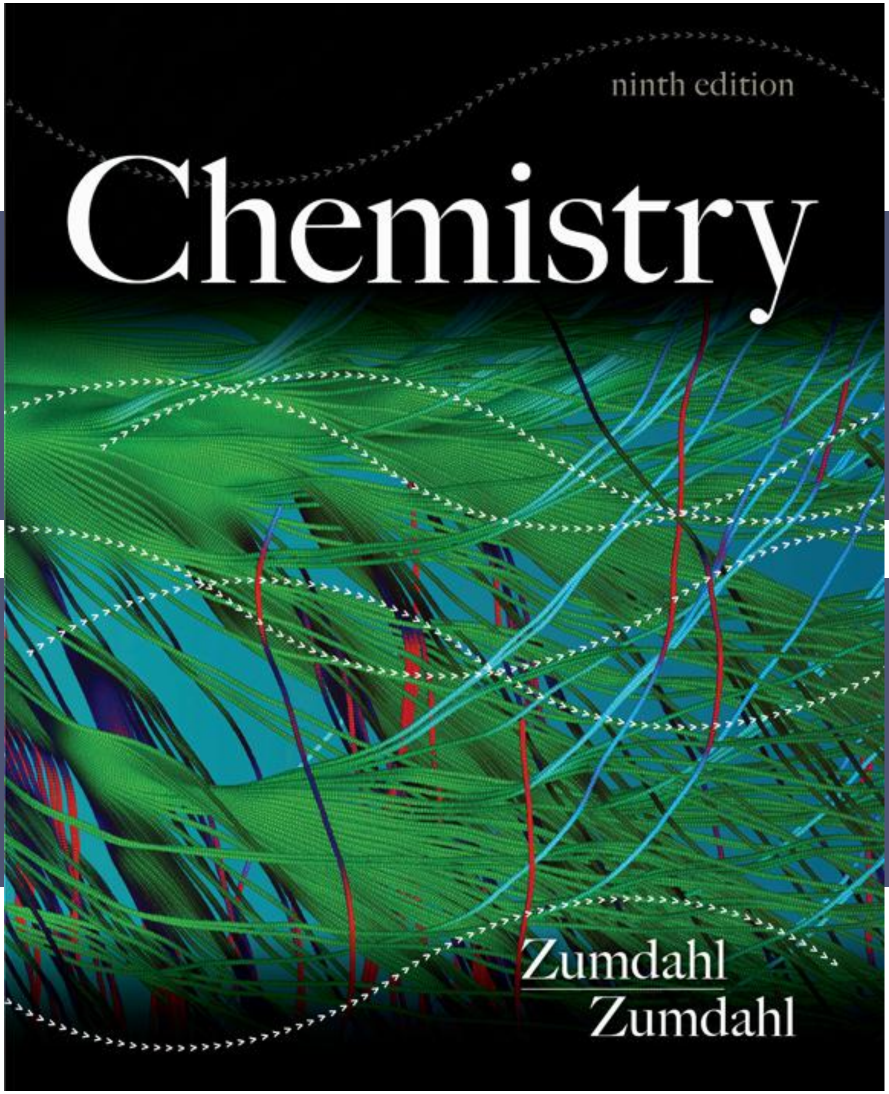


Chapter 12

Chemical Kinetics

Chapter 12
Table of Contents

Reaction Rate

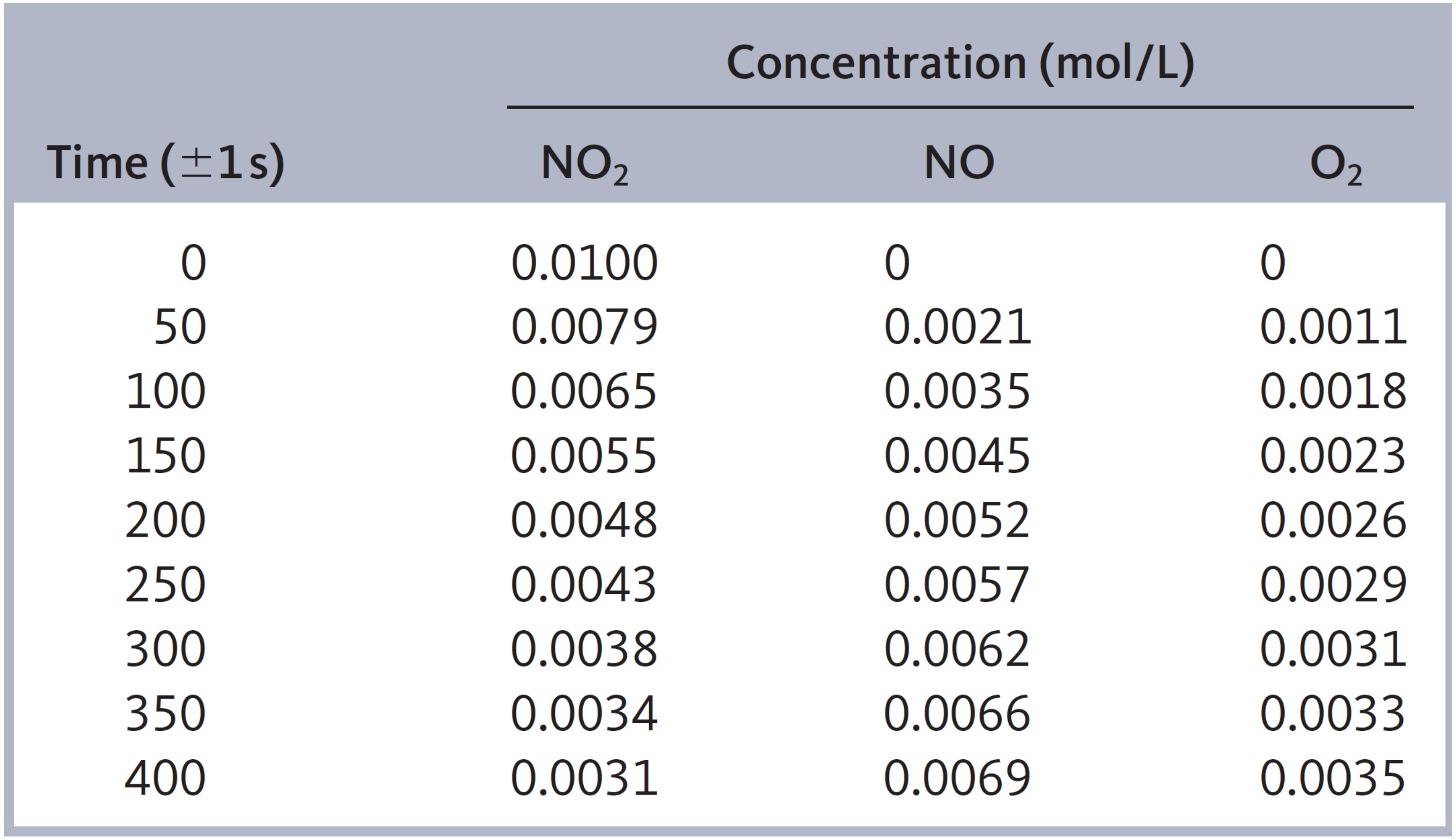
- Change in concentration of a reactant or product per unit time

