

Chemistry, The Central Science, 11th edition
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Chapter 14

Chemical Kinetics



Overview of Kinetics

Section 14.1

- apply the KMT and collision model to explain reaction rates
- factors that affect reaction rates

Section 14.2

- average and instantaneous reaction rates
- apply stoichiometry to determine reaction rates

Sections 14.3 and 14.4**

- identify and apply rate laws and rate constants
- determine the order of a reaction from data
- calculate half-life

Section 14.5

- effects of temperature on reaction rate
- activation energy, including the Arrhenius Equation

Section 14.6

- multi-step reactions

Section 14.7

- catalysts



Kinetics

- In kinetics we study the **rate** at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).



How do the following factors affect rates of reactions?

- Physical state of the reactants
- Concentration of the reactants
- Temperature of the reaction
- Presence or absence of a catalyst



Factors That Affect Reaction Rates

- Physical State of the Reactants
 - In order to react, molecules must come in contact with each other.
 - The more homogeneous the mixture of reactants, the faster the molecules can react.



Factors That Affect Reaction Rates

- Concentration of Reactants
 - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.



Factors That Affect Reaction Rates

- Temperature
 - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

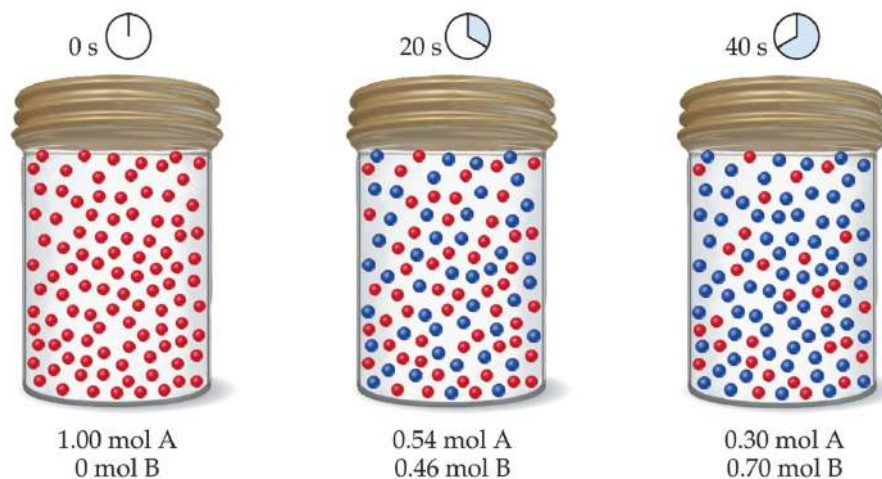


Factors That Affect Reaction Rates

- Presence of a Catalyst
 - Catalysts speed up reactions by changing the mechanism of the reaction.
 - Catalysts are not consumed during the course of the reaction.



Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.



Reaction Rates

- We can measure the rate of the appearance of B:

$$\text{Avg Rate} = \frac{\Delta (\text{Conc B})}{\Delta t} = \frac{(\text{Conc of B at } t = 20\text{s}) - (\text{Conc of B at } t = 0 \text{ s})}{20\text{s} - 0 \text{ min}}$$

- **Average rate = 0.46 M – 0.00 M**
20 s – 0 s
= 0.023 M/s



Reaction Rates

- We can measure the rate of disappearance of A:

$$\text{Average Rate} = \frac{-\Delta(\text{moles of A})}{\Delta t}$$

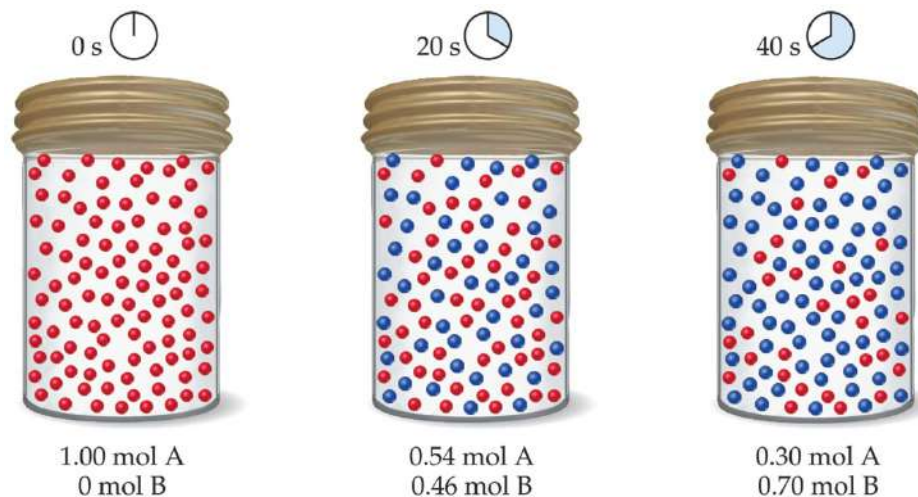
- Note the negative sign! This reminds us that rate is being expressed in terms of the disappearance of a reactant.



Sample Exercise 14.1 (p. 578)

For the reaction pictured at the bottom of this page, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

$(-1.2 \times 10^{-2} \text{ M/s})$



Practice Exercise 1 (14.1)

If the experiment on the previous page is run for 60 s, 0.16 mol A remain. Which of the following statement is or is not 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 $t_1 = 40$ s 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 1 (14.1)

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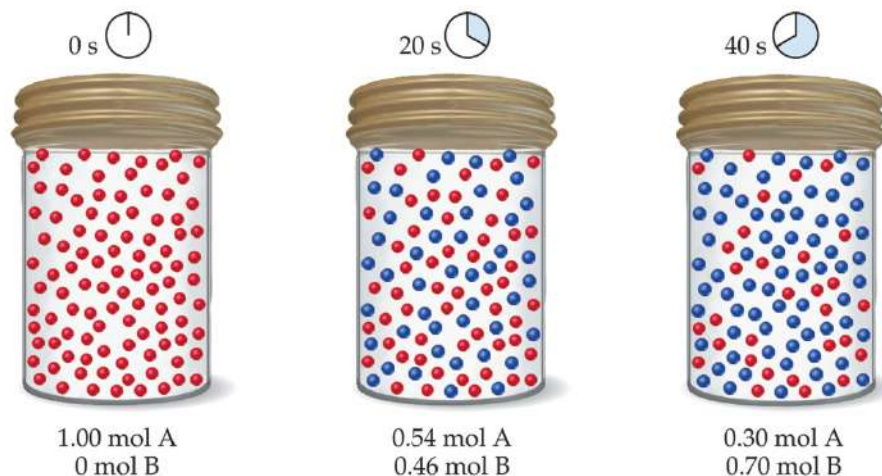
- (i) After 60 s there are 0.84 mol B in the flask.
 - (ii) The decrease in the number of moles of A from $t_1 = 0$ s to $t_2 = 20$ s is greater than that from $t_1 = 40$ s to $t_2 = 60$ s.
 - (iii) The average rate for the reaction from $t_1 = 40$ s to $t_2 = 60$ s is 7.0×10^{-3} M/s.
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- a) Only one of the statements is true.
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 - c) Statements (i) and (iii) are true.
 - d) Statements (ii) and (iii) are true.
 - e) All three statements are true.



Practice Exercise 2 (14.1)

From the reaction pictured, calculate the average rate of appearance of B over the time interval from 0 to 40 s.

$(1.8 \times 10^{-2} \text{ M/s})$



Kinetics

Change of Rate with Time



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}](M)$
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, $\text{C}_4\text{H}_9\text{Cl}$, was measured at various times.



Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}](M)$	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	

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

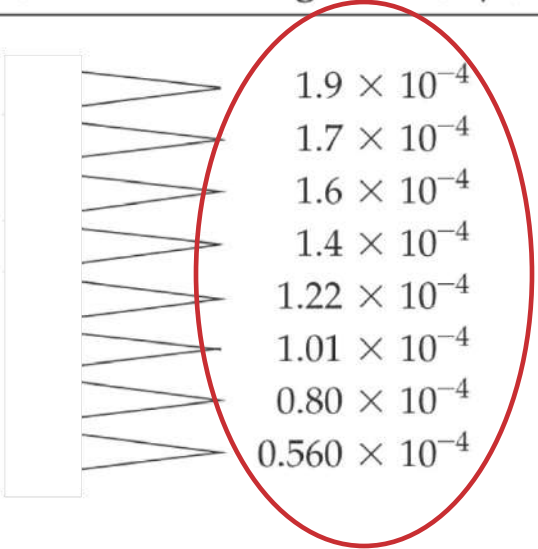
$$\text{Average rate} = \frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t}$$



Reaction Rates



Time, t (s)	$[\text{C}_4\text{H}_9\text{Cl}](M)$	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	



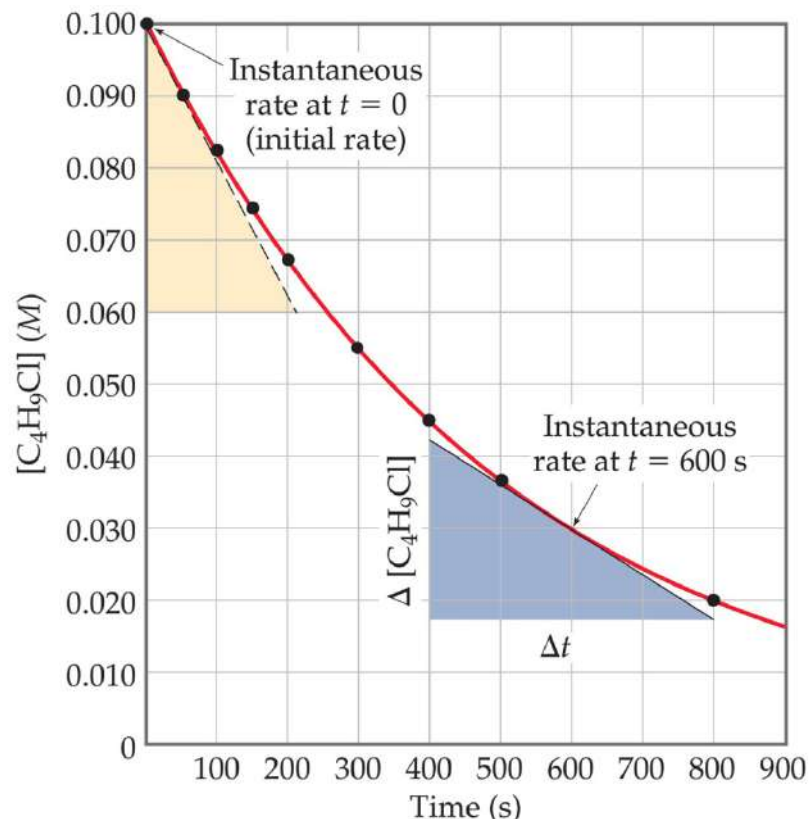
- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.



Reaction Rates



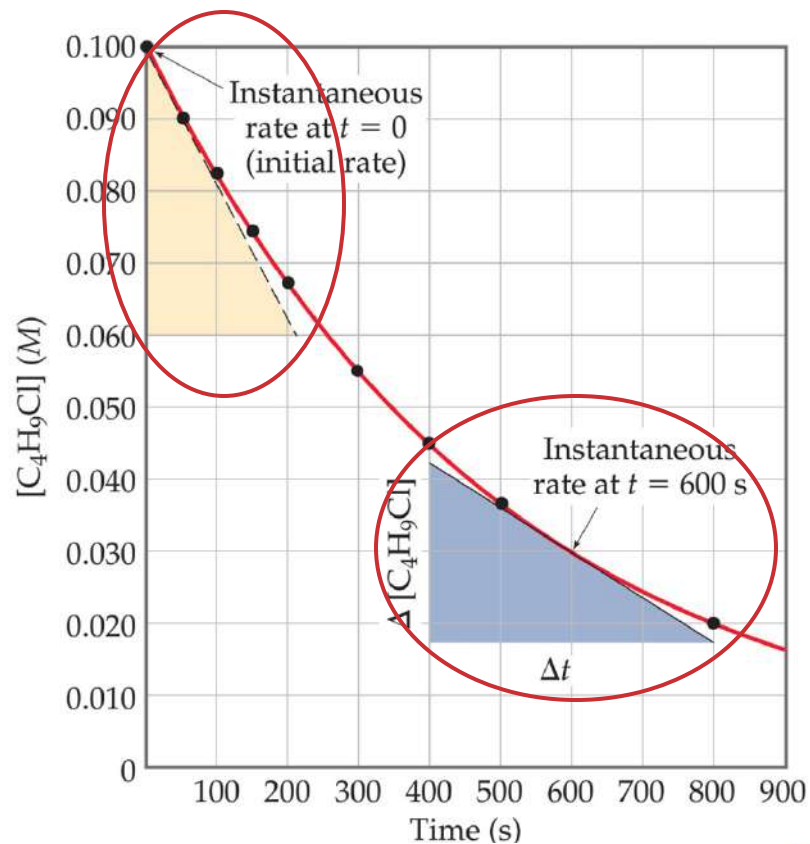
- A plot of $[\text{C}_4\text{H}_9\text{Cl}]$ vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the **instantaneous rate** at that time.



