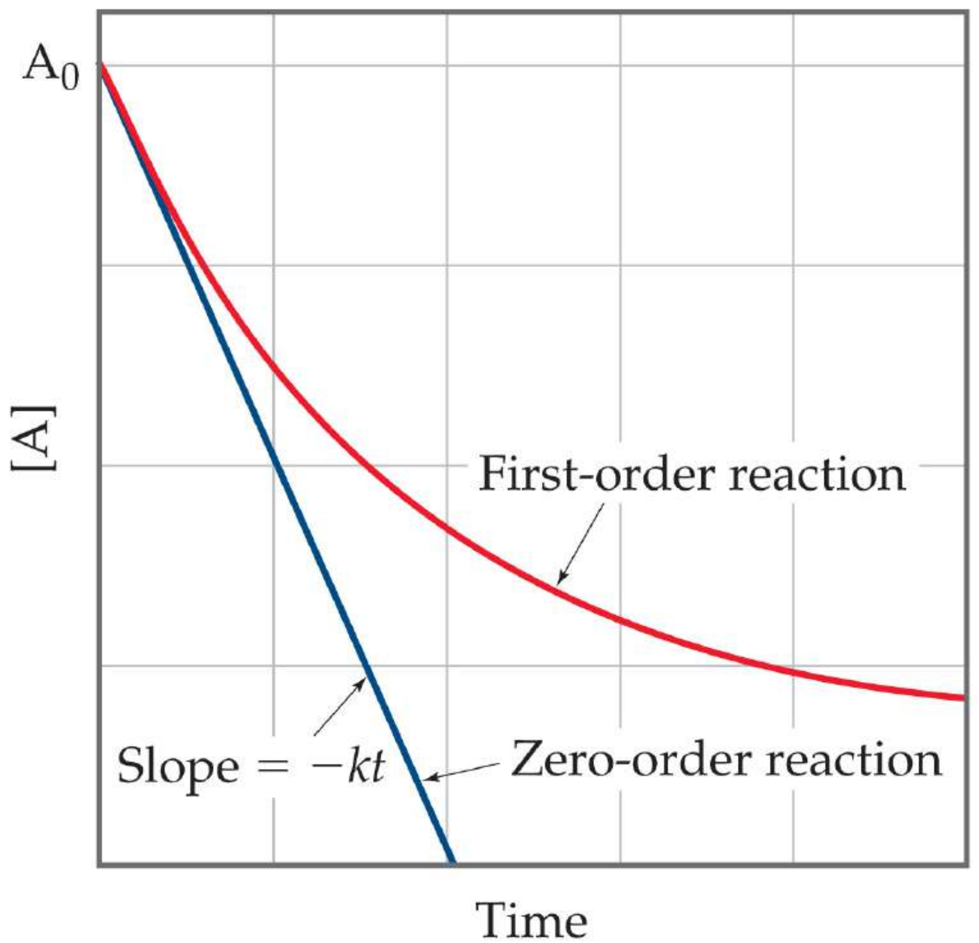
At which times during the reaction would you have trouble distinguishing a zero-order reaction from a first-order reaction?

a. At all times

b. When *t* is close to zero

c. Half-way through the reaction

d. When the concentration of [A] is high



If a solution containing 10.0 g of a substance reacts by first-order kinetics, how many grams remain after three half-lives?

a. 6.00 g

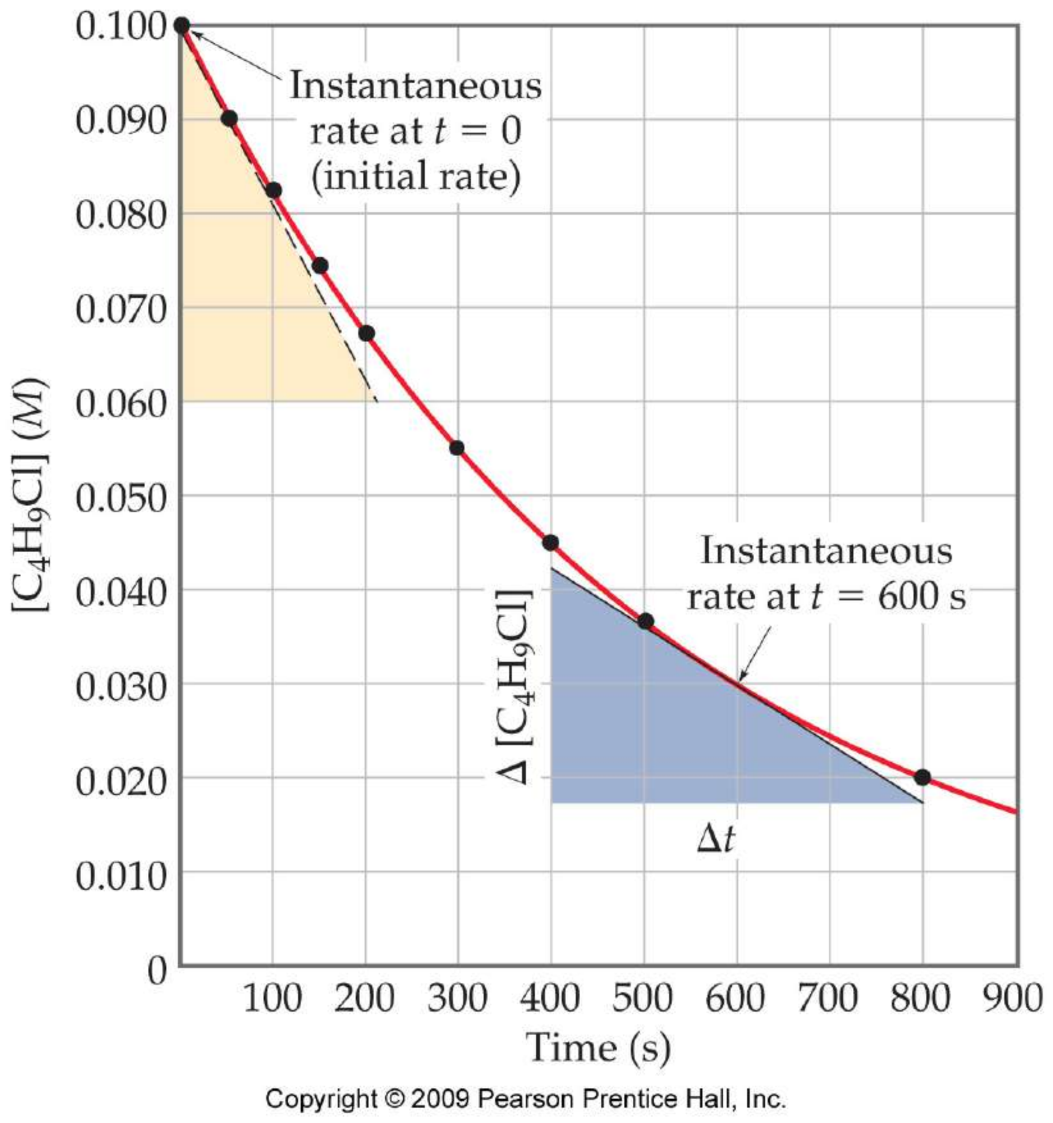
b. 4.50 g

c. 1.25 g

d. 1.11 g

Sample Exercise 14.9

The reaction of C_4H_9Cl with water is a first-order reaction. Figure 14.4 shows how the concentration of C_4H_9Cl changes with time at a particular temperature. **(a)** From that graph, estimate the half-life for this reaction. **(b)** Use the half-life from (a) to calculate the rate constant.



Practice Exercise 1

We noted in an earlier Practice Exercise that at 25 °C the decomposition of $N_2O_5(g)$ into $NO_2(g)$ and $O_2(g)$ follows first-order kinetics with $k = 3.4 \times 10^{-5}\ s^{-1}$. How long will it take for a sample originally containing 2.0 atm of N_2O_5 to reach a partial pressure of 380 torr?

(a) 5.7 h
(b) 8.2 h
(c) 11 h
(d) 16 h
(e) 32 h

Practice Exercise 2

(a) Using Equation 14.15, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of $1.45\ \text{yr}^{-1}$ at 12 ° C

$t_{½} = 0.693/k$

(b) How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Why can we report the half-life for a first-order reaction without knowing the initial concentration, but not for a second-order reaction?

a. The half-life of a first order reaction is independent of the initial concentration.
b. The half-life of a second order reaction is dependent on the initial concentration.
c. Both A and B
d. Neither A nor B

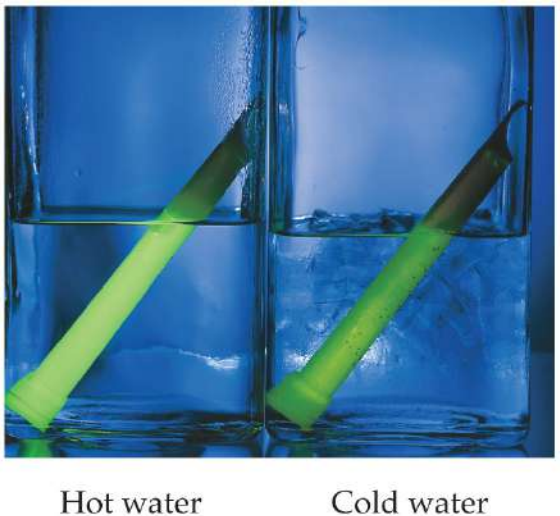
14.5 TEMPERATURE AND RATE

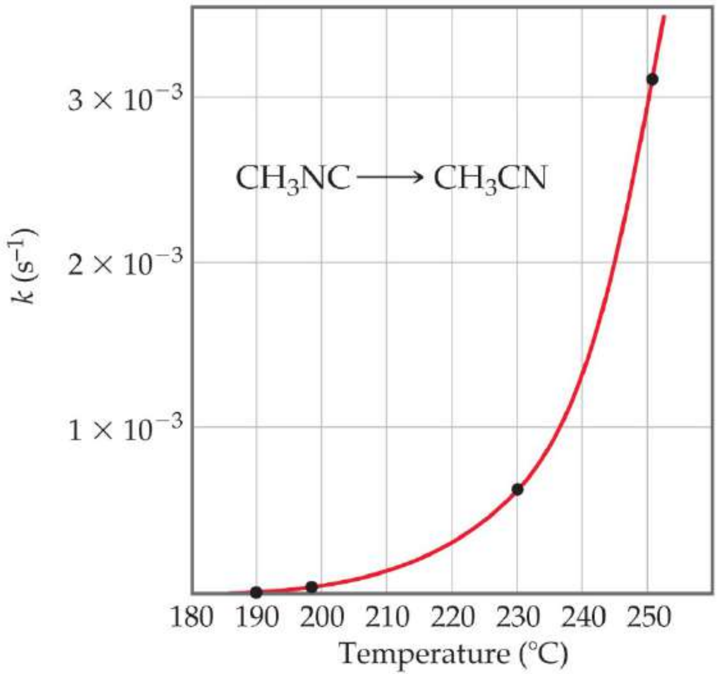
FACTORS THAT AFFECT REACTION RATE

1. Temperature
2. Frequency of collisions
3. Orientation of molecules
4. Energy needed for the reaction to take place (activation energy)

TEMPERATURE AND RATE

- Generally, as temperature increases, rate increases.
- The rate constant is temperature dependent: it increases as temperature increases.
- Rate constant doubles (approximately) with every 10 °C rise.