$$\text{Rate} = \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1}$$

$$= \frac{\Delta\,[\text{A}]}{\Delta t}$$

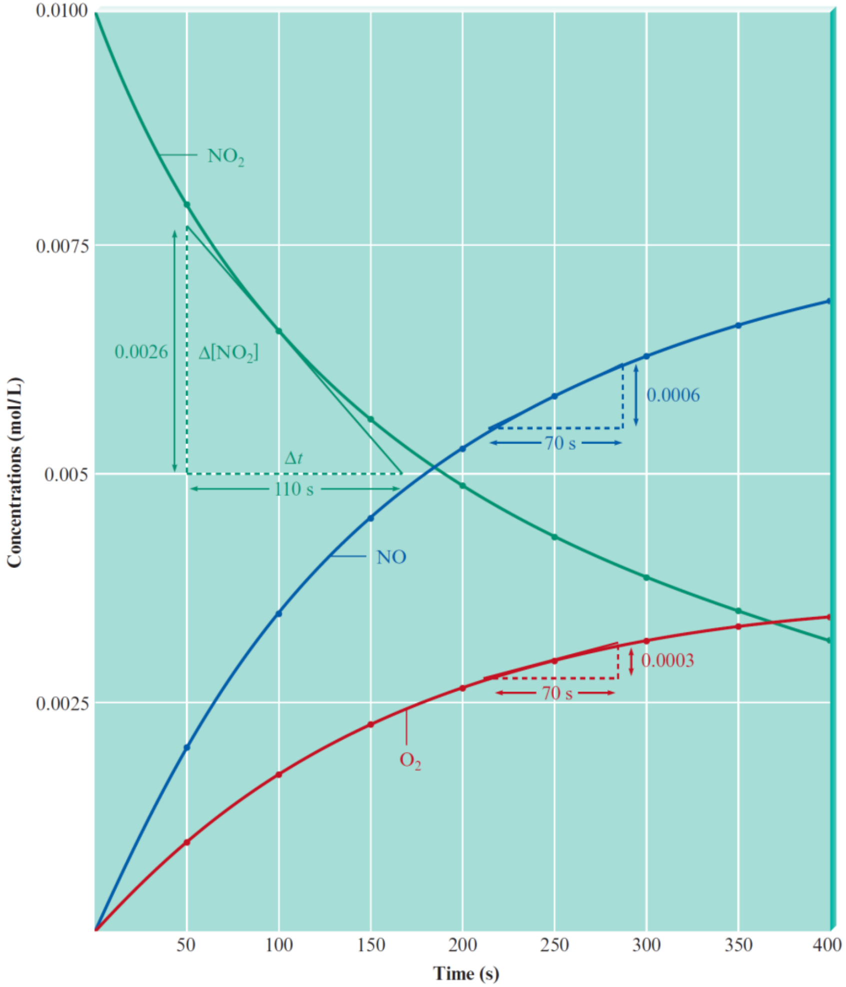
  - [A] = Concentration of the reactant or product in mol/L
  - Δ = Change in a given quantity

Figure 12.1 - Concentrations of Reactant and Products in the Decomposition of Nitrogen Dioxide as a Function of Time



	Concentration (mol/L)		
Time (±1 s)	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

Figure 12.1 - The Decomposition of Nitrogen Dioxide at 300° C



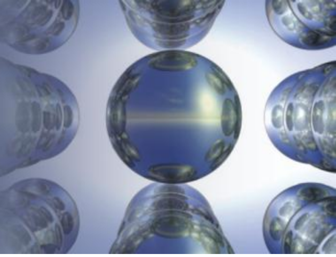
Average Rate at Which the Concentration of NO_2 Changes over the First 50 Seconds

$$\frac{\text{Change in }[NO_2]}{\text{Time elapsed}} = \frac{\Delta\,[NO_2]}{\Delta t}$$

$$= \frac{[NO_2]_{t\,=\,50} - [NO_2]_{t\,=\,0}}{50\text{ s} - 0\text{ s}}$$

$$= \frac{0.0079\text{ mol/L} - 0.0100\text{ mol/L}}{50\text{ s}}$$

$$= -4.2 \times 10^{-5}\text{ mol/L}\cdot\text{s}$$

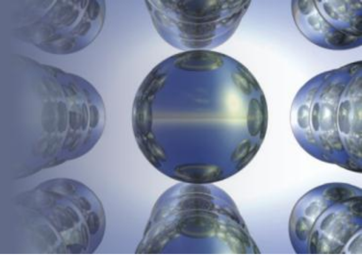


Average Rate at Which the Concentration of NO_2 Changes over the First 50 Seconds (Continued 1)

- Since the concentration of NO_2 decreases with time, [NO_2] is a negative quantity

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

  - Since the concentrations of reactants always decrease with time, any rate expression involving a reactant will include a negative sign