Reaction Rates



- All reactions slow down over time.
- Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the *beginning* of the reaction.



Sample Exercise 14.2 (p. 580)

Using the reaction graphed above, calculate the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 0$ (the initial rate). Hint: use the graph.

$(2.0 \times 10^{-4} \text{ M/s})$



Practice Exercise 1 (14.2)

Which of the following would be the instantaneous rate of the reaction in the previous figure at $t = 1000$ s?

- a) 1.2×10^{-4} M/s
- b) 8.8×10^{-5} M/s
- c) 6.3×10^{-5} M/s
- d) 2.7×10^{-5} M/s
- e) More than one of these.



Practice Exercise 1 (14.2)

Which of the following would be the instantaneous rate of the reaction in the previous figure at $t = 1000$ s?

a) 1.2×10^{-4} M/s

b) 8.8×10^{-5} M/s

c) 6.3×10^{-5} M/s

d) 2.7×10^{-5} M/s

e) More than one of these.



Practice Exercise 2 (14.2)

For the reaction graphed above, calculate the instantaneous rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ at $t = 300 \text{ s}$.

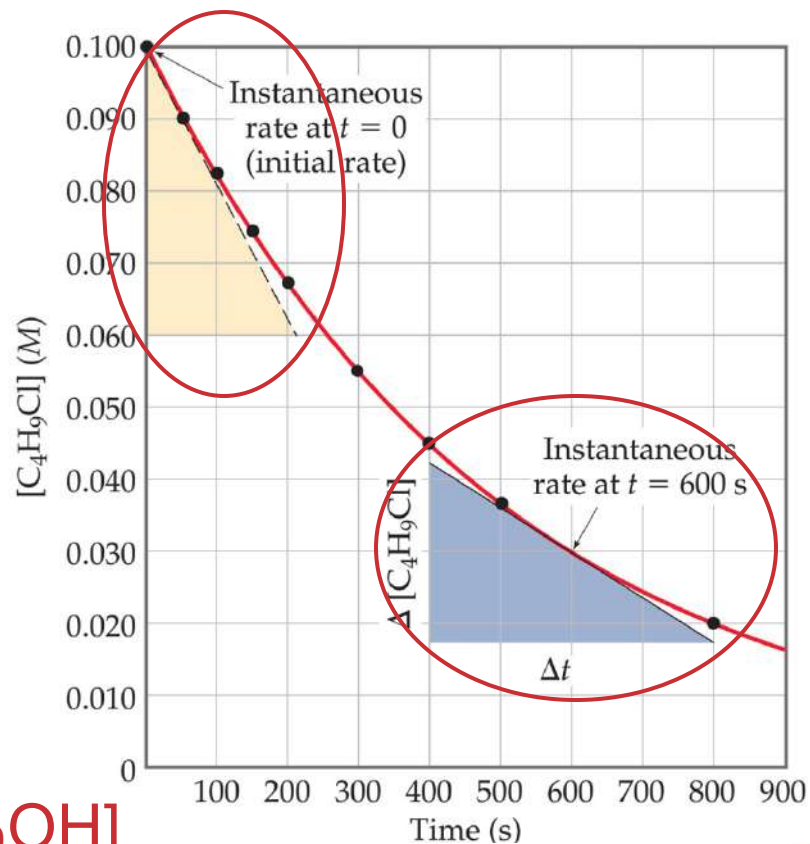
$(1.1 \times 10^{-4} \text{ M/s})$



Reaction Rates and Stoichiometry



- In this reaction, the ratio of $\text{C}_4\text{H}_9\text{Cl}$ to $\text{C}_4\text{H}_9\text{OH}$ is 1:1.
- Thus, the rate of disappearance of $\text{C}_4\text{H}_9\text{Cl}$ is the same as the rate of appearance of $\text{C}_4\text{H}_9\text{OH}$.



$$\text{Rate} = \frac{-\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$



Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?



- In such a case,

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$



Reaction Rates and Stoichiometry

- To generalize, then, for the reaction



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



Sample Exercise 14.3 (p. 581)

a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the following equation? $2 \text{O}_{3(g)} \rightarrow 3 \text{O}_{2(g)}$

$$\left(-\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}\right)$$

b) If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $\Delta[\text{O}_3]/\Delta t$?

$$(-4.0 \times 10^{-5} \text{ M/s})$$



Practice Exercise 2 (14.3)

The decomposition of N_2O_5 proceeds according to the following equation:



If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is

$4.2 \times 10^{-7} \text{ M/s}$, what is the rate of appearance of

a) NO_2 ($8.4 \times 10^{-7} \text{ M/s}$)

b) O_2 ($2.1 \times 10^{-7} \text{ M/s}$)



Practice Exercise 1 (14.3)

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 1 (14.3)

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?



Warmup – Stoich

(p. 617, #20)

For each of the following gas-phase reactions, write the rate expression in terms of the appearance of each product and disappearance of each reactant.



Warmup – Stoich (p. 617, #20)



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



Warmup – Stoich (p. 617, #20)



$$\frac{-\Delta[\text{SO}_2]}{2 \Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{SO}_3]}{2 \Delta t}$$



Warmup – Stoich

(p. 617, #20)



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



Concentration and Rate

We can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration.

In general, rates increase when reactant concentration is increased, and decrease when reactant concentration is reduced.



Concentration and Rate

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}



If we compare Experiments 1 and 2, we see that when $[\text{NH}_4^+]$ doubles, the initial rate doubles.



Concentration and Rate

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}
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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}



Likewise, when we compare Experiments 5 and 6, we see that when $[\text{NO}_2^-]$ doubles, the initial rate doubles.



Concentration and Rate

- This means

$$\text{Rate} \propto [\text{NH}_4^+]$$

$$\text{Rate} \propto [\text{NO}_2^-]$$

Therefore, $\text{Rate} \propto [\text{NH}_4^+][\text{NO}_2^-]$

which, when written as an equation, becomes

$$\text{Rate} = k [\text{NH}_4^+][\text{NO}_2^-]$$

- This equation is called the **rate law**, and k is the **rate constant**.



Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
- The exponents tell the **order** of the reaction with respect to each reactant.
- Since the rate law is

$$\text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

the reaction is

First-order in $[\text{NH}_4^+]$ and

First-order in $[\text{NO}_2^-]$.



Rate Laws



- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is second-order overall.
- In general: $\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n$
- The overall order of the reaction is $m + n + \dots$



Rate Laws

- Reaction orders must be determined experimentally, and do not necessarily correspond to the stoichiometric coefficients in the balanced chemical equation.
- Reaction orders of 0, 1 or 2 are common. Fractional or negative values are possible.



Units of Rate Constants

- depend on the overall reaction order
- e.g. For a reaction that is second order overall:

Units of rate

$$= (\text{units of rate constant})(\text{units of concentration})^2$$

Since the units of rate = M/s, $\text{M}^{-1}\text{s}^{-1}$ must be the units of the rate constant in order to accommodate the squared concentration units



Units of Rate Constants

Rearranging the equation from the page before,

Units of rate constant = units of rate
(units of concentration)²

$$= \frac{\text{M/s}}{\text{M}^2}$$

$$= \text{M}^{-1}\text{s}^{-1}$$



Units of Rate Constants

Using the same principle, what are the units of the rate constant in a first order reaction?

s^{-1}



Using Initial Rates to Determine Rate Laws

- To determine the rate law, we observe the effect of changing initial concentrations.
- If a reaction is zero order in a reactant, changing the initial [reactant] will have no effect on rate (as long as *some* reactant is present).



Using Initial Rates to Determine Rate Laws

- If a reaction is first order, doubling the [reactant] will cause the rate to double.
- If a reaction is second order, doubling the [reactant] will result in a 2^2 increase in rate.
- Similarly, tripling the [reactant] results in a 3^2 increase in rate.



Using Initial Rates to Determine Rate Laws

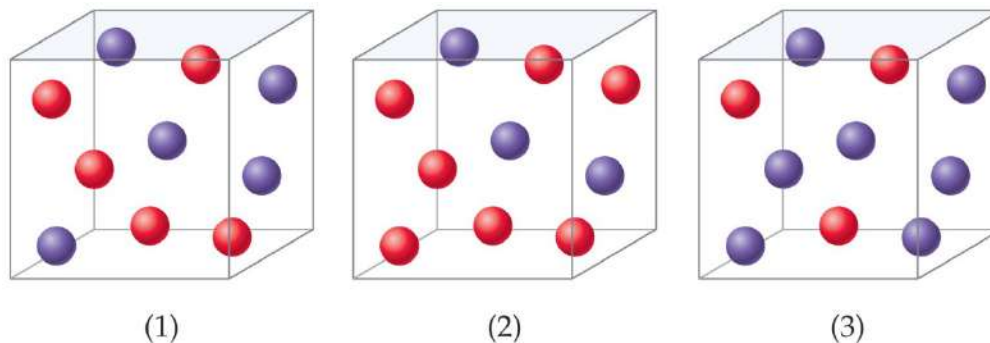
- A reaction is n th order if doubling the concentration causes a 2^n increase in rate.
- Note that the **rate**, not the rate constant, depends on concentration.
- The rate constant IS affected by temperature and by the presence of a catalyst.



Sample Exercise 14.4 (p. 584)

Consider a reaction $A + B \rightarrow C$ 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 blue ones. Rank these mixtures in order of increasing rate of reaction.

(2 < 1 < 3)



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Practice Exercise 1 (14.4)

Suppose the rate law for the reaction in this Sample Exercise were $\text{rate} = k[\text{A}]^2[\text{B}]$. 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 1 (14.4)

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

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Practice Exercise 2 (14.4)

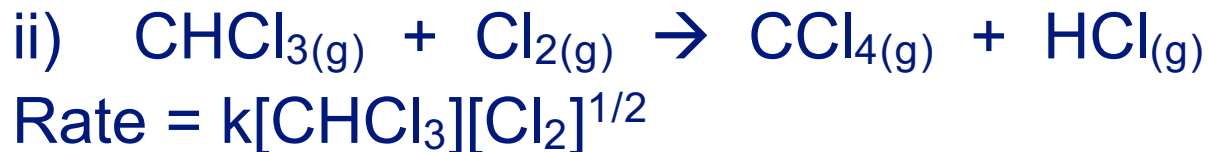
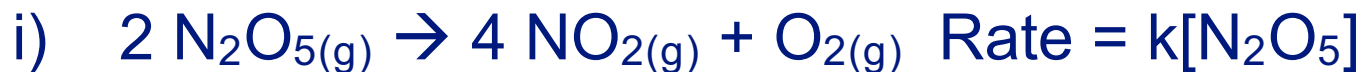
Assuming that the rate = $k[A][B]$, rank the mixtures represented above in order of increasing rate.

$$(2 = 3 < 1)$$



Sample Exercise 14.5 (p. 585)

a) What are the overall reaction orders for the reactions described in the following equations:



b) What are the units of the rate constant for the rate law for Equation (i)?



Practice Exercise 1 (14.5)

Which of the following are the units of the rate constant for (ii)?

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



Practice Exercise 1 (14.5)

Which of the following are the units of the rate constant for (ii)?

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

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

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

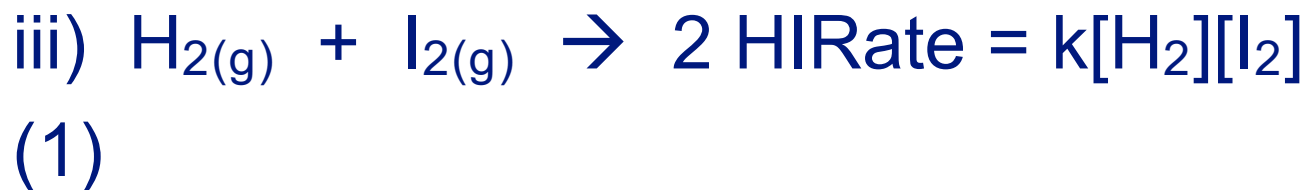
d) $M^{-3/2}s^{-1}$

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



Practice Exercise 2 (14.5)

a) What is the reaction order of the reactant H_2 in Equation (iii)?



b) What are the units of the rate constant for Equation (iii)?