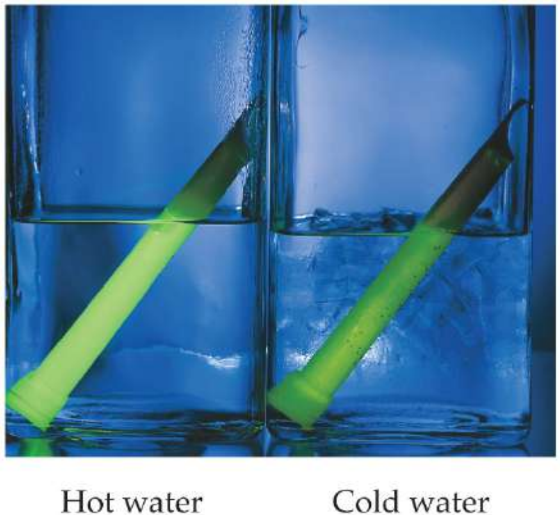


Why does the light stick glow with less light in cold water than in hot water?

a. The light gets absorbed by the cold water more effectively.

b. The cold water reduces the reaction rate.

c. The hot water reduces the reaction rate.

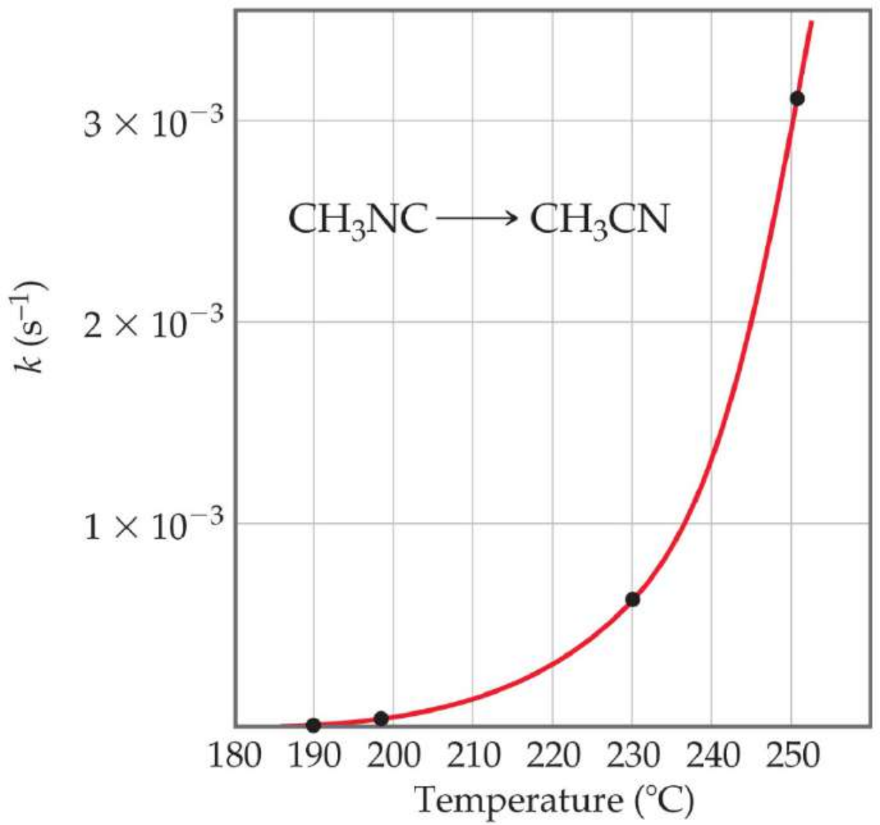


Would you expect this curve to eventually go back down to lower values? Why or why not?

a. Yes, the reaction will eventually reach equilibrium.

b. No, the temperature continues to increase kinetic energy of reactants.

c. Impossible to tell from the information given



FREQUENCY OF COLLISIONS

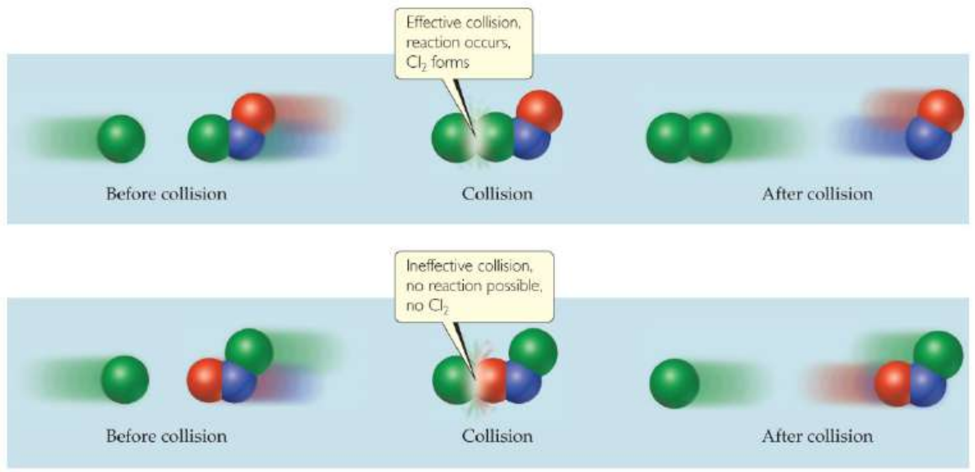
- The **collision model** is based on the kinetic molecular theory.
- Molecules must collide to react.
- If there are more collisions, more reactions can occur.
- So, if there are more molecules, the reaction rate is faster.
- Also, if the temperature is higher, molecules move faster, causing more collisions and a higher rate of reaction.

THE COLLISION MODEL

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.

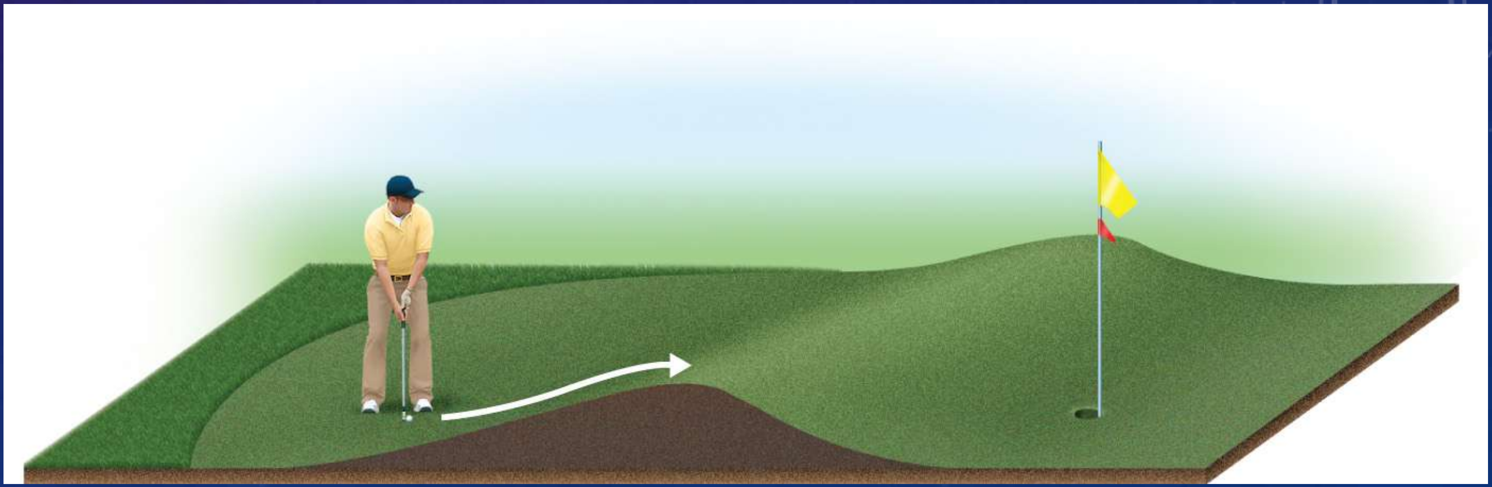
ORIENTATION OF MOLECULES

- Molecules can often collide without forming products.
- Aligning molecules properly can lead to chemical reactions.
- Bonds must be broken and made and atoms need to be in proper positions.



ENERGY NEEDED FOR A REACTION TO TAKE PLACE (ACTIVATION ENERGY)

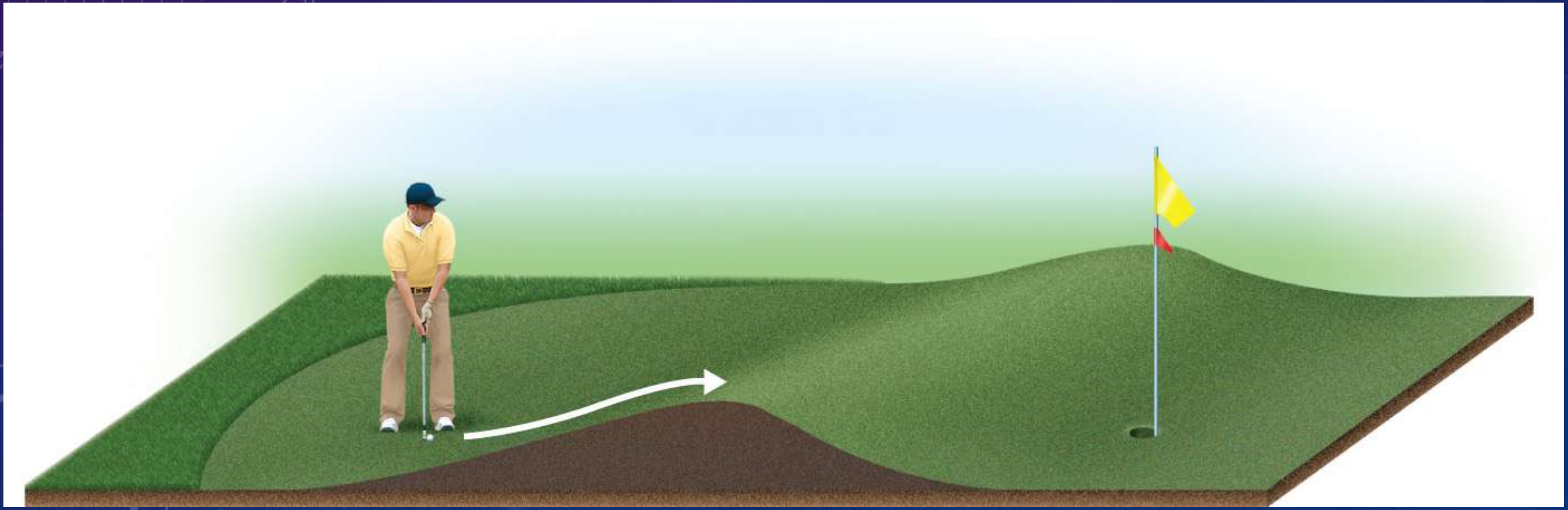
- The minimum energy needed for a reaction to take place is called **activation energy**.
- An energy barrier must be overcome for a reaction to take place, much like the ball must be hit to overcome the barrier in the figure below.