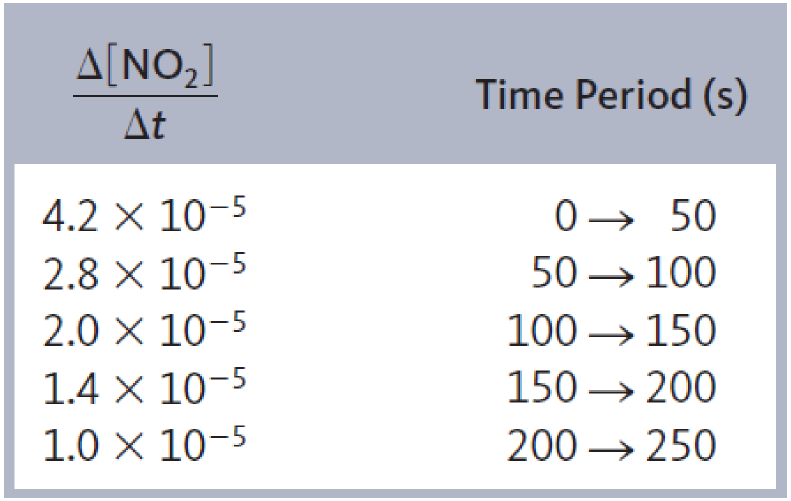


Average Rate at Which the Concentration of NO_2 Changes over the First 50 Seconds (Continued 2)

- Hence,

$$\text{Rate} = -\frac{\Delta[NO_2]}{\Delta t}$$
$$= -(-4.2\times10^{-5}\ \text{mol}/\text{L}\times\text{s})$$
$$= 4.2\ \times\ 10^{-5}\ \text{mol/L}\cdot\text{s}$$

- Rate is not constant
  - Decreases with time



$\frac{\Delta[NO_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	$0 \rightarrow 50$
2.8×10^{-5}	$50 \rightarrow 100$
2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

Instantaneous Rate

- Value of reaction rate at a particular time
- Obtained by computing the slope of a line tangent to the curve at that point
  - Based on figure 12.1

$$\text{Slope of the tangent line} = \frac{\text{change in } y}{\text{change in } x}$$

$$= \frac{\Delta\,[\mathrm{NO_2}]}{\Delta t}$$

Instantaneous Rate (Continued)

- But

$$\text{Rate} = -\frac{\Delta\,[\text{NO}_2]}{\Delta t}$$

- Therefore,

$$\begin{aligned}\text{Rate} &= -\ (\text{slope of the tangent line})\\ &= -\left(\frac{-0.0026\ \text{mol/L}}{110\ \text{s}}\right)\\ &= 2.4\times 10^{-5}\ \text{mol/L}\cdot\text{s}\end{aligned}$$

Determining the Rate of Reaction in Terms of Products

- Consider the reaction

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

  - NO is produced at the same rate as NO_2 is consumed
  - At t = 250 seconds

$$\text{Slope of the tangent to the NO curve} = \frac{6.0 \times 10^{-4}\ \text{mol/L}}{70\ \text{s}}$$

$$= 8.6 \times 10^{-6}\ \text{mol/L}\cdot\text{s}$$

Determining the Rate of Reaction in Terms of Products

(Continued 1)

$$\text{Slope of the tangent to the } O_2 \text{ curve} = \frac{3.0 \times 10^{-4}\ \text{mol/L}}{70\ \text{s}}$$

$$= 4.3 \times 10^{-6}\ \text{mol/L} \cdot \text{s}$$

- Rate of NO production is twice the rate of O_2 production

Determining the Rate of Reaction in Terms of Products

(Continued 2)

- Summary
  - Rate of consumption of NO_2 = Rate of production of NO = 2(rate of production of O_2)

$$-\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = 2\left(\frac{\Delta[O_2]}{\Delta t}\right)$$

Rate Law

- Chemical reactions are reversible
  - As NO and O_2 accumulate, they can react to re-form NO_2

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

- When gaseous NO_2 is placed in an otherwise empty container, initially the dominant reaction is

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

Rate Law (Continued)

- Change in the concentration of NO_2 depends only on the forward reaction
  - Reverse reaction becomes important as enough products accumulate after a period of time
- Expression to be used if the reverse reaction is to be neglected

$$\text{Rate} = k\,[NO_2]^n \qquad (12.1)$$

  - *k* = **rate constant**
  - *n* = **order** of the reactant

Rate Law - Key Points

- The concentrations of the products do not appear in the rate law
    - The reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate
- The value of the exponent *n* must be determined by experiment
    - Cannot be written from the balanced equation

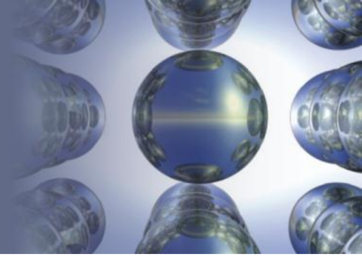
Rate Constant

- Definition of reaction rate in terms of the consumption of NO_2

$$\text{Rate} = -\frac{\Delta\,[\text{NO}_2]}{\Delta t} = k\,[\text{NO}_2]^n$$

- Definition of the reaction rate in terms of production of O_2

$$\text{Rate}' = -\frac{\Delta\,[\text{O}_2]}{\Delta t} = k'\,[\text{NO}_2]^n$$



Rate Constant (Continued)

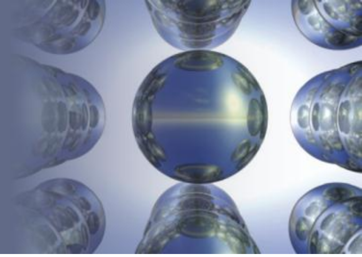
- As two moles of NO_2 molecules are consumed for every O_2 molecule produced,