($\text{M}^{-1}\text{s}^{-1}$)



Sample Exercise 14.6 (p. 586)

The initial rate of a reaction $A + B \rightarrow C$ 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}

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Using these data, determine

a) the rate law for the reaction ($k[A]^2$)

b) the magnitude of the rate constant
($4.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$)

c) the rate of the reaction when $[A] = 0.050 \text{ M}$ and $[B] = 0.100 \text{ M}$. ($1.0 \times 10^{-5} \text{ M/s}$)



Practice Exercise 1 (14.6)

A certain reaction $X + Y \rightarrow Z$ 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: $\text{Rate} = [X][Y]^2$.
- (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 statement 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 1 (14.6)

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- (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 statement 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 (14.6)

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



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}

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- Determine the rate law for this reaction. ($k[\text{NO}]^2[\text{H}_2]$)
- Calculate the rate constant. ($1.2 \text{ M}^{-2}\text{s}^{-1}$)
- Calculate the rate when $[\text{NO}] = 0.050 \text{ M}$ and $[\text{H}_2] = 0.150 \text{ M}$. ($4.5 \times 10^{-4} \text{ M/s}$)



Warmup – Rate Laws

(p. 618, #26)

Consider the following reaction:



- a) The rate law for this reaction is first order in H_2 and second order in NO . Write the rate law.
- b) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4 \text{M}^{-2}\text{s}^{-1}$, what is the reaction rate when $[\text{NO}] = 0.035 \text{ M}$ and $[\text{H}_2] = 0.015 \text{ M}$?
- c) What is the reaction rate at 1000 K when the concentration of NO is increased to 0.10 M, while the concentration of H_2 is 0.010 M?



Warmup – Rate Laws

(p. 618, #26)

- a) The rate law for this reaction is first order in H_2 and second order in NO . Write the rate law.

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

- b) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$, what is the reaction rate when $[\text{NO}] = 0.035 \text{ M}$ and $[\text{H}_2] = 0.015 \text{ M}$?

$$\text{Rate} = (6.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1})(0.035\text{M})^2(0.015\text{M}) = 1.1 \text{ M/s}$$

- c) What is the reaction rate at 1000 K when the concentration of NO is increased to 0.10 M , while the concentration of H_2 is 0.010 M ?

$$\text{Rate} = (6.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1})(0.10\text{M})^2(0.010\text{M}) = 6.0 \text{ M/s}$$



The Change of Concentration with Time

KEY SECTION



Change of Concentration with Time

Goal:

Convert the rate law into a convenient equation that gives concentration as a function of time

Calculus basis – on whiteboard –
background only



Integrated Rate Laws (show details on board)

Using calculus to integrate the rate law for a first-order process gives us

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (\text{Equation 14.12})$$

where

$[A]_0$ is the initial concentration of A, and

$[A]_t$ is the concentration of A at some time, t , during the course of the reaction.



Integrated Rate Laws

Manipulating this equation produces...

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (\text{Equation 14.12})$$

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

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

...which is in the form

$$y = mx + b \quad (\text{Equation 14.13})$$



First-Order Processes

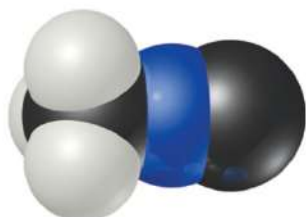
$$\ln [A]_t = -kt + \ln [A]_0$$

Therefore, if a reaction is first-order, a plot of $\ln [A]$ vs. t will yield a straight line, and the slope of the line will be $-k$.

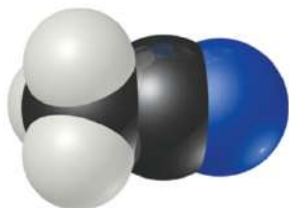
See Appendix A.2 in your textbook to review how to mathematically manipulate logarithms.



First-Order Processes



Methyl isonitrile



Acetonitrile

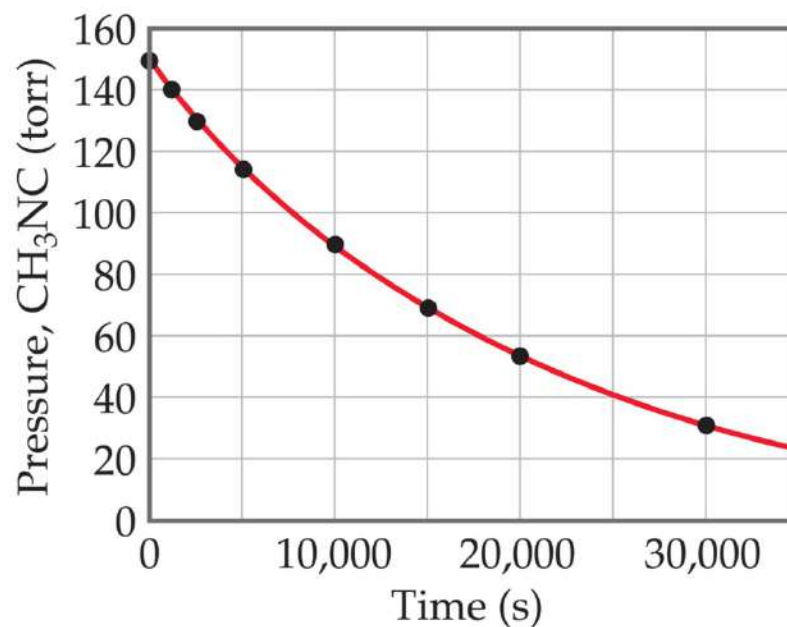
Consider the process in which methyl isonitrile is converted to acetonitrile.



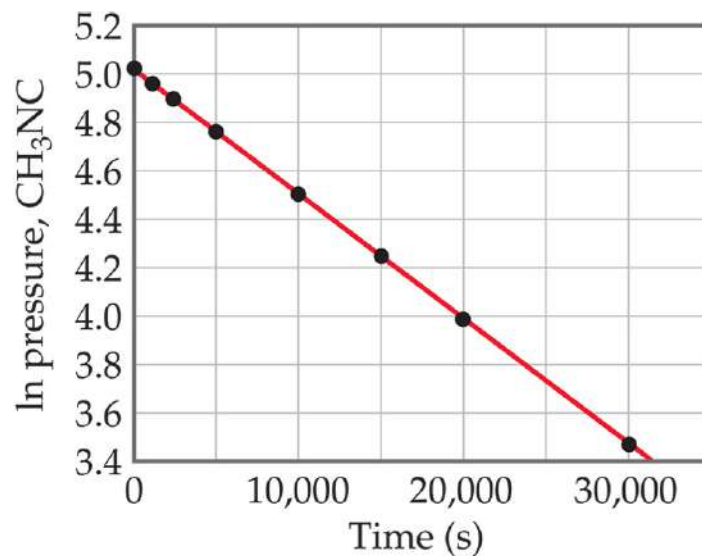
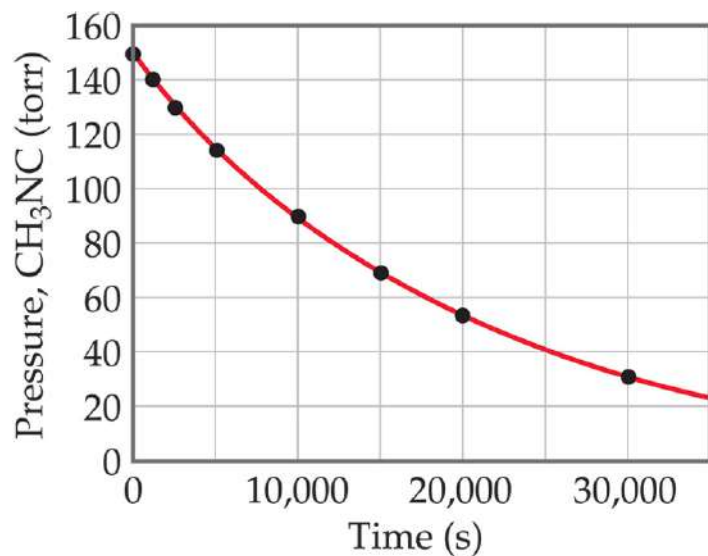
First-Order Processes



This data was collected for this reaction at 198.9 °C.



First-Order Processes



- When $\ln P$ is plotted as a function of time, a straight line results.
- Therefore,
 - The process is first-order.
 - k is the negative of the slope: $5.1 \times 10^{-5} \text{ s}^{-1}$.



Sample Exercise 14.7 (p. 588)

The first-order rate constant for the decomposition of a certain insecticide in water at 12°C is 1.45 yr^{-1} . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$ of water. 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?
($1.2 \times 10^{-7} \text{ g/cm}^3$)

b) How long will it take for the concentration of the insecticide to drop to $3.0 \times 10^{-7} \text{ g/cm}^3$?
(0.35 yr)



Practice Exercise 1 (14.7)

At 25°C, the decomposition of dinitrogen pentoxide, $\text{N}_2\text{O}_{5(g)}$, into $\text{NO}_{2(g)}$ and $\text{O}_{2(g)}$ follows first-order kinetics with $k = 3.4 \times 10^{-5} \text{ s}^{-1}$. 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 1 (14.7)

At 25°C, the decomposition of dinitrogen pentoxide, $\text{N}_2\text{O}_{5(g)}$, into $\text{NO}_{2(g)}$ and $\text{O}_{2(g)}$ follows first-order kinetics with $k = 3.4 \times 10^{-5} \text{ s}^{-1}$. 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 (14.7)

The decomposition of dimethyl ether, CH_3OCH_3 , at 510°C is a first-order process with a rate constant of $6.8 \times 10^{-4} \text{ s}^{-1}$:



If the initial pressure of CH_3OCH_3 is 135 torr, what is its partial pressure after 1420 s?

(51 torr)



Second-Order Reactions

The rate of a second-order reaction depends on the reactant concentration to the second power or on the concentration of two reactants, each raised to the first power.



Second-Order Reactions (show details on board)

Integrating the rate law for a process that is second-order in reactant A, we get

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

also in the form

$$y = mx + b$$



Second-Order Processes

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

So if a process is second-order in A, a plot of $\frac{1}{[A]}$ vs. t will yield a straight line, and the slope of that line is k .

Note: a second-order process can have a rate constant expression of the form:

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



Sample Exercise 14.8 (p. 588)

Second-Order Processes

The decomposition of NO_2 at 300°C is described by the equation



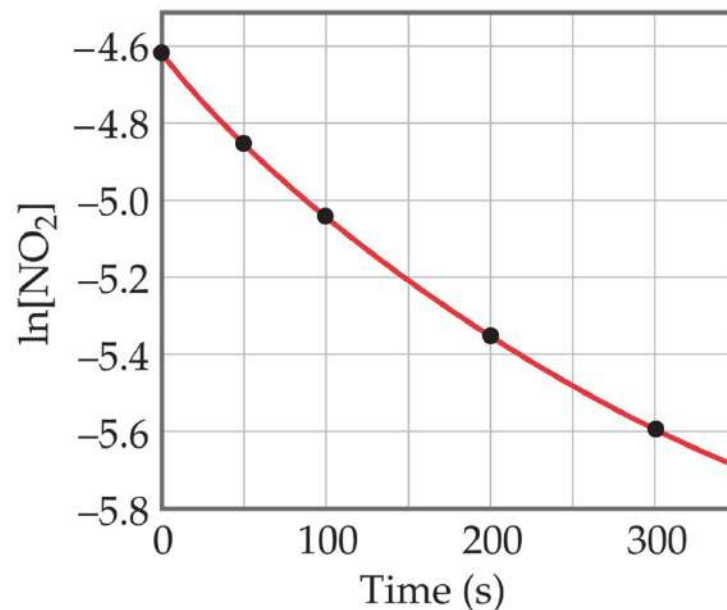
and yields data comparable to this:

Time (s)	$[\text{NO}_2], M$
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380



Second-Order Processes

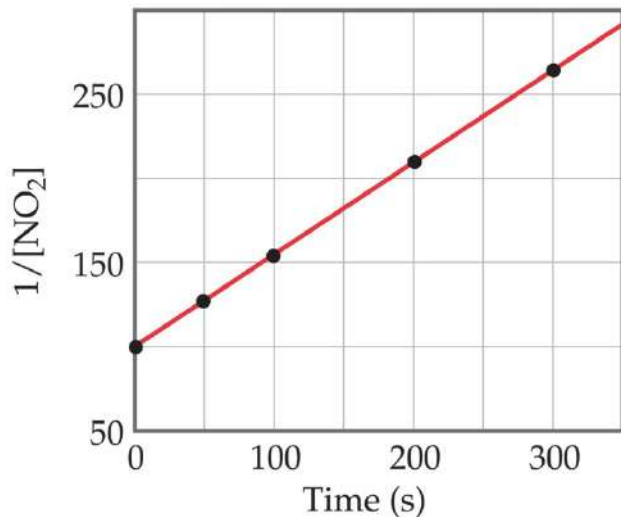
- Plotting $\ln [\text{NO}_2]$ vs. t yields the graph at the right.
- The plot is *not* a straight line, so the process is *not* first-order in $[\text{A}]$.



Time (s)	$[\text{NO}_2], M$	$\ln [\text{NO}_2]$
0.0	0.01000	-4.610
50.0	0.00787	-4.845
100.0	0.00649	-5.038
200.0	0.00481	-5.337
300.0	0.00380	-5.573



Second-Order Processes



- Graphing $\frac{1}{[\text{NO}_2]}$ vs. t , however, gives this plot.
- Because this *is* a straight line, the process is second-order in $[A]$.