If the barrier were lower than as shown in the figure, would the golfer have to hit the ball as hard?

a. Yes

b. No



TRANSITION STATE (ACTIVATED COMPLEX)

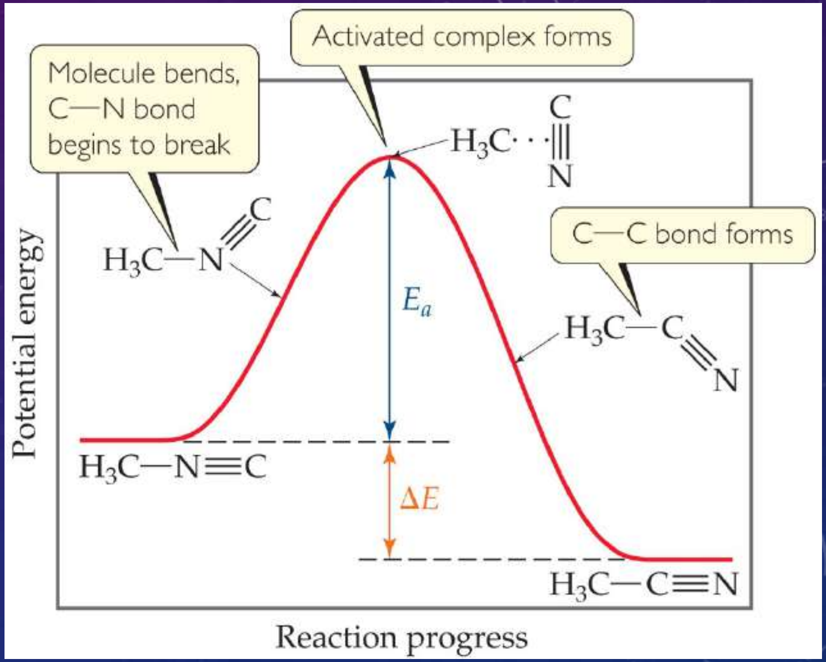
- Reactants gain energy as the reaction proceeds until the particles reach the maximum energy state.
- The organization of the atoms at this highest energy state is called the **transition state** (or activated complex).
- The energy needed to form this state is called the *activation energy*.

REACTION PROGRESS

Plots are made to show the energy possessed by the particles as the reaction proceeds.

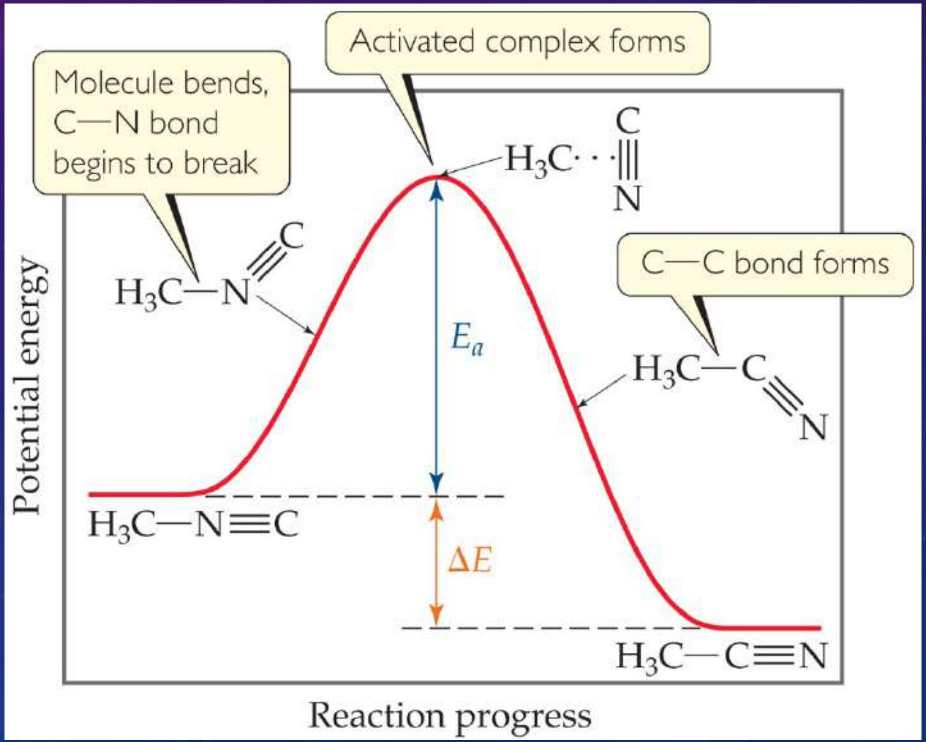
At the highest energy state, the transition state is formed.

Reactions can be endothermic or exothermic after this.



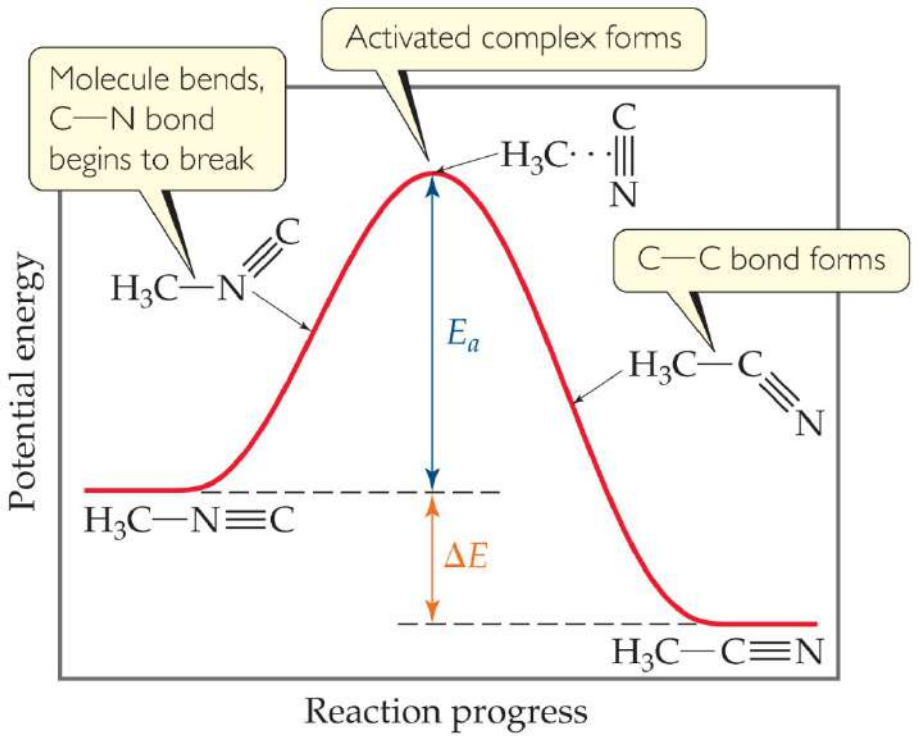
How does the energy needed to overcome the energy barrier compare with the overall change in energy for this reaction?

a. Similar in magnitude
b. Extremely different in magnitude
c. About twice as large as overall change in energy
d. About half as large as the overall change in energy



Suppose you could measure the rates for both the forward and reverse reactions of the process in Figure 14.17. In which direction would the rate be larger? Why?

a. The forward rate would be larger because the activation energy is less.
b. The reverse rate would larger because the activation energy is larger.



Suppose we have two reactions, $A \longrightarrow B$ and $B \longrightarrow C$. You can isolate B, and it is stable. Is B the transition state for the reaction $A \longrightarrow C$?

a. Yes, because B is an intermediate.

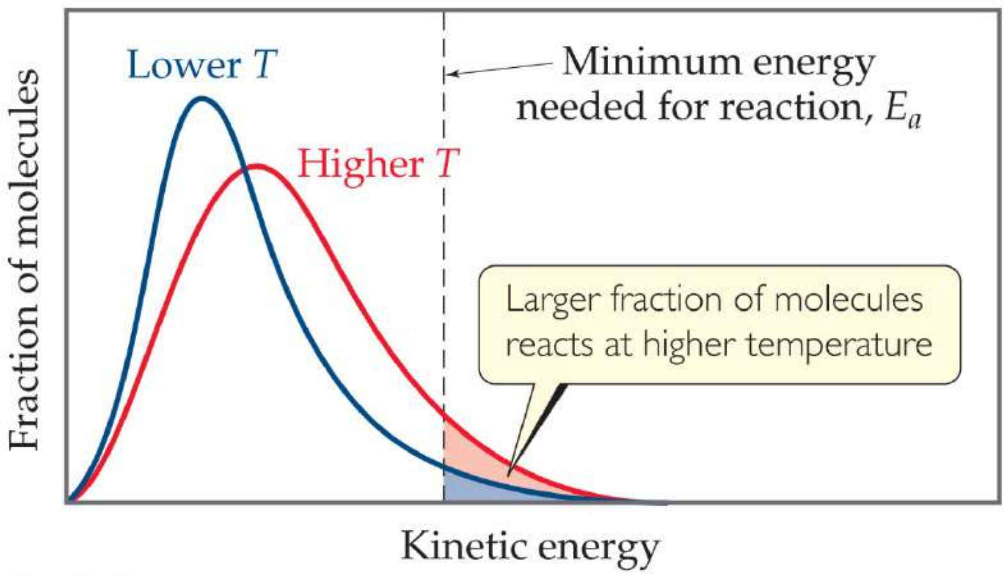
b. Yes, because B can be isolated.

c. No, because B is not stable.

d. No, because B can be isolated and transition states are by definition not stable.

DISTRIBUTION OF THE ENERGY OF MOLECULES

- Gases have an average temperature, but each individual molecule has its own energy.
- At higher energies, more molecules possess the energy needed for the reaction to occur.



What would the curve look like for a temperature higher than that for the red curve in the figure?

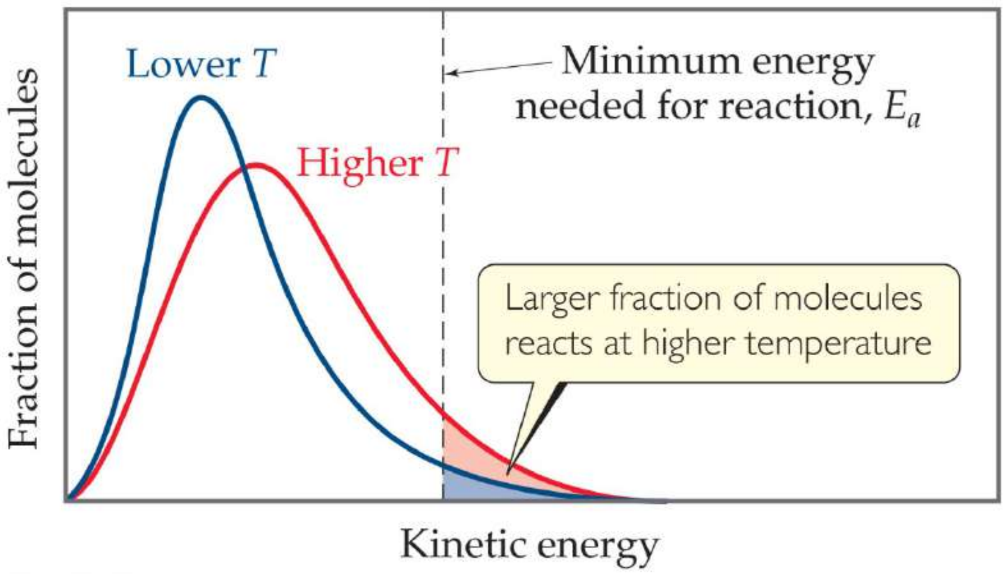
(1) The new curve would be shifted further to the right.