$$\text{Rate} = 2 \times \text{rate}'$$

Or $$k[\text{NO}_2]^n = 2k'[\text{NO}_2]^n$$

and $$k = 2 \times k'$$

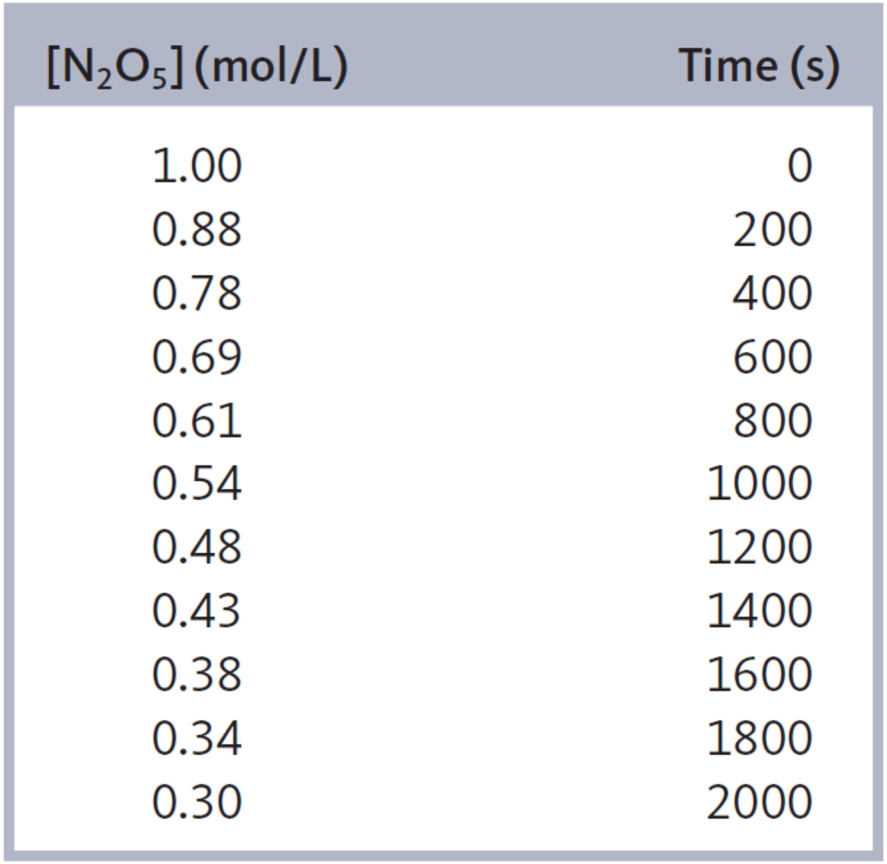
- Value of the rate constant depends on how the rate is defined



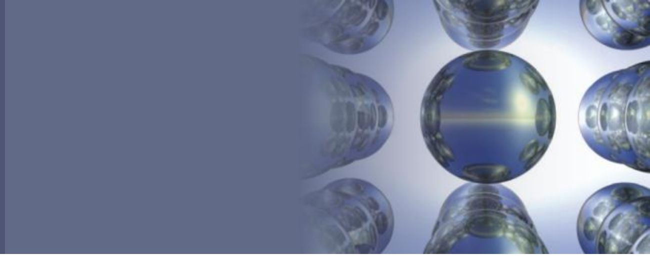
Types of Rate Laws

- **Differential rate law** (**rate law**)
  - Expresses how the rate depends on the concentration of the reactant
- **Integrated rate law**: Expresses how the concentration depends on time
- The type of rate law used depends on what types of data are easiest to collect

Table 12.3 - Concentration/Time Data for the Reaction $2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$ (at 45° C)



$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

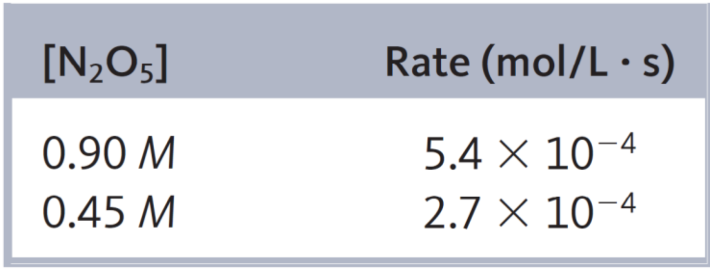


Obtaining the Differential Rate Law for a Reaction

- Consider the following reaction:

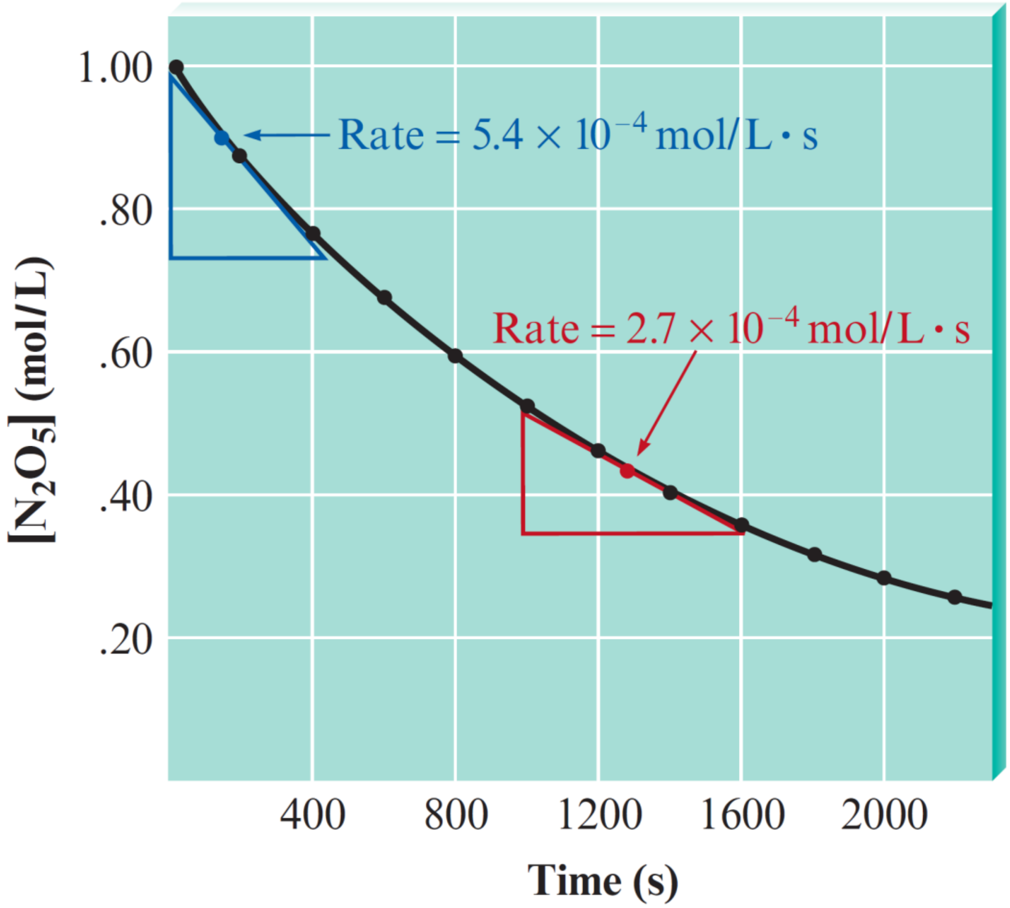
$$2N_2O_5(soln) \longrightarrow 4NO_2\ (soln) + O_2(g)$$