Time (s)	$[\text{NO}_2], M$	$1/[\text{NO}_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263



Practice Exercise 1 (14.8)

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

- (i) The reaction follows first-order kinetics.
 - (ii) The rate constant for the reaction is $3.0 \times 10^{-2} \text{ s}^{-1}$.
 - (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 1 (14.8)

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

- (i) The reaction follows first-order kinetics.
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 - (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 (14.8)

Consider again the decomposition of NO_2 discussed above.

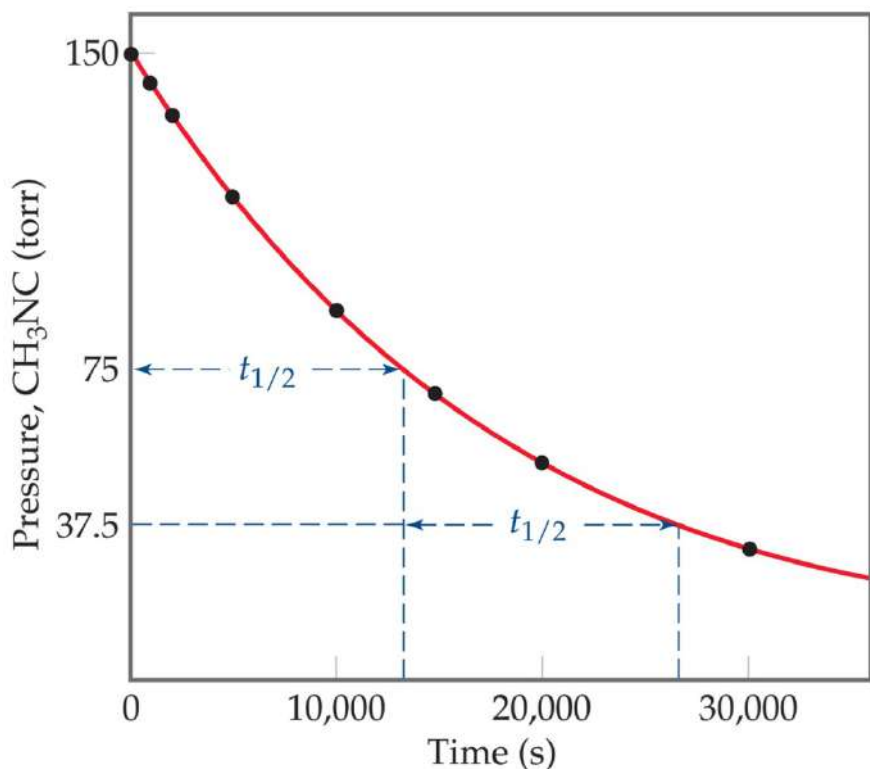
The reaction is second order in NO_2 with $k = 0.543 \text{ M}^{-1}\text{s}^{-1}$.

If the initial concentration of NO_2 in a closed vessel is 0.0500 M , what is the remaining concentration after 0.500 hr ?

$(1.0 \times 10^{-3} \text{ M})$



Half-Life



- Half-life is defined as the time required for one-half of a reactant to react.
- Because $[A]$ at $t_{1/2}$ is one-half of the original $[A]$,
$$[A]_t = 0.5 [A]_0.$$



Half-Life

For a first-order process, this becomes

$$\ln \frac{0.5 [A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

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

NOTE: For a first-order process, then, the half-life *does not* depend on $[A]_0$.



Half-Life

(details not in packet)

For a second-order process,

$$\frac{1}{0.5 [A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2 - 1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

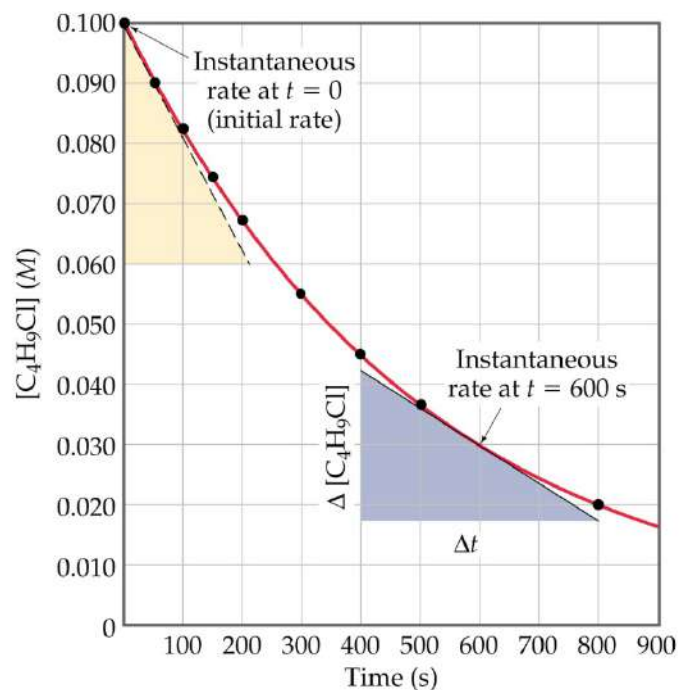
$$\frac{1}{k[A]_0} = t_{1/2}$$



Sample Exercise 14.9 (p. 592)

From the figure below, estimate the half-life of $\text{C}_4\text{H}_9\text{Cl}$ in a reaction with water.

Estimate the second half-life.



(~340 s)



Practice Exercise 1 (14.9)

We noted in an earlier Practice Exercise that at 25°C the decomposition of $\text{N}_2\text{O}_{5(g)}$ into $\text{NO}_{2(g)}$ and $\text{O}_{2(g)}$ follows first-order kinetics with $k = 3.4 \times 10^{-5}\text{s}^{-1}$. 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 1 (14.9)

We noted in an earlier Practice Exercise that at 25°C the decomposition of $\text{N}_2\text{O}_{5(g)}$ into $\text{NO}_{2(g)}$ and $\text{O}_{2(g)}$ follows first-order kinetics with $k = 3.4 \times 10^{-5}\text{s}^{-1}$. 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 (14.9)

a) Calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7.

($k = 1.45 \text{ yr}^{-1}$)

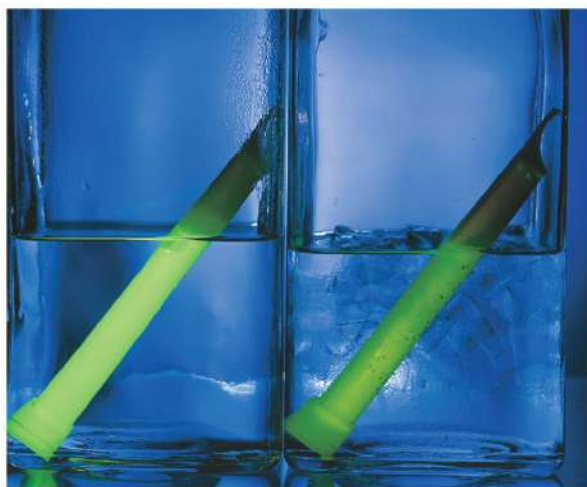
($0.478 \text{ yr} = 1.51 \times 10^7 \text{ s}$)

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

(two half-lives = $2(0.478 \text{ yr}) = 0.956 \text{ yr}$)



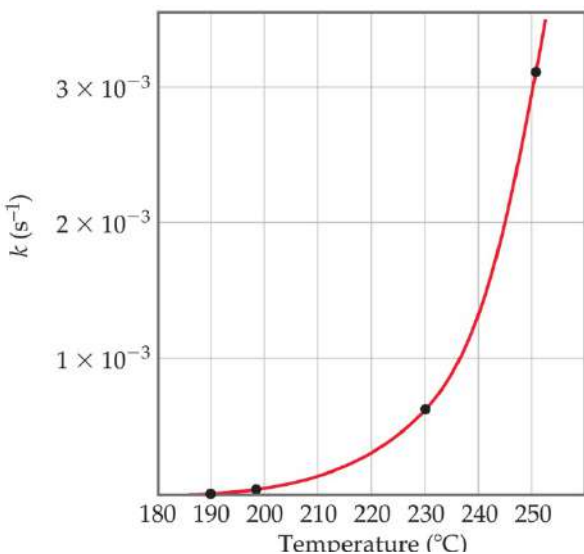
Temperature and Rate



Higher temperature

Lower temperature

- Generally, as temperature increases, so does the reaction rate.
- This is because k is temperature dependent.



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.

Concentration effects:

Thus reaction rate should increase \uparrow with an increase \uparrow in [reactant molecules].

Temperature effects:

The higher the T, the more E available to the molecules and the more frequently the molecules collide. And they collide with more force.

Thus reaction rate should increase \uparrow with an increase \uparrow in T.



The Orientation Factor

Not all collisions lead to products.

- Only a **small fraction** of collisions lead to products.
- In order for a reaction to occur the reactant molecules must collide in the **correct orientation** and with **enough E** to form products.

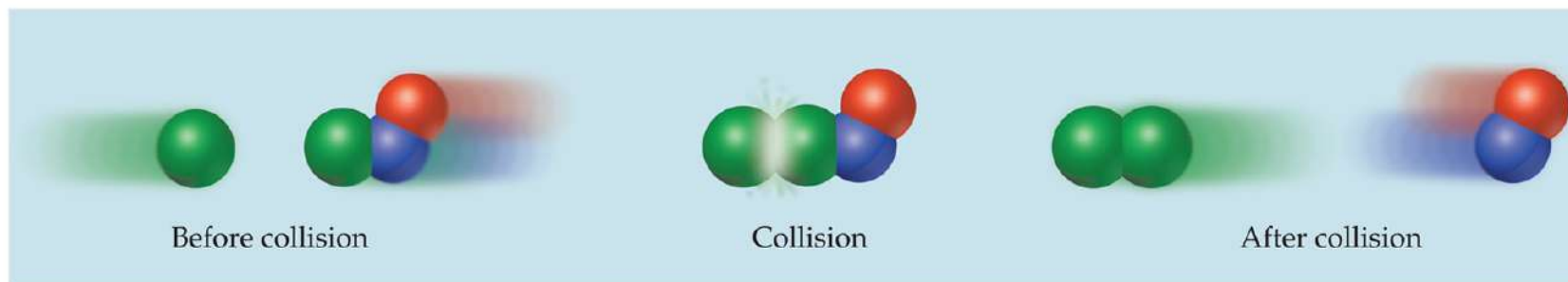


The Collision Model

Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.

Reaction between Cl and NOCl:

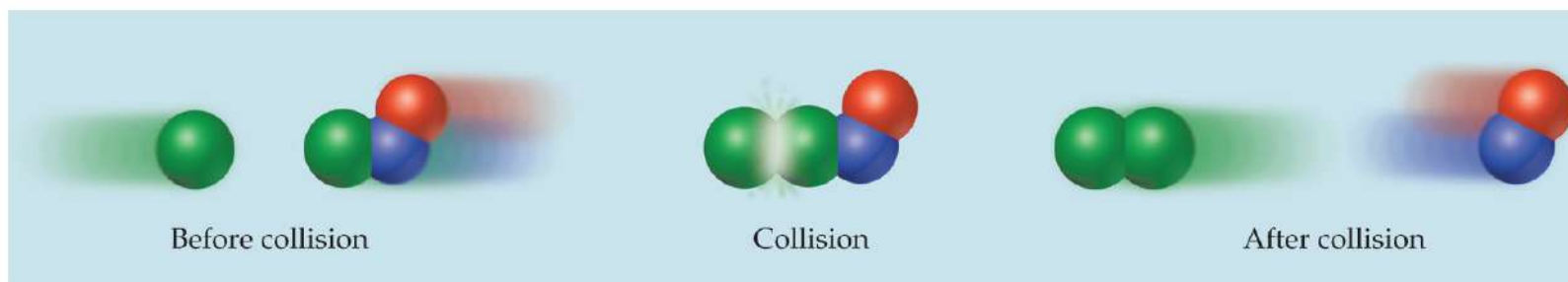
If the Cl collides with the Cl of NOCl, the products are Cl₂ and NO.



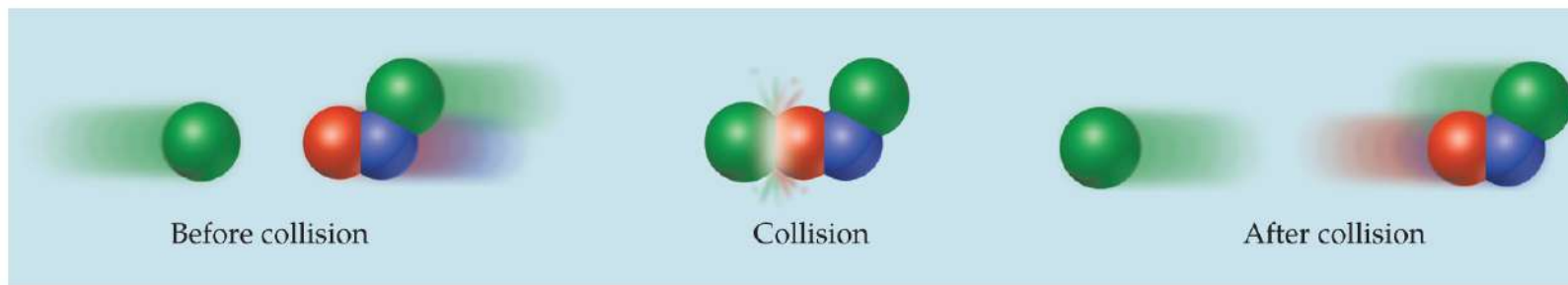
The Collision Model

Reaction between Cl and NOCl:

If the Cl collides with the O of NOCl, no products are formed.