(2) The new curve would have a larger fraction of molecules above E_a.

(3) The new curve would heave a lower peak.

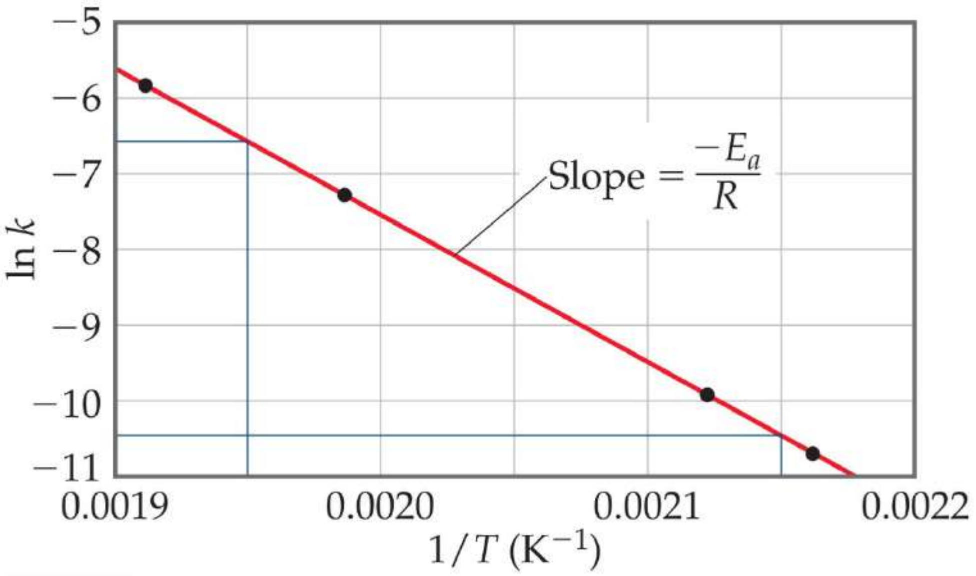
(4) The new curve would have a larger area underneath.

a. (1)
b. (1) and (2)
c. (1), (2), and (3)
d. (1), (2), (3), and (4)



THE RELATIONSHIP BETWEEN ACTIVATION ENERGY & TEMPERATURE

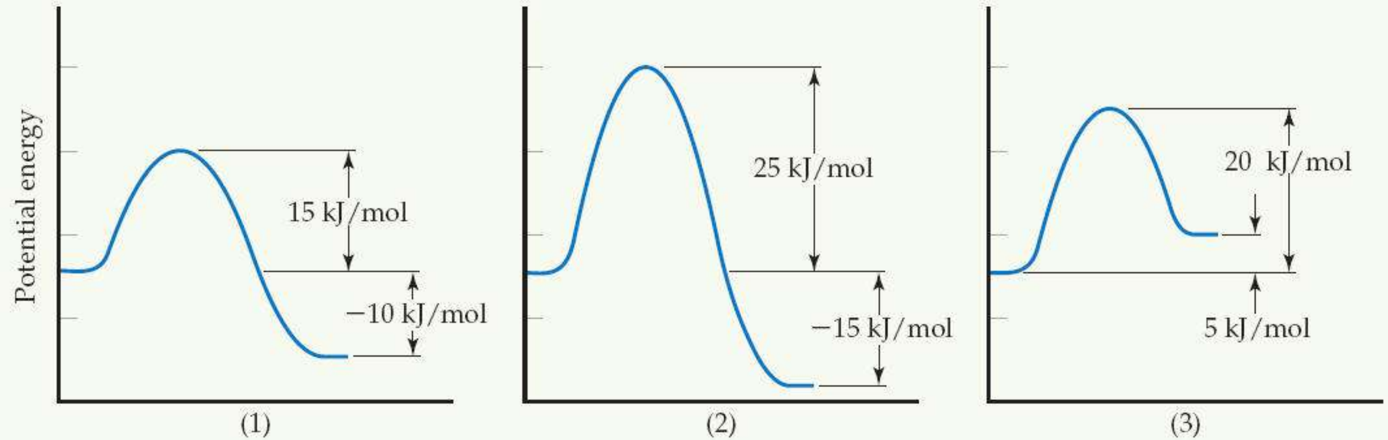
- Arrhenius noted relationship between activation energy and temperature: $k = Ae^{-Ea/RT}$
- Activation energy can be determined graphically by reorganizing the equation: $\ln k = -E_a/RT + \ln A$



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

Sample Exercise 14.10

Consider a series of reactions having the following energy profiles:



Rank the reactions from slowest to fastest assuming that they have nearly the same frequency factors.

Practice Exercise 2

Imagine that these reactions are reversed. Rank these reverse reactions from slowest to fastest.

14.6 REACTION MECHANISMS

LAW VS. THEORY

- Kinetics gives *what* happens. We call the description the *rate law*.
- *Why* do we observe that rate law? We explain with a *theory* called a **mechanism**.
- A mechanism is a series of stepwise reactions that show how reactants become products.

REACTION MECHANISMS

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

MOLECULARITY

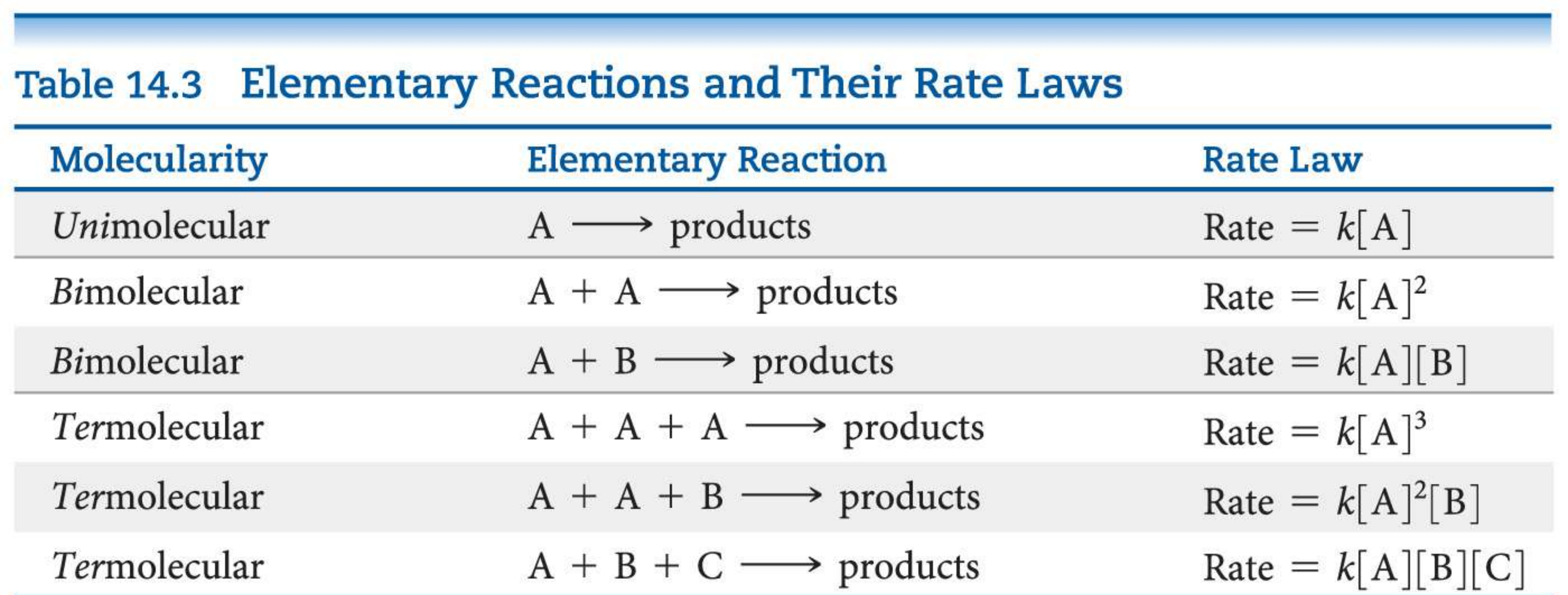


Table 14.3 Elementary Reactions and Their Rate Laws

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

The **molecularity** of an elementary reaction tells how many molecules are involved in that step of the mechanism.

What is the molecularity of the elementary reaction?

$$NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$$

a. Zero molecularity
b. Unimolecular
c. Bimolecular
d. Trimolecular

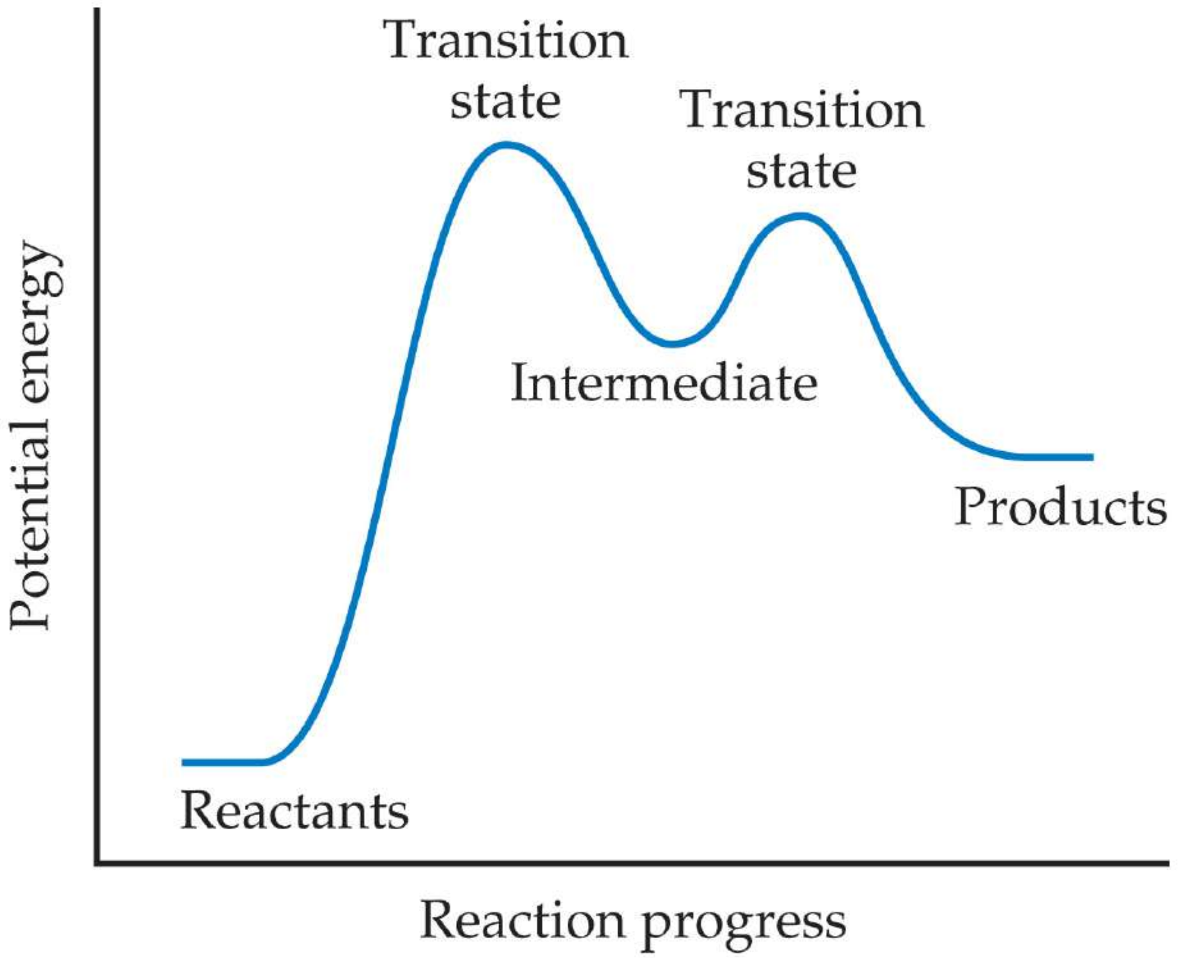
TERMOLECULAR?

