SAMPLE EXERCISE 14.3 Relating Rates at Which Products Appear and Reactants Disappear

(a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction

$2\,O_3(g) \longrightarrow 3\,O_2(g)$?

(b) If the rate at which O_2 appears, $\Delta[O_2]/\Delta t$, is $6.0 \cdot 10^{-5}$ M/s at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[O_3]/\Delta t$?

SAMPLE EXERCISE 14.3 continued

PRACTICE EXERCISE

The decomposition of N_2O_5 proceeds according to the following equation:

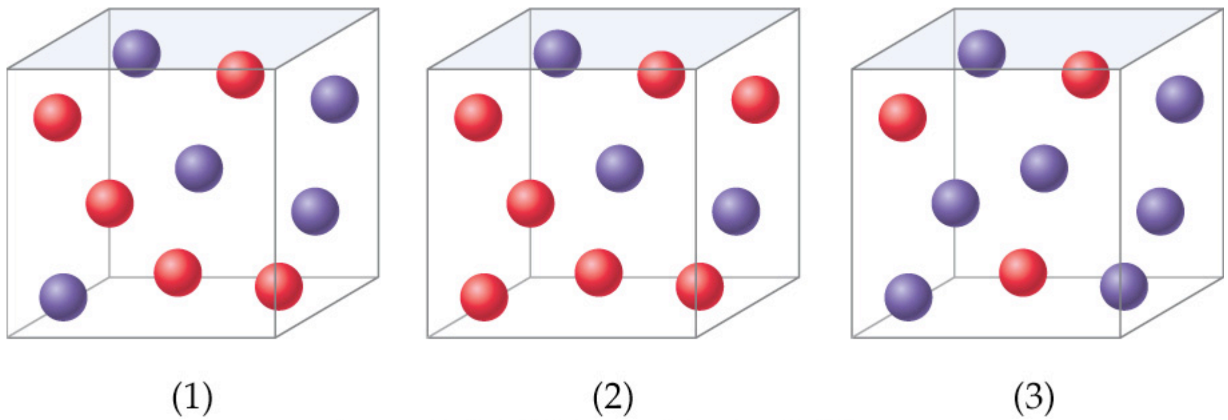
$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is $4.2 \cdot 10^{-7}$ M/s, what is the rate of appearance of (a) NO_2, (b) O_2?

Answers: **(a)** $8.4 \cdot 10^{-7}$ M/s, **(b)** $2.1 \cdot 10^{-7}$ M/s

SAMPLE EXERCISE 14.4 Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction $A + B \longrightarrow C$ for which rate = $k[A][B]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.



SAMPLE EXERCISE 14.4 continued

PRACTICE EXERCISE

Assuming that rate = k[A][B], rank the mixtures represented in this Sample Exercise in order of increasing rate.

Answer: 2 = 3 < 1

SAMPLE EXERCISE 14.5 Determining Reaction Orders and Units for Rate Constants

(a) What are the overall reaction orders for the rate laws described in Equations 14.9 and 14.10? **(b)** What are the units of the rate constant for the rate law for Equation 14.9?

PRACTICE EXERCISE

(a) What is the reaction order of the reactant H_2 in Equation 14.11? **(b)** What are the units of the rate constant for Equation 14.11?

Answers: **(a)** 1, **(b)** M^{-1} s^{-1}

SAMPLE EXERCISE 14.6 Determining a Rate Law from Initial Rate Data

The initial rate of a reaction $A + B \longrightarrow C$ 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 magnitude of the rate constant, **(c)** the rate of the reaction when [A] = 0.050 *M* and [B] = 0.100 *M*.

PRACTICE EXERCISE

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.

Answers: **(a)** rate = $k[NO]^2[H_2]$; **(b)** $k = 1.2\ M^{-2}s^{-1}$; **(c)** rate = $4.5 \cdot 10^{-4}\ M/s$

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 $5.0 \cdot 10^{-7}$ 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 drop to $3.0 \cdot 10^{-7}$ g/cm^3?

PRACTICE EXERCISE

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

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

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

Answer: 51 torr

SAMPLE EXERCISE 14.8 Determining Reaction Order from the Integrated Rate Law

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

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

Time (s)	$[NO_2]$ (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 NO_2?

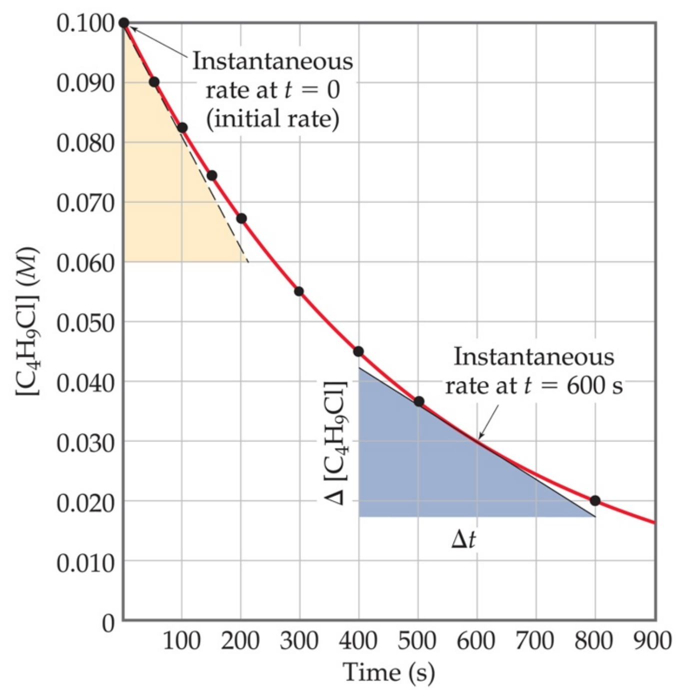
PRACTICE EXERCISE

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?