(a) Effective collision



(b) Ineffective collision

Activation Energy

- In other words, there is a minimum amount of energy required for reaction: the **activation energy**, E_a .
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.



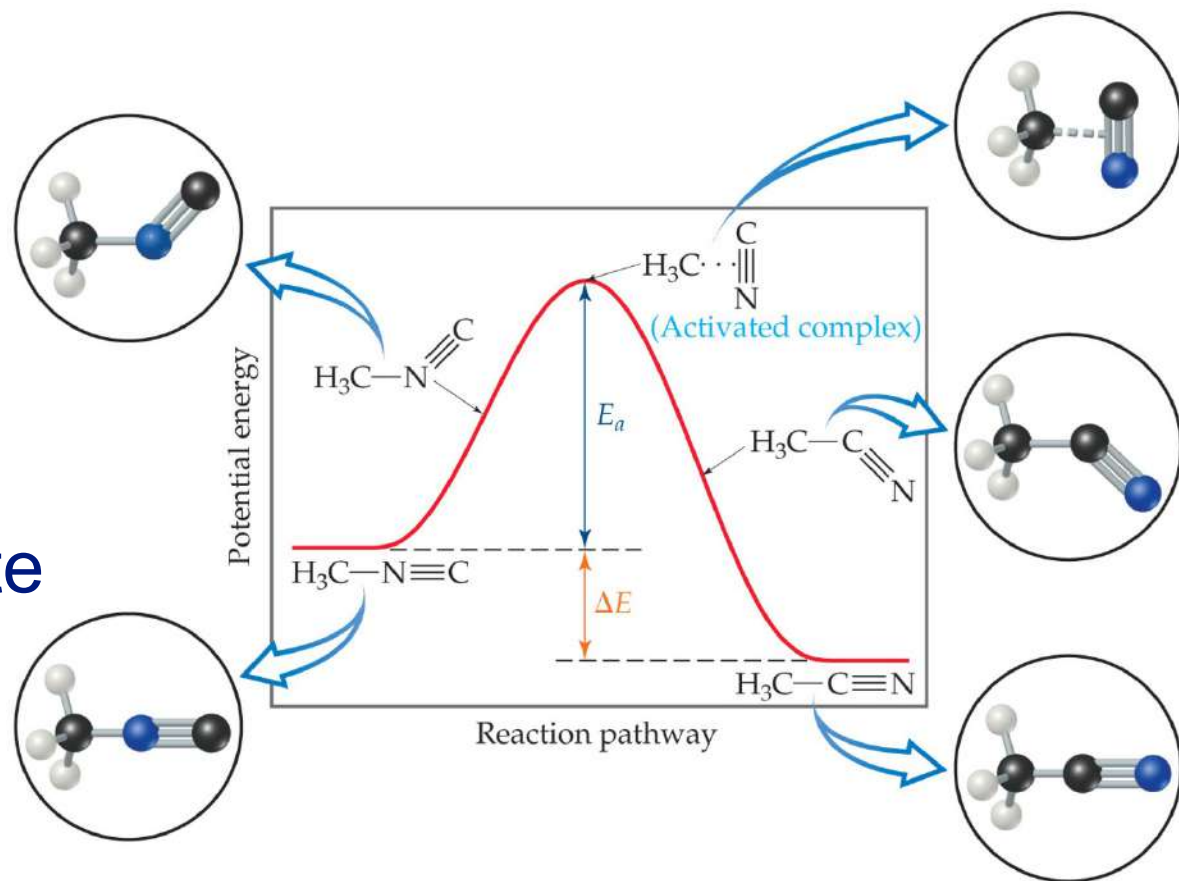
Activation Energy

- Arrhenius: Molecules must possess a minimum amount of E to react. Why?
- In order to form products, bonds must be broken in the reactants.
- Bond breakage requires E .
- Molecules moving too slowly, with too little KE, don't react when they collide.



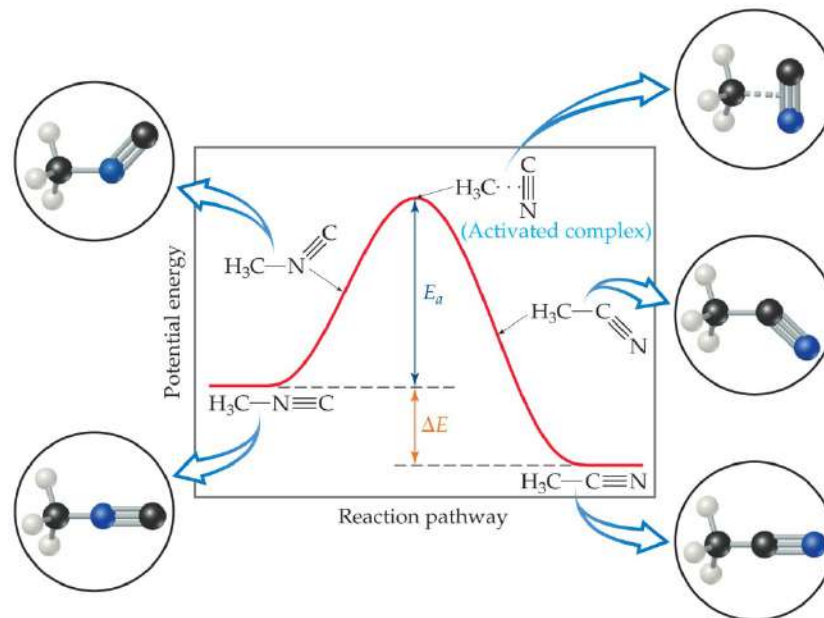
Reaction Coordinate Diagrams

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.

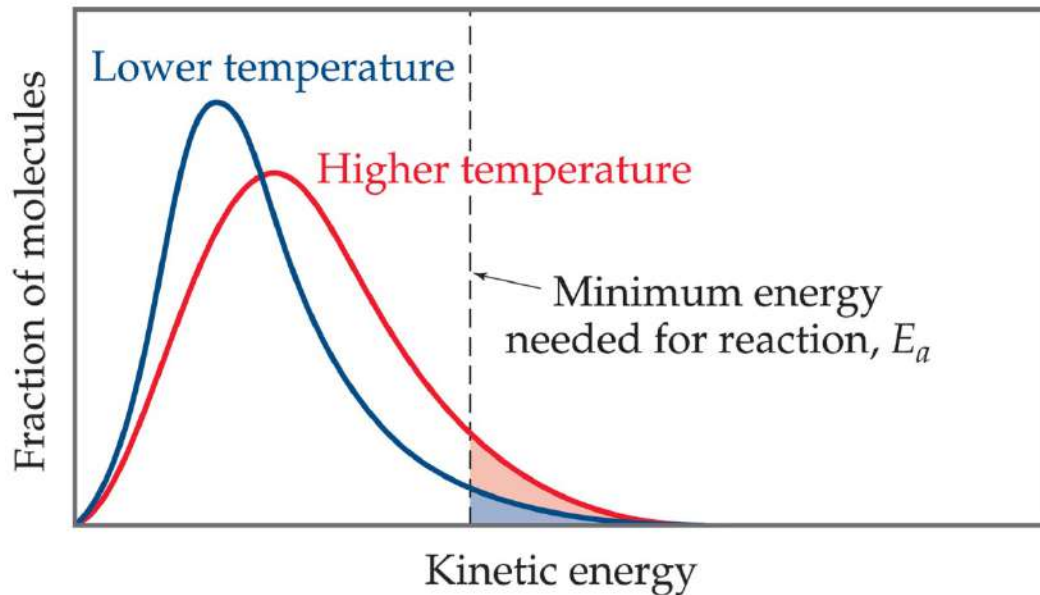


Reaction Coordinate Diagrams

- The diagram shows the energy of the reactants and products (and, therefore, ΔE).
- The high point on the diagram is the **transition state**.
- The species present at the transition state is called the **activated complex**.
- The energy gap between the reactants and the activated complex is the **activation energy barrier**.



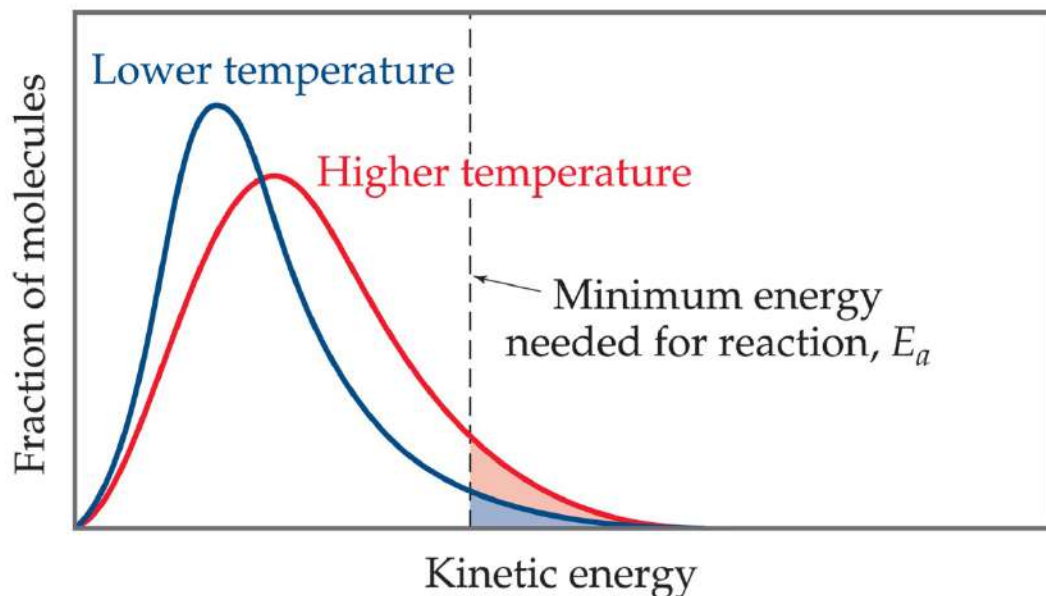
Maxwell–Boltzmann Distribution of Kinetic Energies



- Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.
- At any temperature there is a wide distribution of kinetic energies.



Maxwell–Boltzmann Distributions

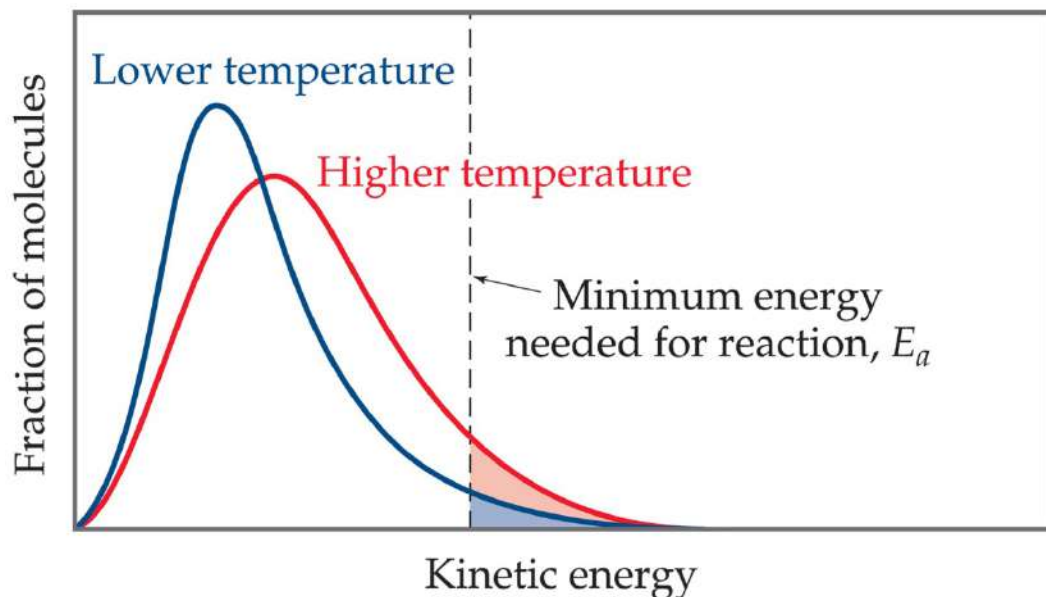


- As the temperature increases, the curve flattens and broadens.
- Thus at higher temperatures, a larger population of molecules has higher energy.