- Termolecular steps require three molecules to simultaneously collide with the proper orientation *and* the proper energy.
- These are rare, if they indeed do occur.
- These *must* be slower than unimolecular or bimolecular steps.
- Nearly *all* mechanisms use *only* unimolecular or bimolecular reactions.

For this profile, is it easier for a molecule of the intermediate to convert to reactants or products?

a. Reactants

b. Products



Sample Exercise 14.12

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$O_3(g) + O(g) \longrightarrow 2\,O_2(g)$$

(a) Describe the molecularity of each elementary reaction in this mechanism. **(b)** Write the equation for the overall reaction. **(c)** Identify the intermediate(s).

Practice Exercise 1

Consider the following two-step mechanism:

$A(g) + B(g) \longrightarrow X(g) + Y(g)$

$X(g) + C(g) \longrightarrow Y(g) + Z(g)$

Which of the following statements is or are true?

(i) Both of the steps in this mechanism are bimolecular.

(ii) The overall reaction is $A(g) + B(g) + C(g) \rightarrow Y(g) + Z(g)$.

(iii) The substance $X(g)$ is an intermediate in this mechanism.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

(c) Statements (i) and (iii) are true.

(d) Statements (ii) and (iii) are true.

(e) All three statements are true.

Practice Exercise 2

For the reaction

$$Mo(CO)_6 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3 + CO$$

the proposed mechanism is

$$\begin{aligned} Mo(CO)_6 &\longrightarrow Mo(CO)_5 + CO \\ Mo(CO)_5 + P(CH_3)_3 &\longrightarrow Mo(CO)_5P(CH_3)_3 \end{aligned}$$

(a) Is the proposed mechanism consistent with the equation for the overall reaction?

(b) What is the molecularity of each step of the mechanism?

(c) Identify the intermediate(s).

Sample Exercise 14.13

If the following reaction occurs in a single elementary reaction, predict its rate law:

$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$$

Practice Exercise 2

Consider the following reaction: $2\,NO(g) + Br_2(g) \rightarrow 2\,NOBr(g)$.

(a) Write the rate law for the reaction, assuming it involves a single elementary reaction.

(b) Is a single step mechanism likely for this reaction?

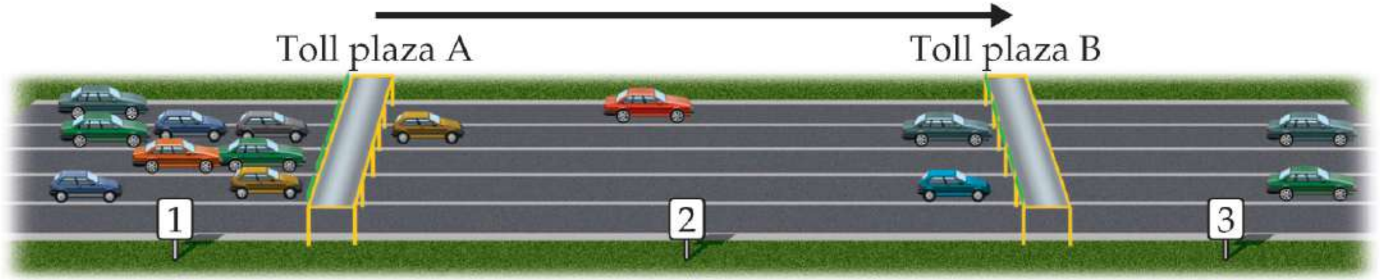
Practice Exercise 1

Consider the following reaction: 2 A + B → X + 2 Y. You are told that the first step in the mechanism of this reaction has the following rate law: Rate = *k*[A][B]. Which of the following could be the first step in the reaction mechanism (Z is an intermediate)?

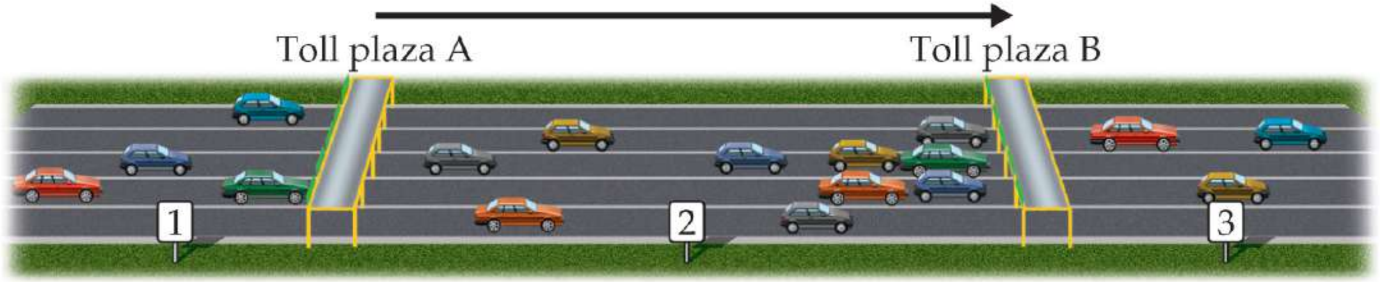
(a)A + A → Y + Z
(b)A → X + Z
(c)A + A + B → X + Y + Y
(d)B → X + Y
(e)A + B → X + Z

WHAT LIMITS THE RATE?

- The overall reaction cannot occur faster than the slowest reaction in the mechanism.
- We call that the **rate-determining step**.



(a) Cars slowed at toll plaza A, rate-determining step is passage through A



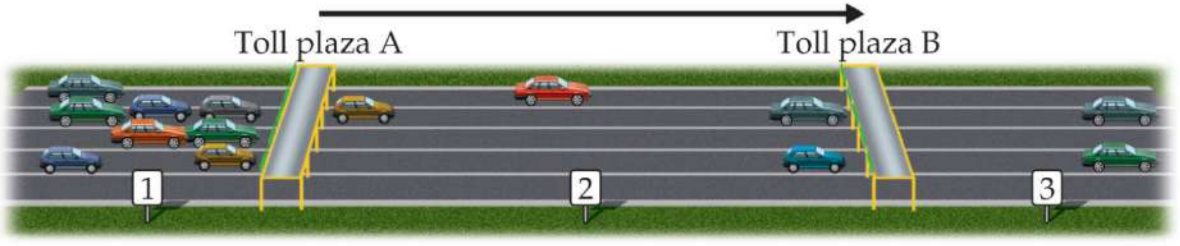
(b) Cars slowed at toll plaza B, rate-determining step is passage through B

For which of the two scenarios in the figure will one get from point 1 to point 3 most rapidly?

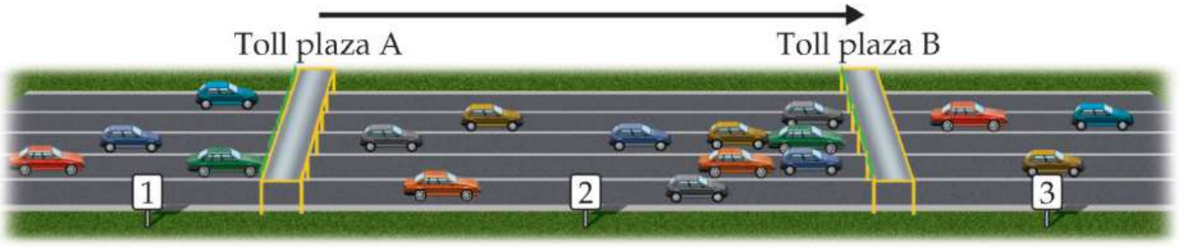
a. Scenario (a)

b. Scenario (b)

c. Need more information



(a) Cars slowed at toll plaza A, rate-determining step is passage through A



(b) Cars slowed at toll plaza B, rate-determining step is passage through B

WHAT IS REQUIRED OF A PLAUSIBLE MECHANISM?

- The *rate law* must be able to be devised from the rate-determining step.
- The *stoichiometry* must be obtained when all steps are added up.
- Each step must balance, like any equation.
- All intermediates are made and used up.
- Any catalyst is used and regenerated.

Why can’t the rate law for a reaction generally be deduced from the balanced equation for the reaction?

a. All reactions are not elementary, single step, as in the balanced equation for the reaction.
b. The balanced equation gives no information about the rate constant, which is part of a rate law.
c. The extent of a reaction as shown by a balanced equation does not depend on concentrations.
d. The rate law depends not on the overall balanced reaction, but on the slowest step in the reaction mechanism.

A MECHANISM WITH A SLOW INITIAL STEP

- Overall equation: $NO_2 + CO \rightarrow NO + CO_2$
- Rate law: Rate = $k\,[NO_2]^2$
- If the first step is the rate-determining step, the coefficients on the reactants side are the same as the order in the rate law!
- So, the first step of the mechanism begins:

$NO_2 + NO_2 \rightarrow$

A MECHANISM WITH A SLOW INITIAL STEP (CONTINUED)

- The easiest way to complete the first step is to make a product:

$NO_2 + NO_2 \longrightarrow NO + NO_3$

- We do not see NO_3 in the stoichiometry, so it is an **intermediate**, which needs to be used in a faster next step.

$NO_3 + CO \longrightarrow NO_2 + CO_2$

A MECHANISM WITH A SLOW INITIAL STEP (COMPLETED)

- Since the first step is the slowest step, it gives the rate law.
- If you add up all of the individual steps (2 of them), you get the stoichiometry.
- Each step balances.
- This is a plausible mechanism.

Sample Exercise 14.14

The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$$N_2O(g) \longrightarrow N_2(g) + O(g) \qquad \text{(slow)}$$

$$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g) \qquad \text{(fast)}$$

(a) Write the equation for the overall reaction.

(b) Write the rate law for the overall reaction.

Practice Exercise 1

Let's consider a hypothetical reaction: 2 C + D → J + 2 K. You are told that the rate of this reaction is second order overall and second order in [C]. Could any of the following be a rate-determining first step in a reaction mechanism that is consistent with the observed rate law for the reaction (Z is an intermediate)?

(a) C + C → K + Z

(b) C → J + Z

(c) C + D → J + Z

(d) D → J + K

(e) None of these are consistent with the observed rate law.

Practice Exercise 2

Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

$$O_3(g) + 2\,NO_2(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction is believed to occur in two steps:

$$O_3(g) + NO_2(g) \longrightarrow NO_3(g) + O_2(g)$$
$$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$$

The experimental rate law is rate = $k[O_3][NO_2]$. What can you say about the relative rates of the two steps of the mechanism?

A MECHANISM WITH A FAST INITIAL STEP

- Equation for the reaction:

$2\ NO + Br_2 \rightleftharpoons 2\ NOBr$

- The rate law for this reaction is found to be

$\text{Rate} = k\,[NO]^2\,[Br_2]$

- Because termolecular processes are rare, this rate law suggests a multistep mechanism.