- The reverse reaction is negligible
- Evaluation of reaction rates at concentrations of N_2O_5 of 0.90 *M* and 0.45 *M* yields the following data:



$[N_2O_5]$	Rate (mol/L · s)
0.90 *M*	5.4×10^{-4}
0.45 *M*	2.7×10^{-4}

Figure 12.3 - A Plot of the Concentration of N_2O_5 as a Function of Time



Obtaining the Differential Rate Law for a Reaction

(Continued)

- When $[N_2O_5]$ is halved, the rate is also halved
  - The (differential) rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]$$

    - The order of a particular reactant must be obtained by observing how the reaction rate depends on the concentration of that reactant

$$\text{Rate law for the decomposition of N}_2\text{O}_5 = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

Method of Initial Rates

- **Initial rate**: The instantaneous rate determined just after $t = 0$
- Several experiments are carried out using different initial concentrations of each of the reactants
  - The initial rate is determined for each run
    - The results are then compared to see how the initial rate depends on the initial concentrations

Interactive Example 12.1 - Determining a Rate Law

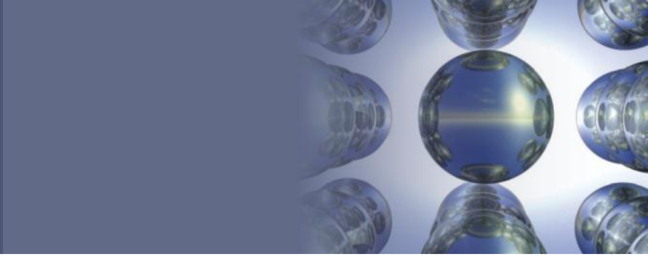
- The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the following equation:

$$\mathrm{BrO_3^-}(aq) + 5\mathrm{Br^-}(aq) + 6\mathrm{H^+}(aq) \rightarrow 3\mathrm{Br_2}(l) + 3\mathrm{H_2O}(l)$$

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}

Interactive Example 12.1 - Determining a Rate Law
(Continued)

- Determine the orders for all three reactants, the overall reaction order, and the value of the rate constant



Interactive Example 12.1 - Solution

- General form of the rate law

$$\text{Rate} = k\,[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

- Step 1 - Determine the value of *n*
  - Use the results from Experiments 1 and 2

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.6\times10^{-3}\ \text{mol/L}\cdot\text{s}}{8.0\times10^{-4}\ \text{mol/L}\cdot\text{s}} = \frac{k(0.20\ \text{mol/L})^n(0.10\ \text{mol/L})^m(0.10\ \text{mol/L})^p}{k(0.10\ \text{mol/L})^n(0.10\ \text{mol/L})^m(0.10\ \text{mol/L})^p}$$

$$2.0 = \left(\frac{0.20\ \text{mol/L}}{0.10\ \text{mol/L}}\right)^n = (2.0)^n$$

  - Thus, *n* = 1

Interactive Example 12.1 - Solution (Continued 1)

- Step 2 - Determine the value of *m*
  - Use the results from Experiments 2 and 3

$$\frac{\text{Rate } 3}{\text{Rate } 2} = \frac{3.2\times10^{-3}\ \text{mol/L}\cdot\text{s}}{1.6\times10^{-3}\ \text{mol/L}\cdot\text{s}} = \frac{k(0.20\ \text{mol/L})^{n}(0.20\ \text{mol/L})^{m}(0.10\ \text{mol/L})^{p}}{k(0.20\ \text{mol/L})^{n}(0.10\ \text{mol/L})^{m}(0.10\ \text{mol/L})^{p}}$$

$$2.0 = \left(\frac{0.20\ \text{mol/L}}{0.10\ \text{mol/L}}\right)^{m} = (2.0)^{m}$$

  - Thus, $m = 1$

Interactive Example 12.1 - Solution (Continued 2)

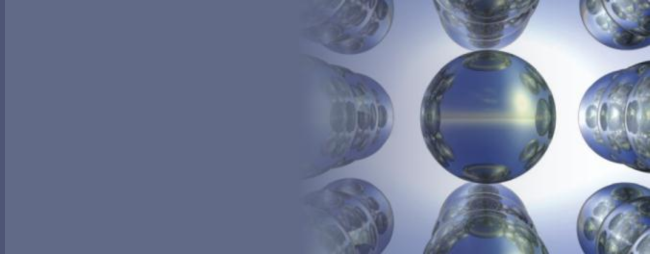
- Step 3 - Determine the value of *p*
  - Use the results from Experiments 1 and 4

$$\frac{\text{Rate } 4}{\text{Rate } 1} = \frac{3.2\times10^{-3}\ \text{mol}/\text{L}\cdot\text{s}}{8.0\times10^{-4}\ \text{mol}/\text{L}\cdot\text{s}} = \frac{k(0.10\ \text{mol}/\text{L})^{n}(0.10\ \text{mol}/\text{L})^{m}(0.20\ \text{mol}/\text{L})^{p}}{k(0.10\ \text{mol}/\text{L})^{n}(0.10\ \text{mol}/\text{L})^{m}(0.10\ \text{mol}/\text{L})^{p}}$$

$$4.0 = \left(\frac{0.20\ \text{mol}/\text{L}}{0.10\ \text{mol}/\text{L}}\right)^{p}$$

$$4.0 = (2.0)^{p} = (2.0)^{2}$$

  - Thus, $p = 2$
  - The overall reaction order is $n + m + p = 4$



Interactive Example 12.1 - Solution (Continued 3)