Maxwell–Boltzmann Distributions

- If the dotted line represents the activation energy, then as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.



- As a result, the reaction rate increases.

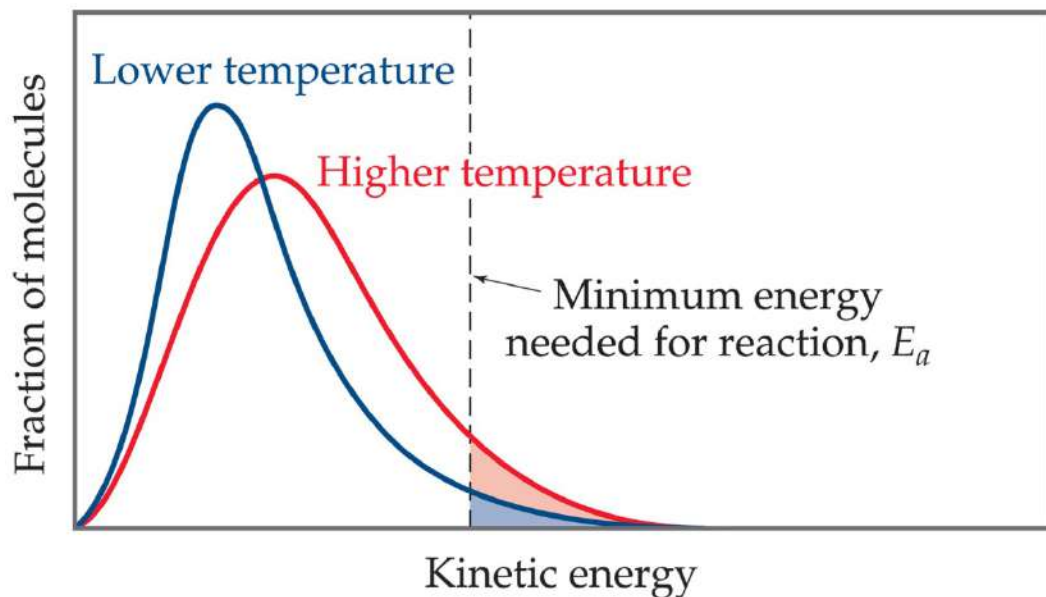


Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

$$f = e^{\frac{-E_a}{RT}}$$

where R is the gas constant and T is the Kelvin temperature.



Arrhenius



Svante Arrhenius –
Swedish – 1859-1927
- one of the founders of
the field of physical
chemistry, worked in
chemical kinetics and
electrochemistry



Arrhenius

Nobel Prize in Chemistry - 1903 - electrolytic theory of dissociation – i.e. that some chemical compounds break apart in solution to form electrolytes – he applied this to colligative properties (worked with van't Hoff)

- one of the first scientists to associate the amount of CO_2 in the air with climate



Arrhenius Equation

Svante Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:

- The number of collisions per unit time
- The fraction of collisions that occur with the correct orientation.
- The fraction of the colliding molecules that have an $E \geq E_a$.



Arrhenius Equation

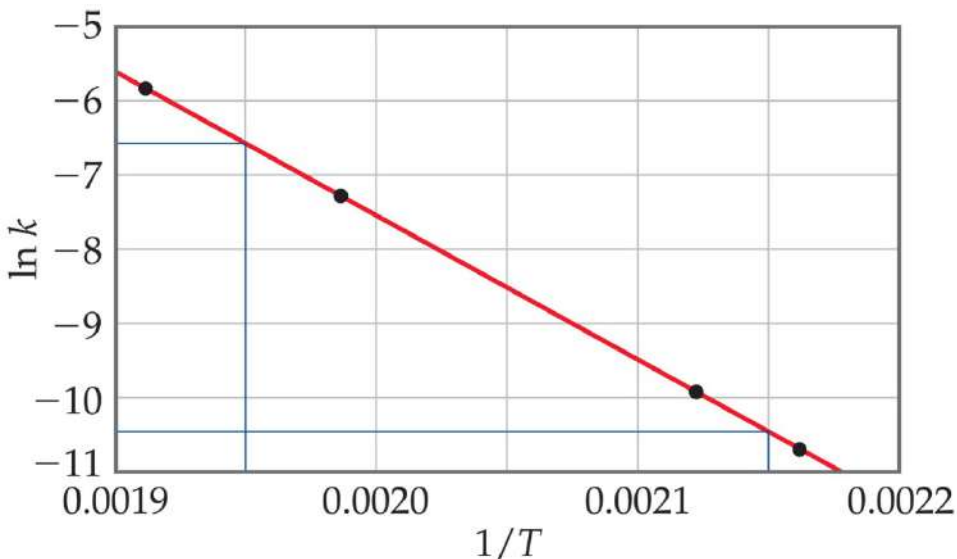
Svante Arrhenius developed a mathematical relationship between k and E_a :

$$k = A e^{\frac{-E_a}{RT}}$$

where A is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.



Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

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

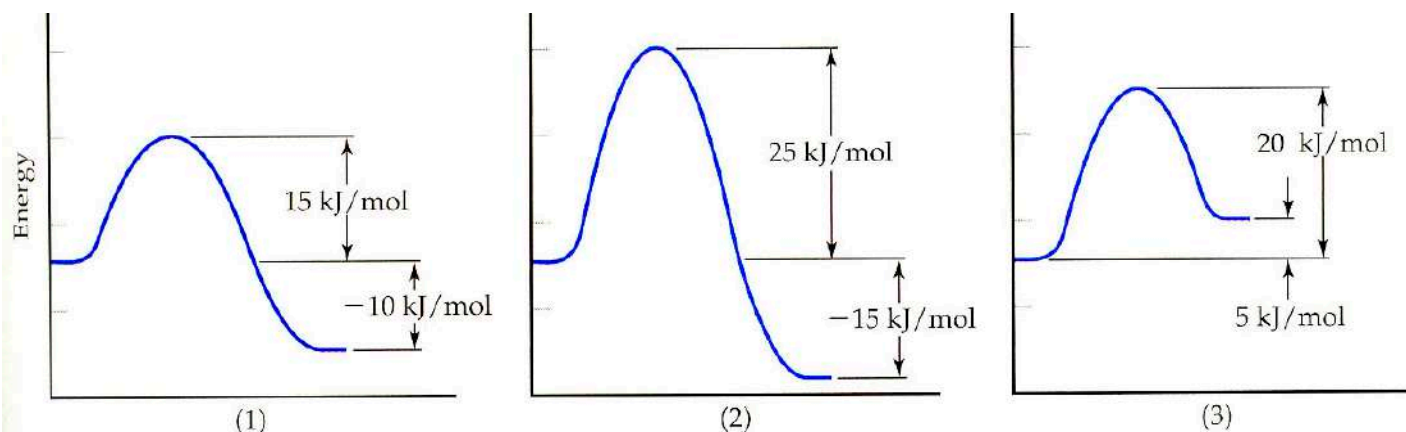
$$y = m x + b$$

Therefore, if k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of $\ln k$ vs. $\frac{1}{T}$.



Sample Exercise 14.10 (p. 597)

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.

((2) < (3) < (1))



Practice Exercise 1 (14.10)

Which of the following statement is or are true?

- (i) The activation energies for the forward and reverse directions of a reaction can be different.
 - (ii) Assuming that A is constant, if both E_a and T increase, then k will increase.
 - (iii) For two different reactions, the one with the smaller value of E_a will necessarily have the larger value for k .
-
- a) Only one of the statements is true.
 - b) Statements (i) and (ii) are true.
 - c) Statements (ii) and (iii) are true.
 - d) All three statements are true.



Practice Exercise 1 (14.10)

Which of the following statement is or are true?

(i) The activation energies for the forward and reverse directions of a reaction can be different.

(ii) Assuming that A is constant, if both E_a and T increase, then k will increase.

(iii) For two different reactions, the one with the smaller value of E_a will necessarily have the larger value for k .

a) Only one of the statements is true.

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

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

d) All three statements are true.



Practice Exercise 2 (14.10)

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

((2) < (1) < (3))



Sample Exercise 14.11 (p. 598)

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}

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- a) From these data, calculate E_a for the reaction. (160 kJ/mol)
(Hint: make a table of T , $1/T$ and $\ln k$)
- b) What is the value of the rate constant at 430.0 K? ($1.0 \times 10^{-6} \text{ s}^{-1}$)



Practice Exercise 1 (14.11)

Using the data in Sample Exercise 14.11, which of the following is the rate constant for the rearrangement of methyl isonitrile at 320°C?

- a) $8.1 \times 10^{-15} \text{ s}^{-1}$
- b) $2.2 \times 10^{-13} \text{ s}^{-1}$
- c) $2.7 \times 10^{-9} \text{ s}^{-1}$
- d) $2.3 \times 10^{-1} \text{ s}^{-1}$
- e) $9.2 \times 10^3 \text{ s}^{-1}$



Practice Exercise 1 (14.11)

Using the data in Sample Exercise 14.11, which of the following is the rate constant for the rearrangement of methyl isonitrile at 320°C?

- a) $8.1 \times 10^{-15} \text{ s}^{-1}$
- b) $2.2 \times 10^{-13} \text{ s}^{-1}$
- c) $2.7 \times 10^{-9} \text{ s}^{-1}$
- d) $2.3 \times 10^{-1} \text{ s}^{-1}$
- e) $9.2 \times 10^3 \text{ s}^{-1}$



Practice Exercise 2 (14.11)

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

$$(2.2 \times 10^{-2} \text{ s}^{-1})$$



Reaction Mechanisms

The sequence of events that describes the actual process by which reactants become products is called the **reaction mechanism**.



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 step.**



Elementary Steps

- **Elementary steps** are any processes that occur in a **single step**.
- The number of molecules present in an elementary step is the **molecularity** of that elementary step.
- **Unimolecular**: one molecule in the elementary step
- **Bimolecular**: collision of two molecules in the elementary step
- **Termolecular**: simultaneous collision of three molecules in the elementary step
- very uncommon (statistically improbable)



Reaction Mechanisms

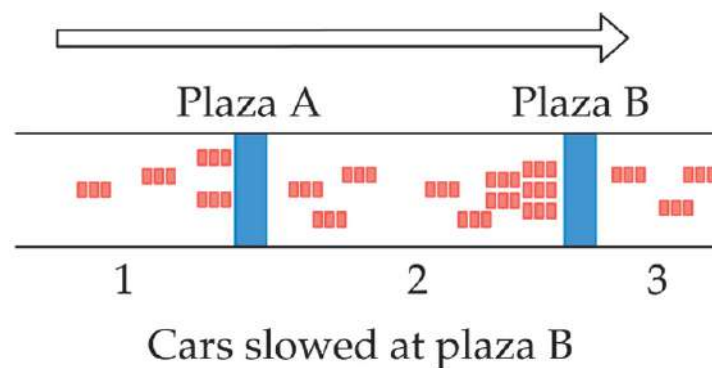
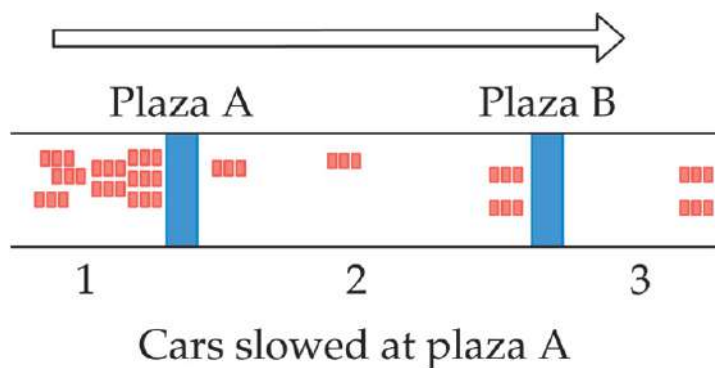
Elementary Reactions and Their Rate Laws		
Molecularity	Elementary Reaction	Rate Law
<i>Unimolecular</i>	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
<i>Bimolecular</i>	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
<i>Bimolecular</i>	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
<i>Termolecular</i>	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
<i>Termolecular</i>	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
<i>Termolecular</i>	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

The **molecularity** of a process tells how many molecules are involved in the process.



Multistep Mechanisms

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, **rate-determining step**.



Slow Initial Step



- The rate law for this reaction is found experimentally to be

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

- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.

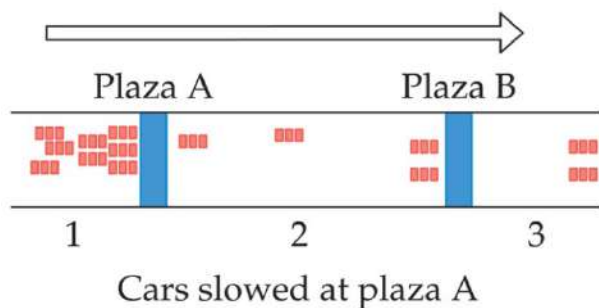


Slow Initial Step

- A proposed mechanism for this reaction is



- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.