Why are termolecular elementary steps rare in gas-phase reactions?

a. Gas reactions do not require three reactants.
b. Unimolecular gas reactions are more likely.
c. Odds of three particles simultaneously colliding together and properly oriented are very low.
d. All of the above

A MECHANISM WITH A FAST INITIAL STEP (CONTINUED)

- The rate law indicates that a quickly established equilibrium is followed by a slow step.
- Step 1:$NO + Br_2 \rightleftharpoons NOBr_2$
- Step 2:$NOBr_2 + NO \rightarrow 2\ NOBr$

WHAT IS THE RATE LAW?

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

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

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

[$NOBR_2$] (AN INTERMEDIATE)?

- $NOBr_2$ can react two ways:
  - With NO to form NOBr.
  - By decomposition to reform NO and Br_2.
- The reactants and products of the first step are in equilibrium with each other.
- For an equilibrium (as we will see in the next chapter):

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

THE RATE LAW (FINALLY!)

- Substituting for the forward and reverse rates:

k_1 [NO] [Br_2] = k_{-1} [$NOBr_2$]

- Solve for [$NOBr_2$], then substitute into the rate law:

Rate = k_2 (k_1/k_{-1}) [NO] [Br_2] [NO]

- This gives the observed rate law!

Rate = k $[NO]^2$ [Br_2]

Sample Exercise 14.15

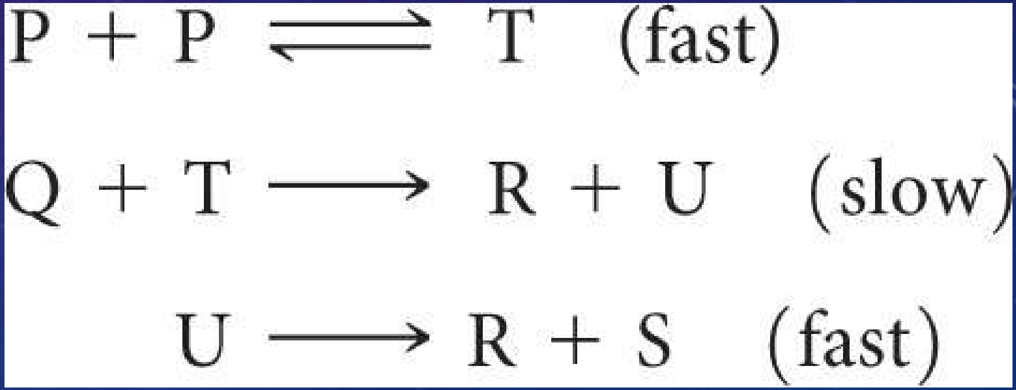
Show that the following mechanism for Equation 14.24 ($2NO + Br_2 \rightarrow 2NOBr$) also produces a rate law consistent with the experimentally observed one:

$$\text{Step 1:}\quad NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g) \qquad \text{(fast equilibrium)}$$

$$\text{Step 2:}\quad N_2O_2(g) + Br_2(g) \xrightarrow{k_2} 2\,NOBr(g) \qquad \text{(slow)}$$

Practice Exercise 1

Consider the following hypothetical reaction: $2\ P + Q \rightarrow 2\ R + S$. The mechanism below is proposed for this reaction:



$$P + P \rightleftharpoons T \quad \text{(fast)}$$

$$Q + T \longrightarrow R + U \quad \text{(slow)}$$

$$U \longrightarrow R + S \quad \text{(fast)}$$

Substances T and U are intermediates. What rate law is predicted by this mechanism?

(a) Rate = $k[P]^2$

(b) Rate = $k[P][Q]$

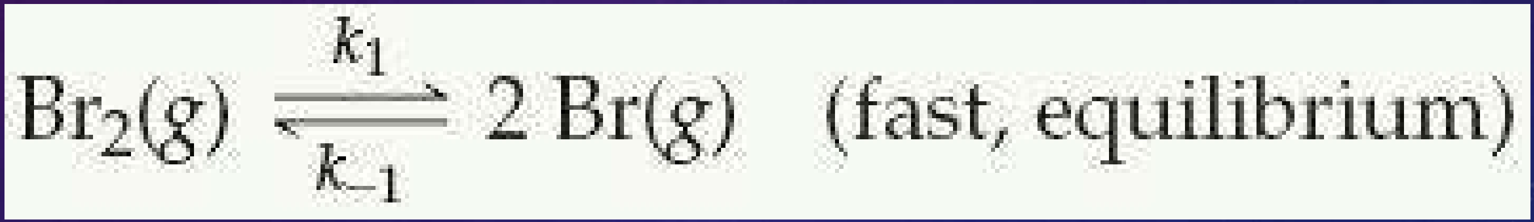
(c) Rate = $k[P]^2[Q]$

(d) Rate = $k[P][Q]^2$

(e) Rate = $k[U]$

Practice Exercise 2

The first step of a mechanism involving the reaction of bromine is



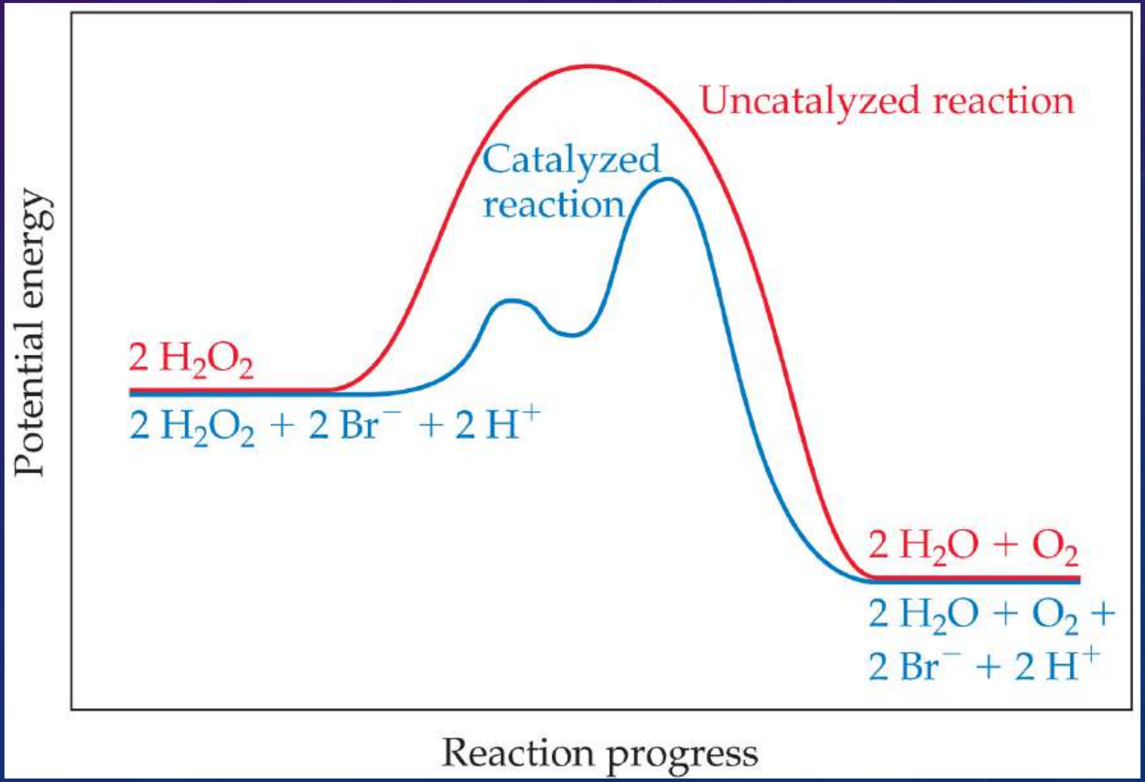
$$Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Br(g) \quad \text{(fast, equilibrium)}$$

What is the expression relating the concentration of Br(g) to that of Br_2(g)?

14.7 CATALYSIS

CATALYSTS

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

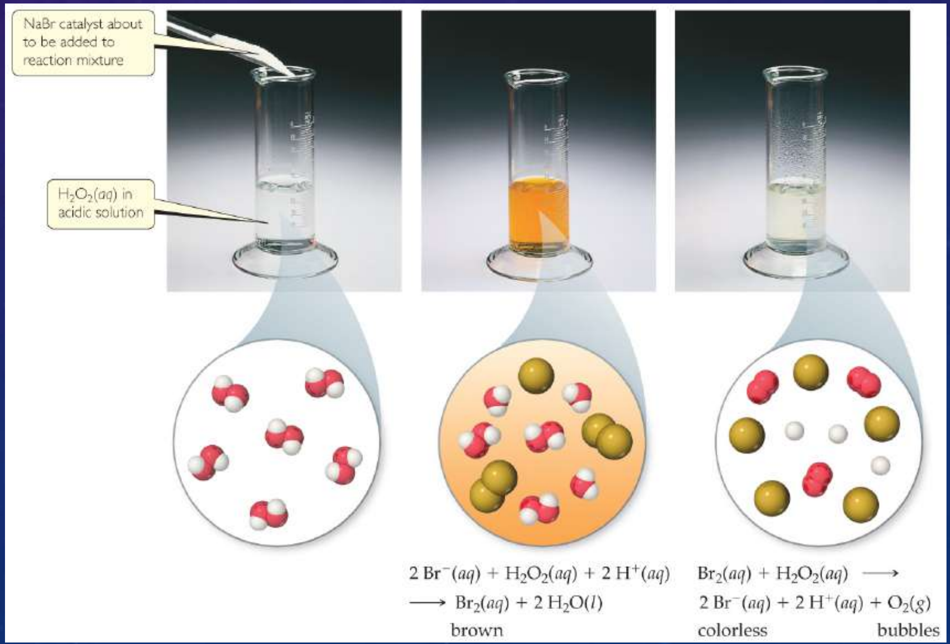


TYPES OF CATALYSTS

1) Homogeneous catalysts
2) Heterogeneous catalysts
3) Enzymes

HOMOGENEOUS CATALYSTS

- The reactants and catalyst are in the same phase.
- Many times, reactants and catalyst are dissolved in the same solvent, as seen below.