- The rate law for the reaction

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

- The value of the rate constant *k* can be calculated from the results of any of the four experiments
- For Experiment 1, the initial rate is 8.0×10^{-4} mol/L·s

$$[\text{BrO}_3^-] = 0.100\,M, [\text{Br}^-] = 0.10\,M, \text{and}\,[\text{H}^+] = 0.10\,M$$

Interactive Example 12.1 - Solution (Continued 4)

- Using the values from the initial rate in the rate law

$$8.0\times10^{-4}\ \text{mol}/\text{L}\cdot\text{s} = k(0.10\ \text{mol}/\text{L})\,(0.10\ \text{mol}/\text{L})\,(0.10\ \text{mol}/\text{L})^2$$

$$8.0\times10^{-4}\ \text{mol}/\text{L}\cdot\text{s} = k(1.0\times10^{-4}\,\text{mol}^4/\text{L}^4)$$

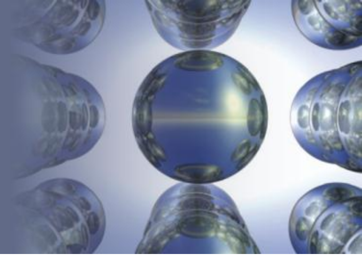
$$k = \frac{8.0\times10^{-4}\ \text{mol}/\text{L}\cdot\text{s}}{1.0\times10^{-4}\ \text{mol}^4/\text{L}^4} = 8.0\ \text{L}^3/\text{mol}^3\cdot\text{s}$$

- Reality Check
  - Verify that the same value of *k* can be obtained from the results of the other experiments

Integrated Rate Law

- Used to express the reactant concentrations as a function of time
- Basic formula

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^n$$



First-Order Rate Laws

- Rate law for the decomposition of dinitrogen pentoxide

$$\text{Rate} = -\frac{\Delta[\mathrm{N_2O_5}]}{\Delta t} = k[\mathrm{N_2O_5}]$$

  - This is a **first-order reaction**
    - Rate of formation of products increases with the increase in the concentration of the reactant

First-Order Rate Laws (Continued)

- The first-order reaction can be converted into an integrated rate law
  - Integrated rate law - Expresses the concentration of the reactant as a function of time

$$\ln [N_2O_5] = -kt + \ln [N_2O_5]_0$$

    - ln - Natural algorithm
    - *t* - Time
    - $[N_2O_5]$ - Concentration of N_2O_5 at time *t*
    - $[N_2O_5]_0$ - Initial concentration of N_2O_5

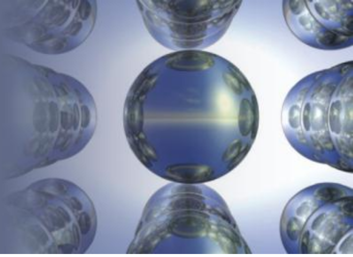
Integrated First-Order Rate Law

- Consider a reaction with the following rate law

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

- The integrated first-order rate law is

$$\ln\,[\text{A}] = -kt + \ln\,[\text{A}]_0 \qquad (12.2)$$



Integrated First-Order Rate Law - Key Points

- The equation expresses the influence of time on the concentration of A
  - The initial concentration of A and the rate constant *k* can be used to calculate the concentration of A at any time
- The equation is of the form $y = mx + b$
  - $y = \ln[A]$, $x = t$, $m = -k$, and $b = \ln[A]_0$
  - For a first-order reaction, a plot of ln[A] versus *t* is always a straight line

Integrated First-Order Rate Law - Key Points (Continued)

- The equation can be expressed in terms of a ratio of [A] and $[A]_0$

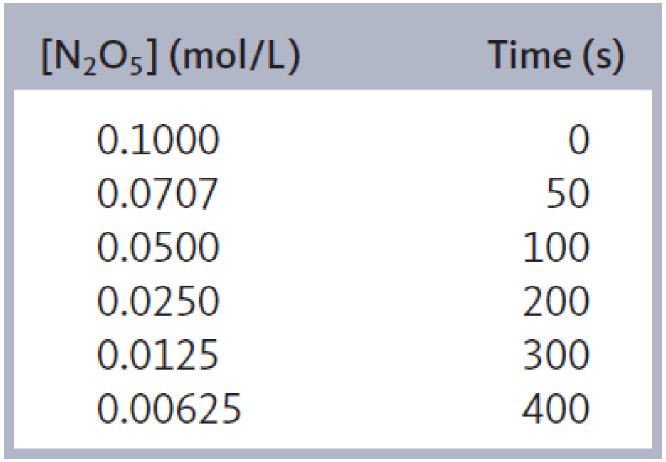
$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

Interactive Example 12.3 - First-Order Rate Laws II

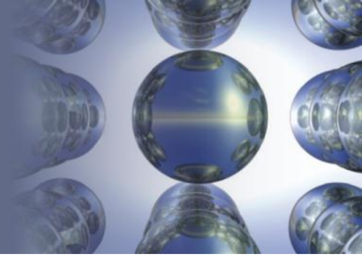
- Calculate $[N_2O_5]$ at 150 s after the start of the following reaction:

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

  - Use the following information:



$[N_2O_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400



Interactive Example 12.3 - Solution

- Information available
  - $[N_2O_5] = 0.0500$ mol/L at 100 s
  - $[N_2O_5] = 0.0250$ mol/L at 200 s
- Formula required to calculate $[N_2O_5]$ after 150 s

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$$

  - Where $t = 150$ s, $k = 6.93 \times 10^{-3}\ \text{s}^{-1}$, and $[N_2O_5]_0 =$ 0.1000 mol/L

Interactive Example 12.3 - Solution (Continued)

$$\ln([N_2O_5]_{t=150}) = -(6.93\times10^{-3}\,\text{s}^{-1})(150\,\text{s}) + \ln(0.100)$$

$$= -1.040 - 2.303 = -3.343$$

$$([N_2O_5]_{t=150}) = \text{antilog}\,(-3.343) = 0.0353\ \text{mol/L}$$

- Note that this value of $[N_2O_5]$ is not halfway between 0.0500 and 0.0250 mol/L