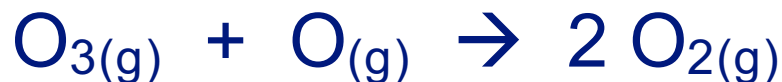
Multistep mechanisms = sequence of elementary steps

- Elementary steps must add to give the balanced chemical equation.
- **Intermediate**: a species which appears in an elementary step which is **not a reactant or product**.
- **formed in one elementary step and consumed in another.**
- **not found** in the balanced equation for the overall reaction.



Sample Exercise 14.12 (p. 600)

It has been proposed that the conversion of ozone into O_2 proceeds via two elementary steps:



- Describe the molecularity of each step in this mechanism.
- Write the equation for the overall reaction.
- Identify the intermediate(s).



Practice Exercise 1 (14.12)

Consider the two-step reaction mechanism:



Which of the following statements about this mechanism 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 these statements is true.
 - b) Statements (i) and (ii) are true.
 - c) Statements (i) and (iii) are true.
 - d) Statements (ii) and (iii) are true.



Practice Exercise 1 (14.12)

Consider the two-step reaction mechanism:



Which of the following statements about this mechanism 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 these statements is true.
 - b) Statements (i) and (ii) are true.
 - c) Statements (i) and (iii) are true.
 - d) Statements (ii) and (iii) are true.



Practice Exercise 2 (14.12)

For the reaction



the proposed mechanism is



- Is the proposed mechanism consistent with the equation for the overall reaction?
- Identify the intermediates.



Where we have been

- Reaction mechanisms – series of elementary steps
- Slow first step \rightarrow rate law
- Next: slow second step \rightarrow rate law
More difficult!



Reaction Laws for Elementary Steps

- determine the overall rate law of the reaction
- The rate law of an elementary step is determined by its molecularity:
 - Unimolecular processes are first order.
 - Bimolecular processes are second order.
 - Termolecular processes are third order.

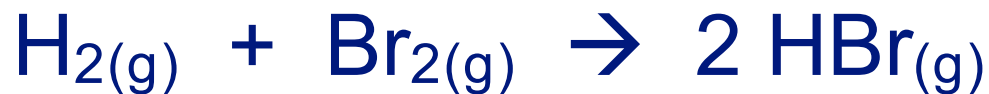
TABLE 14.3 ■ Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	Rate = $k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$



Sample Exercise 14.13 (p. 602)

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



Practice Exercise 1 (14.13)

Consider the following reaction:

$2A + B \rightarrow X + 2Y$. You are told that the first step in the mechanism of this reaction has the following rate law: $\text{Rate} = k[A][B]$. Which of the following could be the first step in the reaction mechanism (note that substance Z is an intermediate)?



Practice Exercise 1 (14.13)

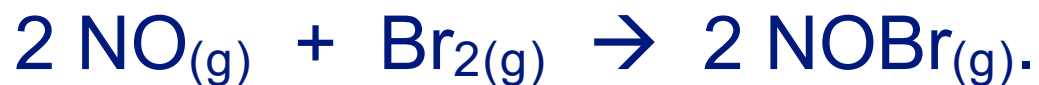
Consider the following reaction:

$2A + B \rightarrow X + 2Y$. You are told that the first step in the mechanism of this reaction has the following rate law: $\text{Rate} = k[A][B]$. Which of the following could be the first step in the reaction mechanism (note that substance Z is an intermediate)?



Practice Exercise 2 (14.13)

Consider the following reaction:



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

- b) Is a single-step mechanism likely for this reaction? Why or why not?



Rate Laws for Multistep Mechanisms

- Most reactions occur by mechanisms with $>$ one elementary step.
- **Rate-determining step** (rate-limiting step) of the reaction = the **slowest** of the elementary steps.
- governs the overall rate law for the overall reaction.



Rate Laws for Multistep Mechanisms

- Consider the reaction:



- The experimentally derived rate law is:
Rate = $k[\text{NO}_2]^2$



Rate Laws for Multistep Mechanisms

- We propose a mechanism for the reaction:

k_1



k_2



- Note that NO_3 is an **intermediate**.



Rate Laws for Multistep Mechanisms

- If $k_2 \gg k_1$, then the overall reaction rate will depend on the first step (the **rate-limiting step**).

$$\text{Rate} = k_1[\text{NO}_2]^2$$

- This theoretical rate law is in agreement with the experimental rate law.
→ (but does not prove) our mechanism



Fast Initial Step



- The rate law for this reaction is found to be

$$\text{Rate} = k [\text{NO}]^2 [\text{Br}_2]$$

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



Fast Initial Step

- A proposed mechanism is



Step 1 includes the forward *and* reverse reactions.



Fast Initial Step

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

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

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



Fast Initial Step

- 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.
- Therefore,

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



Fast Initial Step

- Because $\text{Rate}_f = \text{Rate}_r$,



- Solving for $[\text{NOBr}_2]$ gives us

$$\frac{k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$



Fast Initial Step

Substituting this expression for $[\text{NOBr}_2]$ in the rate law for the rate-determining step gives

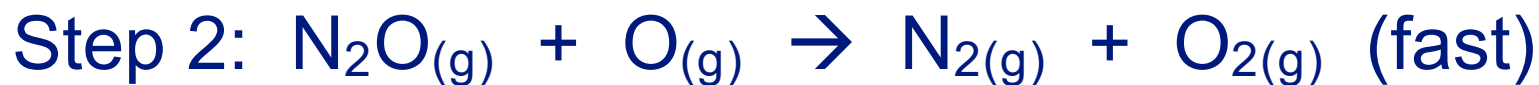
$$\begin{aligned}\text{Rate} &= \frac{k_2 k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] [\text{NO}] \\ &= k [\text{NO}]^2 [\text{Br}_2]\end{aligned}$$

This final rate law is consistent with the experimentally-determined rate law.



Sample Exercise 14.14 (p. 604)

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



a) Write the equation for the overall reaction.



b) Write the rate law for the overall reaction.



Practice Exercise 1 (14.14)

Let's consider a hypothetical reaction similar to that in Practice Exercise 1 of Sample Exercise 14.13:

$2\text{C} + \text{D} \rightarrow \text{J} + 2\text{K}$. You are told that the rate of this reaction is second order overall and second order in $[\text{C}]$. 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 (note that substance Z is an intermediate)?



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



Practice Exercise 1 (14.14)

Let's consider a hypothetical reaction similar to that in Practice Exercise 1 of Sample Exercise 14.13:

$2\text{C} + \text{D} \rightarrow \text{J} + 2\text{K}$. You are told that the rate of this reaction is second order overall and second order in $[\text{C}]$. 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 (note that substance Z is an intermediate)?



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

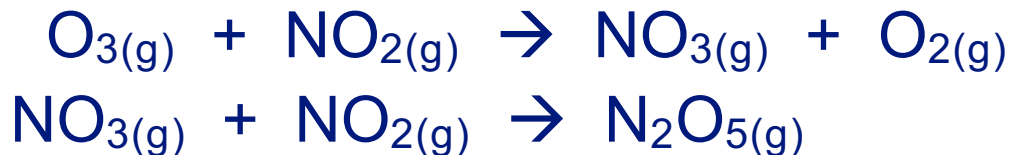


Practice Exercise 2 (14.14)

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



The reaction is believed to occur in two steps:



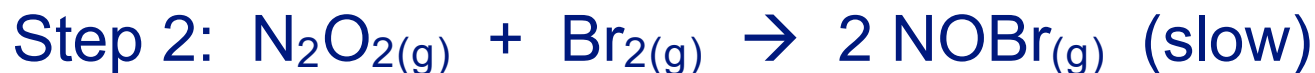
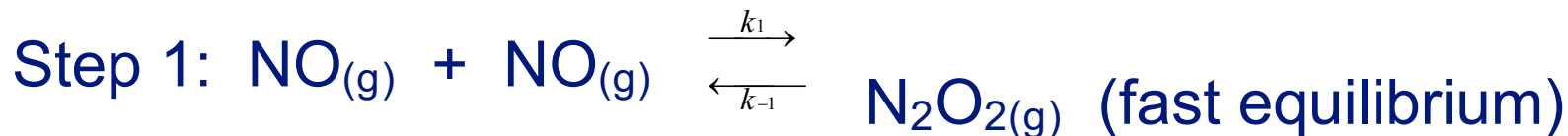
The experimental rate law is $\text{rate} = k[\text{O}_3][\text{NO}_2]$.

What can you say about the relative rates of the two steps of the mechanism?



Sample Exercise 14.15 (p. 606)

Show that the following mechanism for the equation $2 \text{NO}_{(g)} + \text{Br}_{2(g)} \rightarrow 2 \text{NOBr}_{(g)}$ also produces a rate law consistent with the experimentally observed one:



Practice Exercise 1 (14.15)

Consider the following hypothetical reaction:



The following mechanism is proposed for this reaction:



Substances T and U are unstable 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 1 (14.15)

Consider the following hypothetical reaction:



The following mechanism is proposed for this reaction:



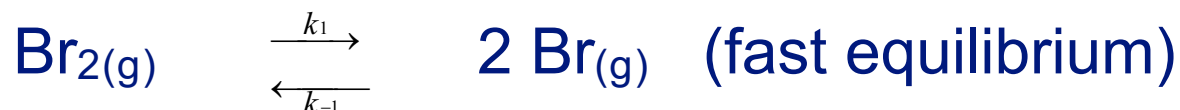
Substances T and U are unstable intermediates. What rate law is predicted by this mechanism?

- 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 (14.15)

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



What is the expression relating the concentration of $\text{Br}_{(g)}$ to that of $\text{Br}_{2(g)}$?



Catalysts

- **catalyst** = a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.

Two types of catalysts:

- Homogeneous
- Heterogeneous



Homogeneous Catalysts

Homogeneous catalysts are present in the same phase as the reacting molecules.

e.g. H_2O_2 decomposes very slowly without a catalyst:



Homogeneous Catalysts

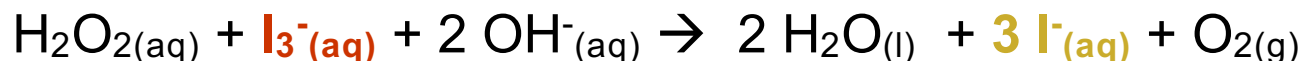
Old Foamey Demo

In the presence of iodide ions, the decomposition occurs rapidly:

Step 1:



Step 2:



Overall:



Old Foamey Demo

1. What is the effect of concentration of H_2O_2 on the rate of the reaction?

(30%, 6%, 3%)

2. Observe the reaction intermediate and product. Watch for colors and other products in the cylinder.

3. What is the effect of changing the concentration of the catalyst?



Old Foamey (with NaBr instead of NaI)

HOMOGENEOUS CATALYSIS
A catalyst that is present in the same phase as the reacting molecules is a homogeneous catalyst.

In the absence of a catalyst, $\text{H}_2\text{O}_2(\text{aq})$ decomposes very slowly.

Shortly after the addition of a small amount of $\text{NaBr}(\text{aq})$ to $\text{H}_2\text{O}_2(\text{aq})$, the solution turns brown because Br_2 is generated (Equation 14.30). The buildup of Br_2 leads to rapid evolution of O_2 according to Equation 14.31.

After all of the H_2O_2 has decomposed, a colorless solution of $\text{NaBr}(\text{aq})$ remains. Thus, NaBr has catalyzed the reaction even though it is not consumed during the reaction.

Old Foamey Demo

What volume of O_2 should be produced, theoretically?

Start here:

30% H_2O_2 , 15 mL, 1.11 g/mL, 100°C

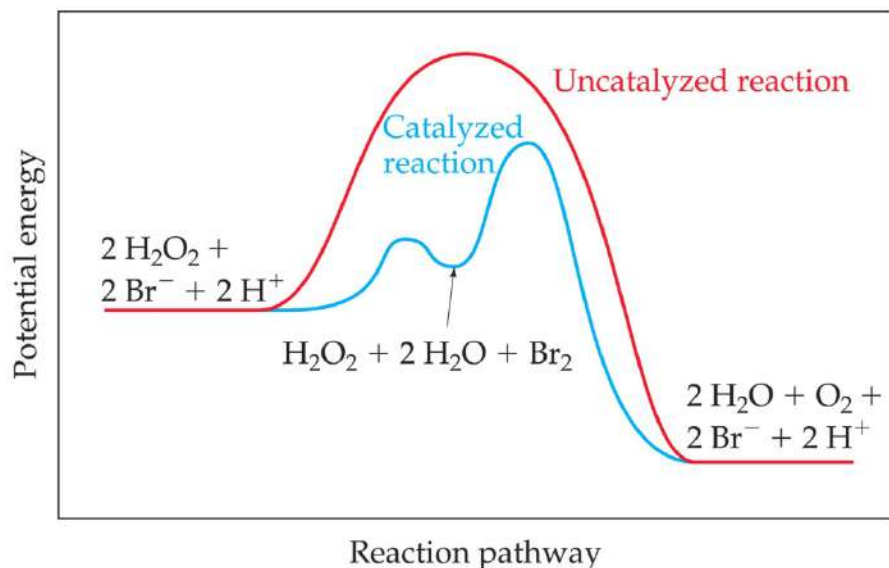
Hint: use $PV = nRT$

(A: 2.3 L O_2)



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.