Answer: Using Equation 14.14, we find $[NO2] = 1.00 \cdot 10^{-3}\ M$

SAMPLE EXERCISE 14.9 Determining the Half-life of a First-Order Reaction

The reaction of C_4H_9Cl with water is a first-order reaction. The figure below 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.



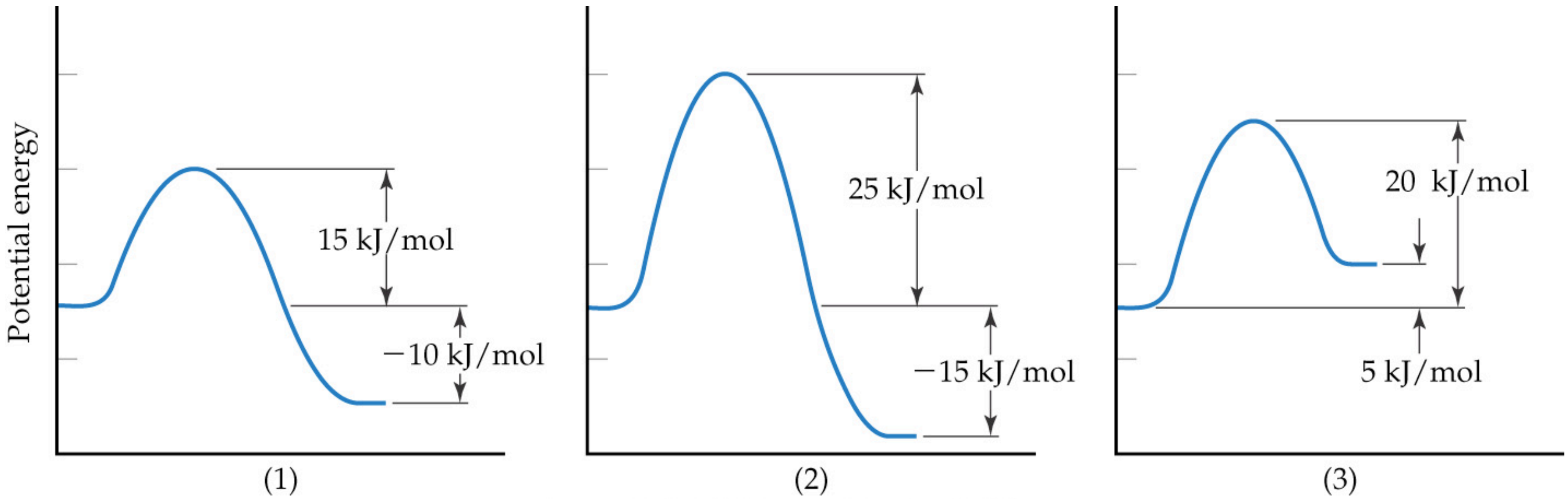
PRACTICE EXERCISE

(a) Using Equation 14.15, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. **(b)** How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Answers: **(a)** 0.478 yr = $1.51 \cdot 10^{-7}$ s; **(b)** it takes two half-lives, 2(0.478 yr) = 0.956 yr

SAMPLE EXERCISE 14.10 Relating Energy Profiles to Activation Energies and Speeds of Reaction

Consider a series of reactions having the following energy profiles:



Assuming that all three reactions have nearly the same frequency factors, rank the reactions from slowest to fastest.

PRACTICE EXERCISE

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

Answer: (2) < (1) < (3) because E_a values are 40, 25, and 15 kJ/mol, respectively

SAMPLE EXERCISE 14.11 Determining the Energy of Activation

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures

Temperature (°C)	$k(s^{-1})$
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(a) From these data, calculate the activation energy for the reaction. **(b)** What is the value of the rate constant at 430.0 K?

PRACTICE EXERCISE

Using the data in Sample Exercise 14.11, calculate the rate constant for the rearrangement of methyl isonitrile at 280°C.

Answer: $2.2 \cdot 10^{-2} s^{-1}$

SAMPLE EXERCISE 14.12 Determining Molecularity and Identifying Intermediates

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

For the reaction

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

the proposed mechanism is

$$Mo(CO)_6 \longrightarrow Mo(CO)_5 + CO$$
$$Mo(CO)_5 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3$$

(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).

Answers: **(a)** Yes, the two equations add to yield the equation for the reaction. **(b)** The first elementary reaction is unimolecular, and the second one is bimolecular. **(c)** $Mo(CO)_5$

SAMPLE EXERCISE 14.13 Predicting the Rate Law for an Elementary Reaction

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

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

PRACTICE EXERCISE

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

Answers: **(a)** Rate = $k[NO]^2[Br_2]$ **(b)** No, because termolecular reactions are very rare

SAMPLE EXERCISE 14.14 Determining the Rate Law for a Multistep Mechanism

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

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

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

(a) Write the equation for the overall reaction. **(b)** Write the rate law for the overall reaction.

SAMPLE EXERCISE 14.14 continued

PRACTICE EXERCISE

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?

Answer: Because the rate law conforms to the molecularity of the first step, that must be the rate-determining step. The second step must be much faster than the first one.

SAMPLE EXERCISE 14.15 Deriving the Rate Law for a Mechanism with a Fast Initial Step

Show that the following mechanism for Equation 14.24 also produces a rate law consistent with the experimentally observed one:

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

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

PRACTICE EXERCISE

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

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

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

Answer: $[Br] = \left(\frac{k_1}{k_{-1}}[Br_2]\right)^{1/2}$