$2\,Br^-(aq) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l)$

$Br_2(aq) + H_2O_2(aq) \longrightarrow 2\,Br^-(aq) + 2\,H^+(aq) + O_2(g)$

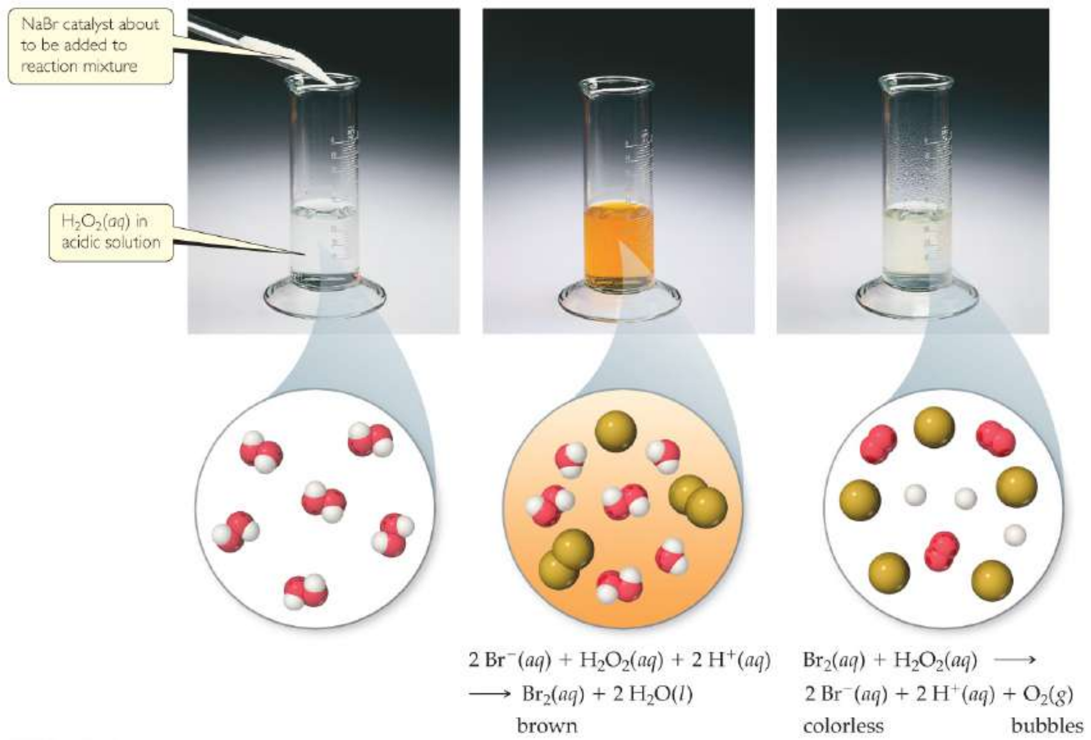
Why does the solution in the middle cylinder have a brownish color?

a. Br^- colors the solution.

b. Br_2 colors the solution

c. H_2O_2 colors the solution.

d. O_2 colors the solution.



$$2\,Br^-(aq) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l)$$

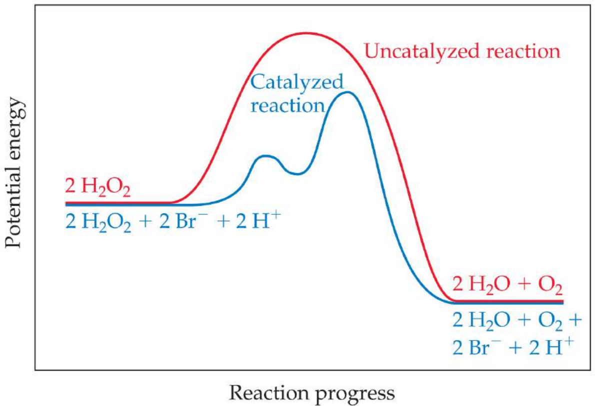
brown

$$Br_2(aq) + H_2O_2(aq) \longrightarrow 2\,Br^-(aq) + 2\,H^+(aq) + O_2(g)$$

colorless bubbles

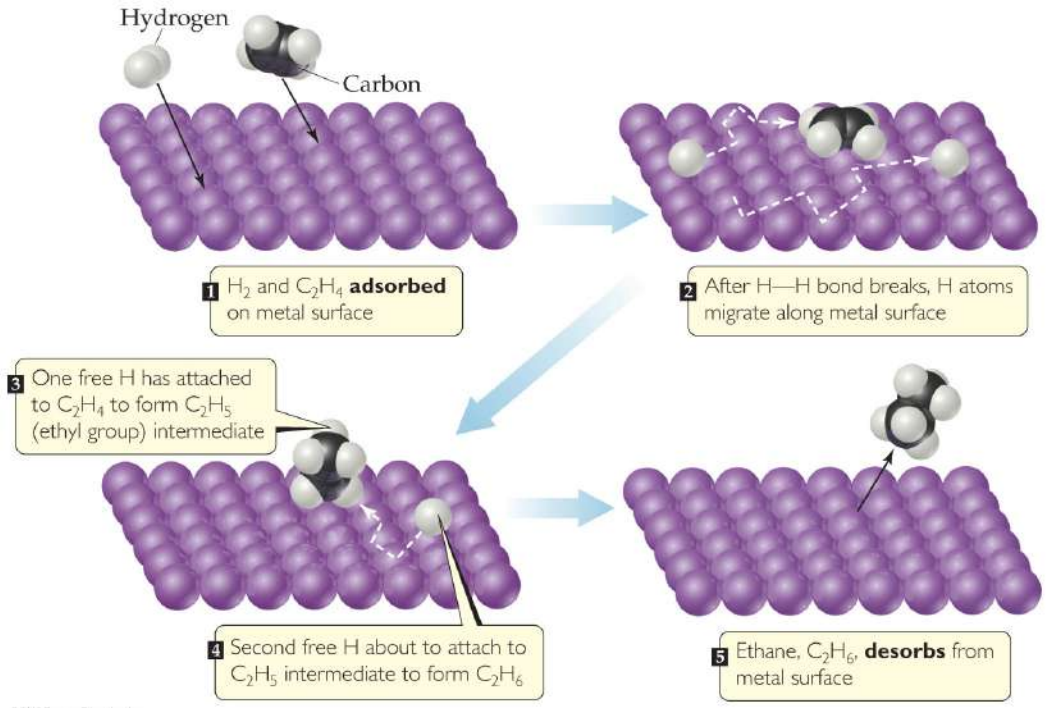
Where are the intermediates and transition states in this diagram?

	Red curve	Blue curve
a.	Top of peak; no intermediates	top of first peak; top of second peak
b.	Top of peak; top of peak	both in the “valley” between peaks
c.	Top of peak; top of peak	top of both peaks; no intermediates
d.	Top of peak; no intermediates	top of both peaks; in the “valley” between the peaks



HETEROGENEOUS CATALYSTS

- The catalyst is in a different phase than the reactants.
- Often, gases are passed over a solid catalyst.
- The adsorption of the reactants is often the rate-determining step.



1 H_2 and C_2H_4 **adsorbed** on metal surface

2 After H—H bond breaks, H atoms migrate along metal surface

3 One free H has attached to C_2H_4 to form C_2H_5 (ethyl group) intermediate

4 Second free H about to attach to C_2H_5 intermediate to form C_2H_6

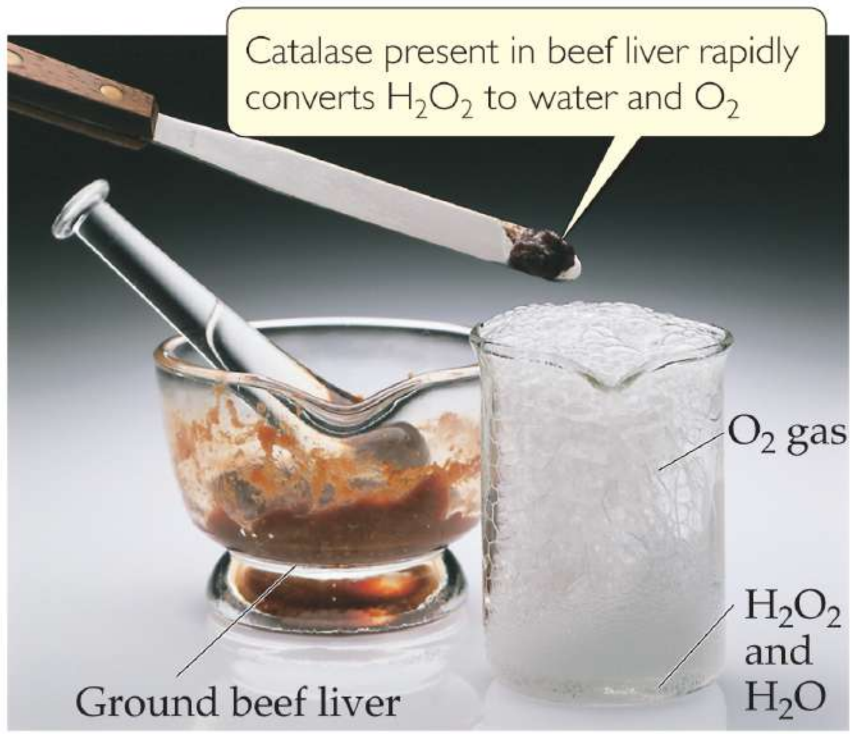
5 Ethane, C_2H_6, **desorbs** from metal surface

How does a homogeneous catalyst compare with a heterogeneous one regarding the ease of recovery of the catalyst from the reaction mixture?

a. A heterogeneous catalyst is easier to remove from a reaction mixture because of phase differences.
b. A heterogeneous catalyst is easier to remove from a reaction mixture because it is present in the greatest quantity.
c. A homogeneous catalyst is easier to remove from a reaction mixture because of phase differences.
d. A homogenous catalyst is easier to remove from a reaction mixture because it is easier to identify in the reaction mixture.

ENZYMES

- **Enzymes** are biological catalysts.
- They have a region where the reactants attach. That region is called the **active site**. The reactants are referred to as **substrates**.

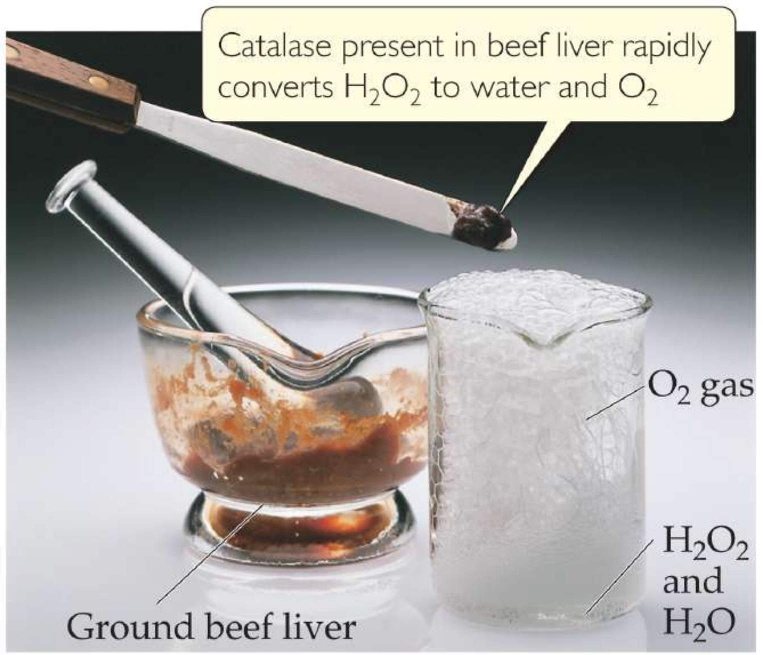


Why is the reaction faster when the liver is ground up?

a. The grinding motion activates the reaction.