The Pink Catalyst



Cobalt chloride forms pink complex with water:

$\text{Co}(\text{H}_2\text{O})_6^{2+}$ → forms complex with $\text{C}_4\text{H}_4\text{O}_6^{2-}$, and causes the Co to be oxidized to Co^{3+} , which is green.

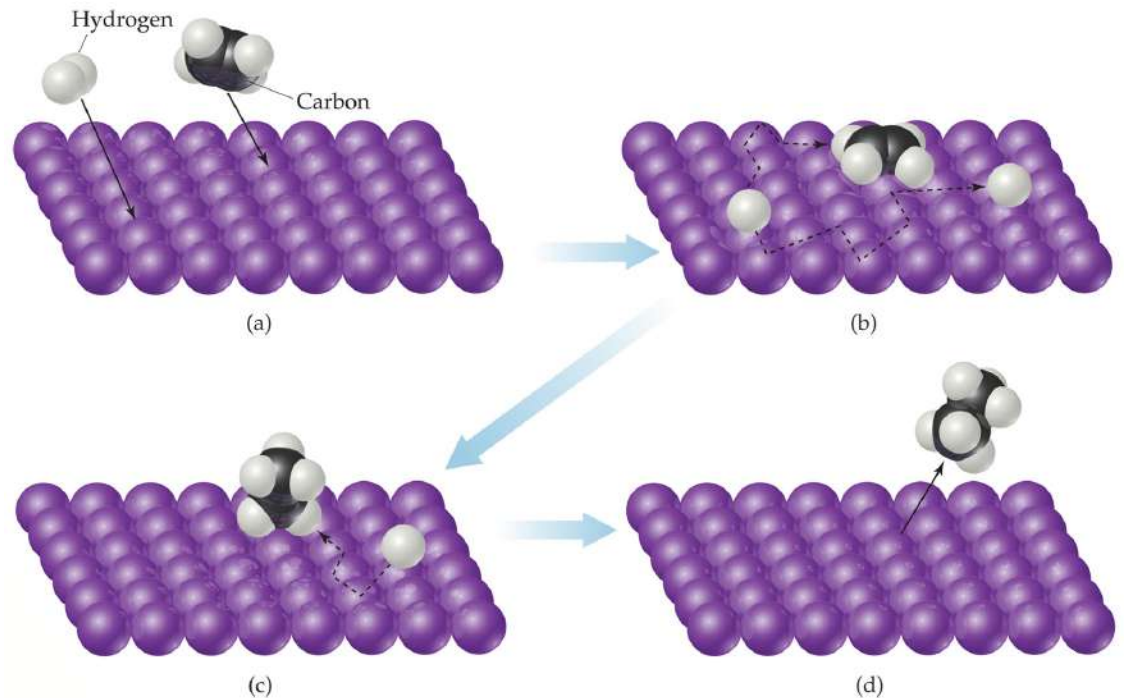
As the $\text{C}_4\text{H}_4\text{O}_6^{2-}$ is oxidized to CO_2 , etc.,
 Co^{3+} is reduced back to Co^{2+}



Catalysts

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.

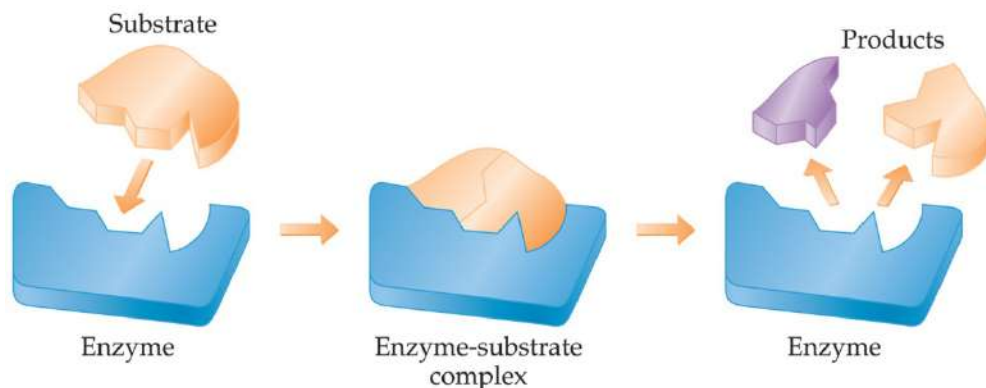
(example of heterogeneous catalyst)



Enzymes



- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.



Acid-Base Catalysts

- Proton transfers to or from charged intermediates or transition states that would otherwise break down to their reactants.

Water is often produced or involved, acting as a Brønsted-Lowry acid or base.

- Stabilizes the intermediate long enough to go on to the next step.

- The acid or base participates in one of the early steps in a multi-step reaction before or during the slow step, then is regenerated in a later step.



Acid-Base Catalysts

- one of the mechanisms by which enzymes catalyze reactions, via amino acid acidic or basic side-chains in the active site.

(general acid-base catalysis)

- Specific acid-base catalysis = reaction rate is dependent on pH only, i.e. the solvent acts as an acid or base.

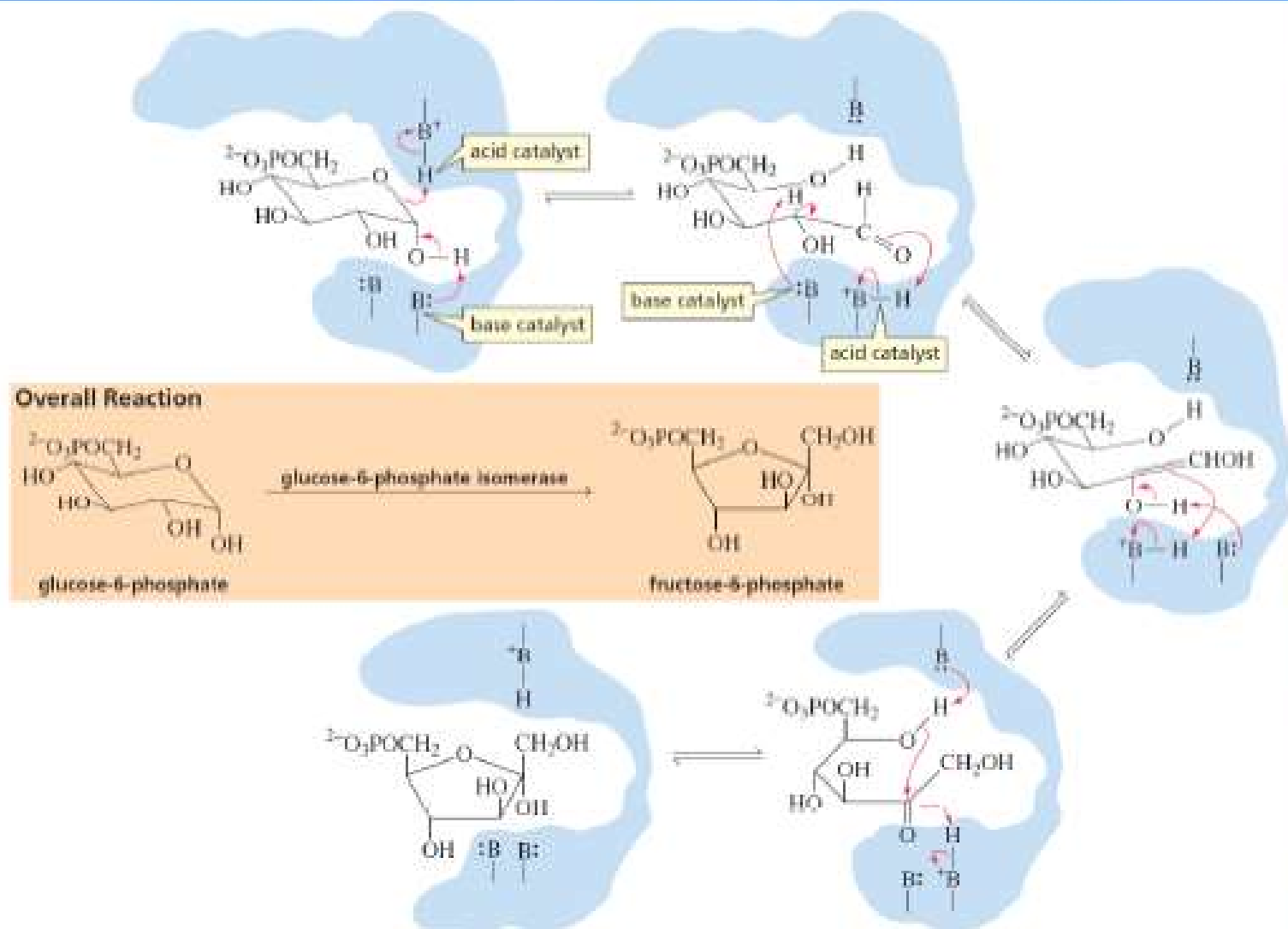
- Examples – organic chemistry, such as ester hydrolysis (enzymatic) or decomposition of hydrocarbons in the conversion of petroleum to gasoline (industrial)



Enzymes – acid-base catalysis

Glucose-6-Phosphate Isomerase

Zhang
Chem 109C



Sample Integrative Exercise 14: Putting Concepts Together (p. 613)

Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:



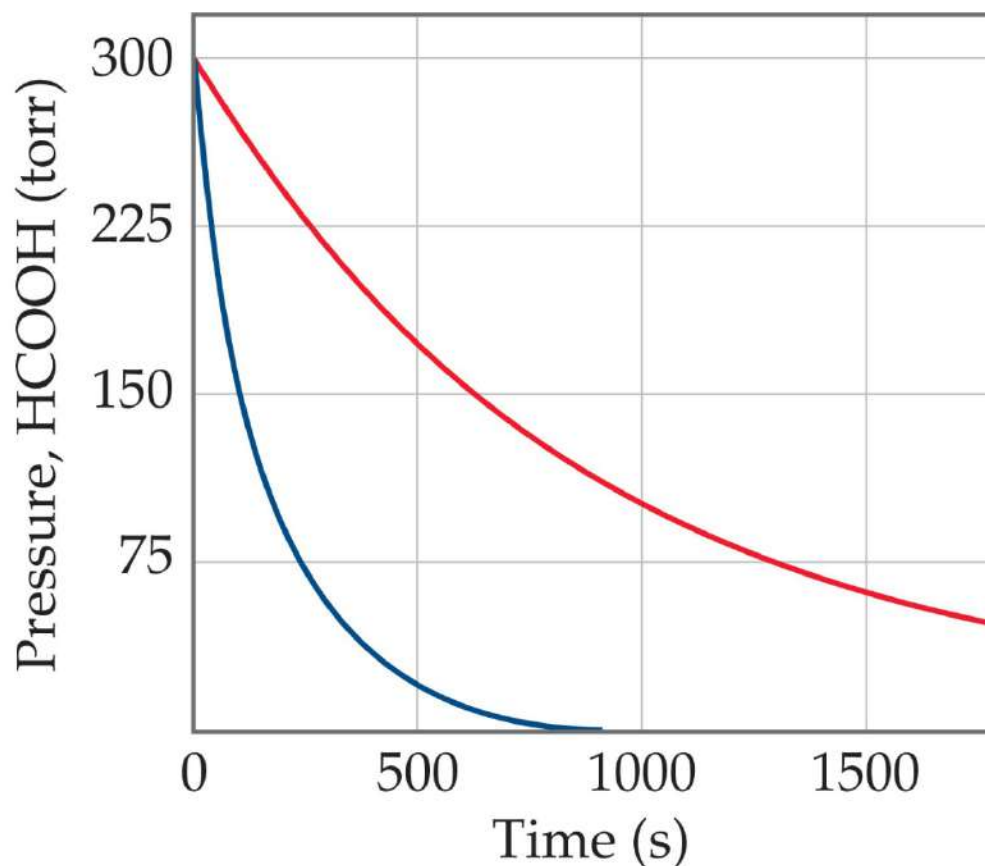
The decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in the figure below. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies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



Sample Integrative Exercise

14: Putting Concepts Together

(p. 611)



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Sample Integrative Exercise

14: Putting Concepts Together

(p. 611)

- 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 ?



Sample Integrative Exercise

14: Putting Concepts Together

(p. 611)

- d) The pressure of formic acid vapor at the start of the reaction is 3.00×10^2 torr. Assuming constant temperature and ideal-gas behavior, 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.
Assuming that 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.