Half-Life of a First-Order Reaction

- **Half-life of a reactant** ($t_{1/2}$): Time required for a reactant to reach half its original concentration
- Consider the general reaction aA → products
  - If the reaction is first order in [A], then

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

  - When $t = t_{1/2}$,

$$[A] = \frac{[A]_0}{2}$$

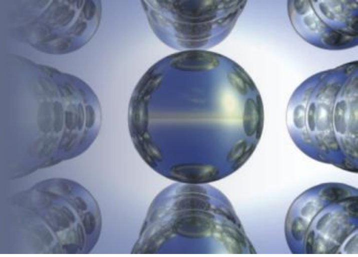
Half-Life of a First-Order Reaction (Continued 1)

- For $t = t_{1/2}$, the integrated rate law becomes

$$\ln\left(\frac{[A]_0}{[A]_0 / 2}\right) = kt_{1/2} \qquad \text{or} \qquad \ln(2) = kt_{1/2}$$

- Substituting the value for ln(2) and solving for $t_{1/2}$

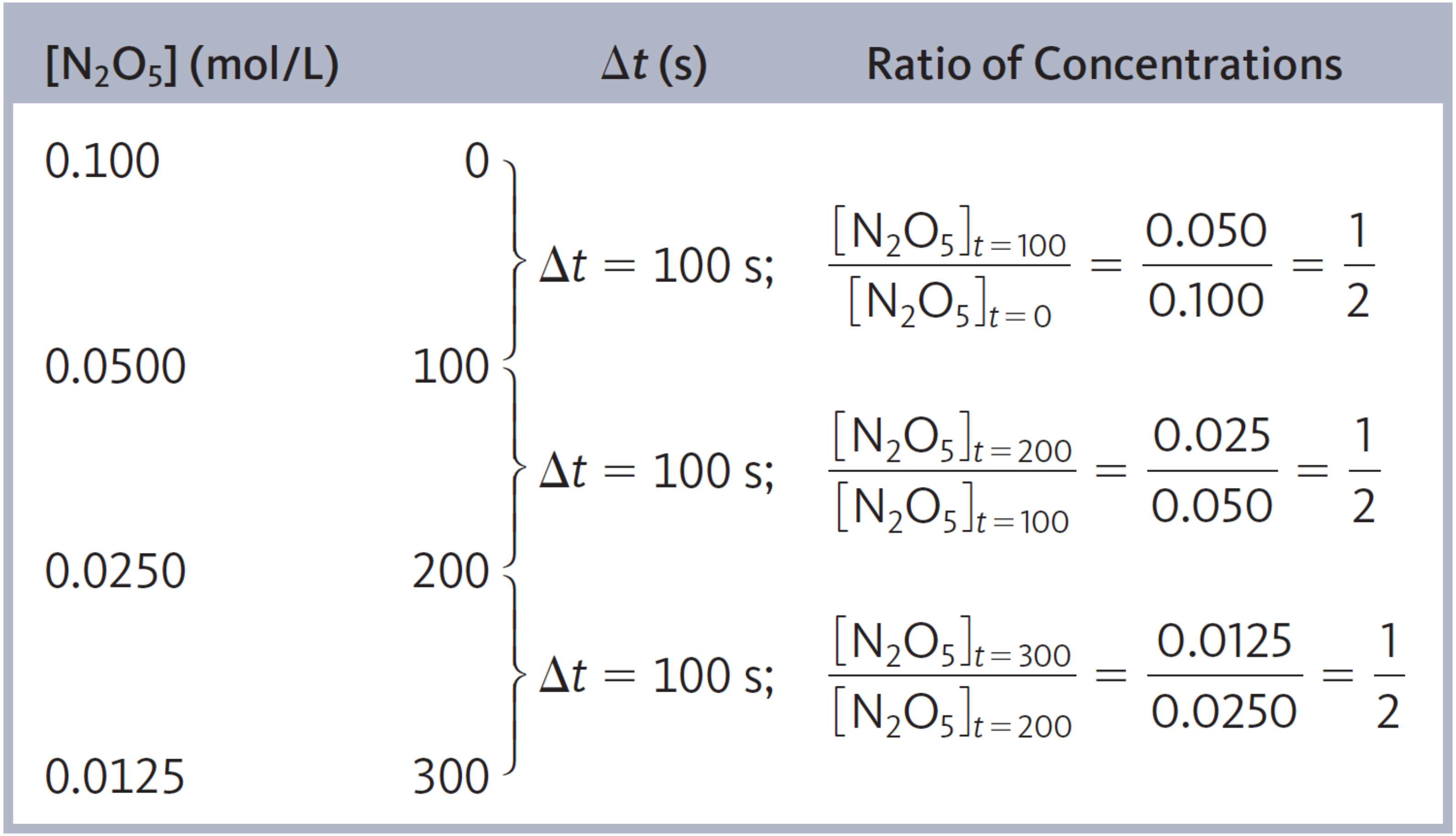
$$t_{1/2} = \frac{0.693}{k} \qquad (12.3)$$



Half-Life of a First-Order Reaction (Continued 2)