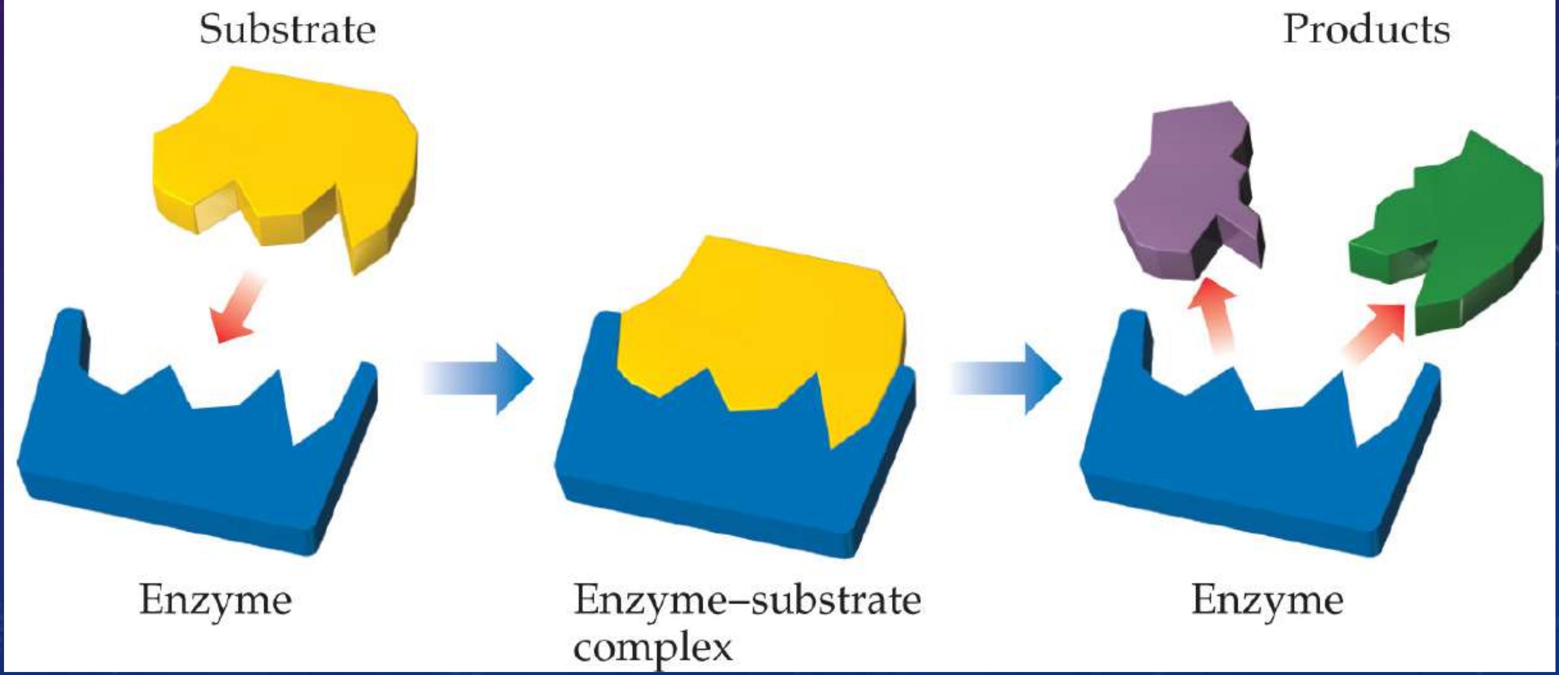
b. The glass from the mortar and pestle act as a catalyst.

c. Grinding produces smaller particles of liver and more surface area for reaction.



LOCK-AND-KEY MODEL

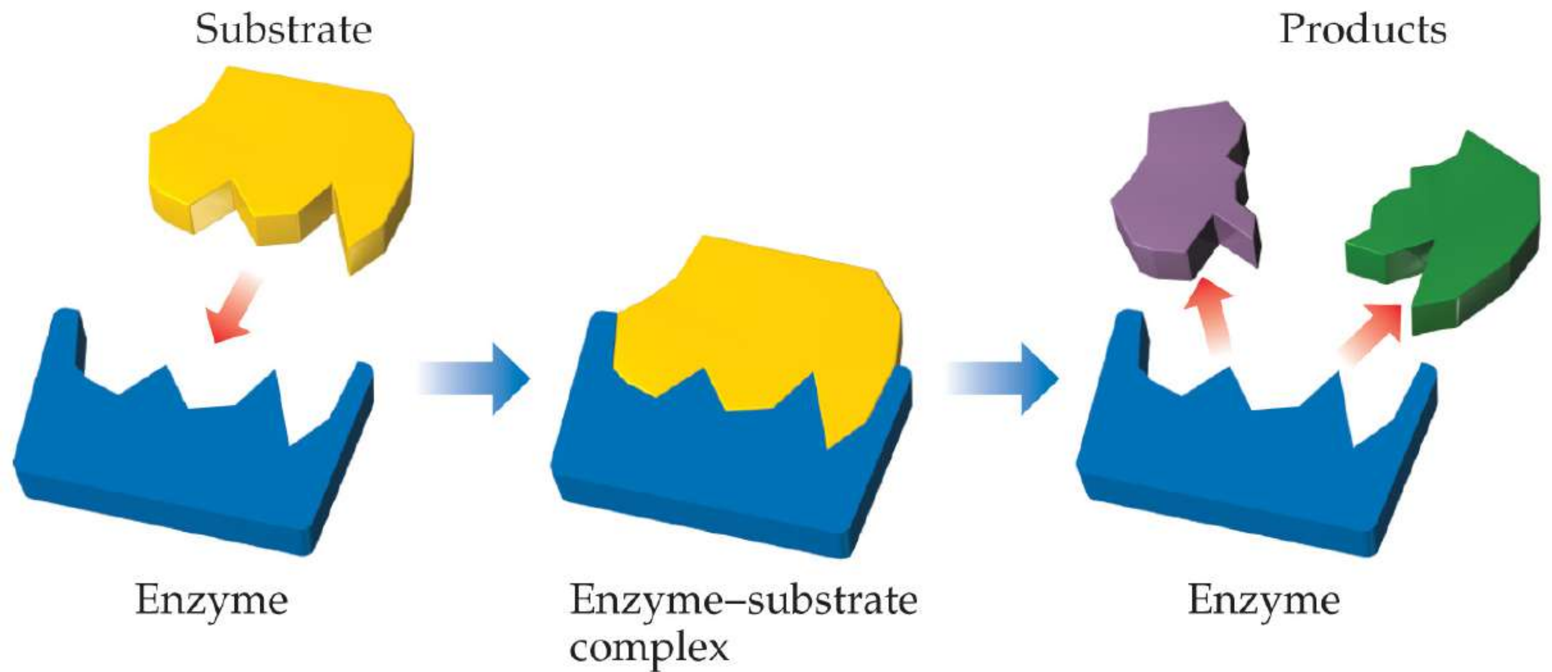
- In the enzyme–substrate model, the substrate fits into the active site of an enzyme, much like a key fits into a lock.
- They are specific.



Which molecules must bind more tightly to the active site, substrates or products?

a. Substrate

b. Products



Is it reasonable to say that enzymes lower the energy of the transition state for a reaction?

a. Yes, because an enzyme is a catalyst.

b. No, because enzymes are different in structure and their properties than typical catalysts in non-biochemical reactions.

c. Possibly, but the nature of the transition states in the catalyzed and uncatalyzed reaction can be significantly different.

d. Yes, because it should form a stable intermediate, transition state.

Sample Integrative Exercise

Putting Concepts Together

Formic acid (HCOOH) decomposes as follows:

$HCOOH(g) \rightarrow CO_2(g) + H_2(g)$

The uncatalyzed decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in Figure 14.31. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in Figure 14.31.

(a) Estimate the half-life and first-order rate constant for formic acid decomposition.

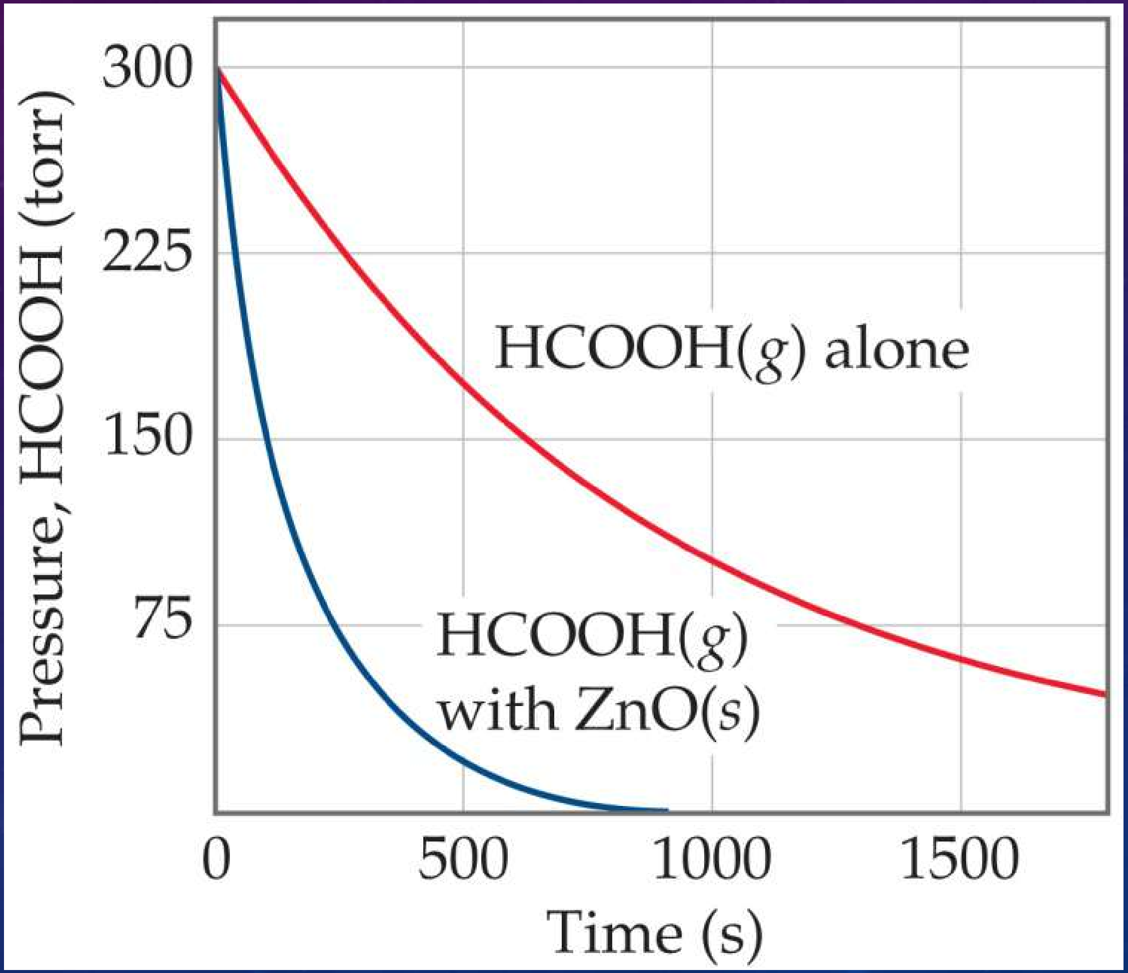
(b) What can you conclude from the effect of added ZnO on the decomposition of formic acid?

(c) The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of k?

(d) The pressure of formic acid vapor at the start of the reaction is 3.00×10^2 torr. What is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm^3, how many moles of gas occupy the reaction chamber at the end of the reaction?

(e) The standard heat of formation of formic acid vapor is $\Delta H^\circ_f = -378.6$ kJ/mol. Calculate ΔH° for the overall reaction. If the activation energy (E_a) for the reaction is 184 kJ/mol, sketch an approximate energy profile for the reaction, and label E_a, ΔH°, and the transition state.

FIGURE 14.31


300
225
150
75
Pressure, HCOOH (torr)
HCOOH(g) alone
HCOOH(g) with ZnO(s)
0
500
1000
1500
Time (s)