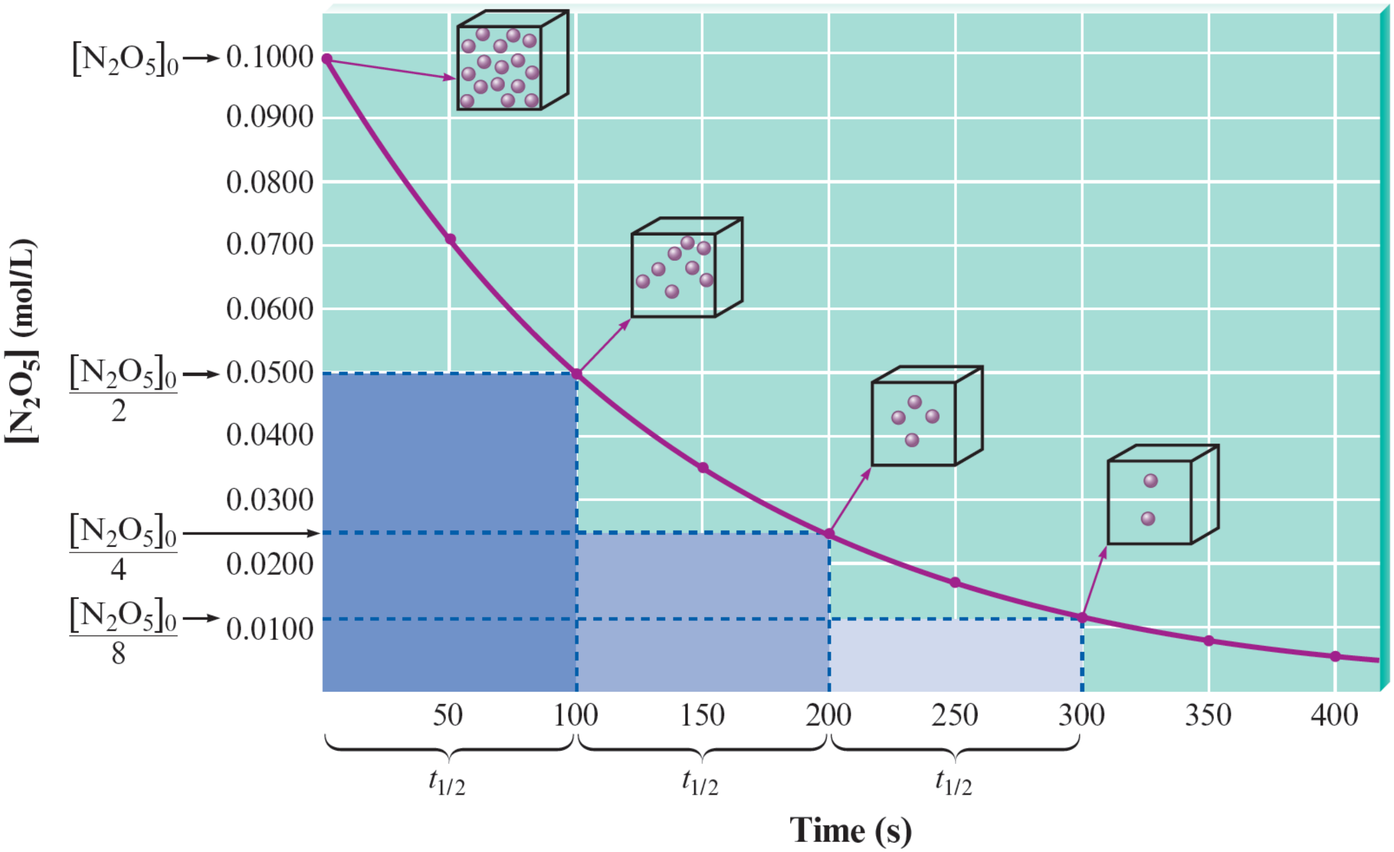
- Equation 12.3 can be used to determine:
    - $t_{1/2}$ if k is known
    - k if $t_{1/2}$ is known
- For a first-order reaction, half-life does not depend on concentration

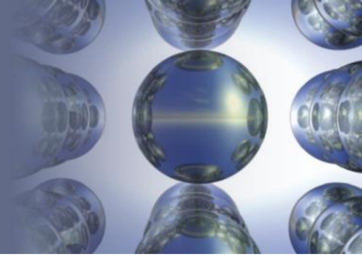
Half-Life for the Decomposition of Dinitrogen Pentoxide



$[N_2O_5]$ (mol/L)	Δt (s)	Ratio of Concentrations
0.100	0	
	$\Delta t = 100$ s;	$\frac{[N_2O_5]_{t=100}}{[N_2O_5]_{t=0}} = \frac{0.050}{0.100} = \frac{1}{2}$
0.0500	100	
	$\Delta t = 100$ s;	$\frac{[N_2O_5]_{t=200}}{[N_2O_5]_{t=100}} = \frac{0.025}{0.050} = \frac{1}{2}$
0.0250	200	
	$\Delta t = 100$ s;	$\frac{[N_2O_5]_{t=300}}{[N_2O_5]_{t=200}} = \frac{0.0125}{0.0250} = \frac{1}{2}$
0.0125	300	

Figure 12.4 - A Plot of $[N_2O_5]$ versus Time for the Decomposition of N_2O_5





Interactive Example 12.4 - Half-Life for a First-Order Reaction

- A certain first-order reaction has a half-life of 20.0 minutes
  1. Calculate the rate constant for this reaction
  2. How much time is required for this reaction to be 75% complete?

Interactive Example 12.4 - Solution (a)

- Solving equation (12.3) for *k* gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0\ \text{min}} = 3.47 \times 10^{-2}\ \text{min}^{-1}$$

Interactive Example 12.4 - Solution (b)

- We use the integrated rate law in the form

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

  - If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form

$$\frac{[A]}{[A]_0} \times 100\% = 25\%$$

Interactive Example 12.4 - Solution (b) (Continued 1)

$$\frac{[A]}{[A]_0} = 0.25 \text{ or } \frac{[A]_0}{[A]} = \frac{1}{0.25} = 4.0$$

$$\ln\left(\frac{[A]_0}{[A]}\right) = \ln(4.0) = kt = \left(\frac{3.47 \times 10^{-2}}{\text{min}}\right)t$$

$$t = \frac{\ln(4.0)}{\frac{3.47 \times 10^{-2}}{\text{min}}} = 40 \text{ min}$$

- It takes 40 minutes for this particular reaction to reach 75% completion

Interactive Example 12.4 - Solution (b) (Continued 2)

- Alternate way of solving the problem using the definition of half-life
  - After one half-life the reaction has gone 50% to completion
  - If the initial concentration were 1.0 mol/L, after one half-life the concentration would be 0.50 mol/L
    - One more half-life would produce a concentration of 0.25 mol/L

Interactive Example 12.4 - Solution (b) (Continued 3)

  - Comparing 0.25 mol/L with the original 1.0 mol/L shows that 25% of the reactant is left after two half-lives
- What percentage of reactant remains after three half-lives?
  - Two half-lives for this reaction is 2(20.0 min), or 40.0 min, which agrees with the preceding answer

Second-Order Rate Laws

- Consider a general reaction

$$aA \longrightarrow \text{products}$$

  - Rate law for a second-order reaction

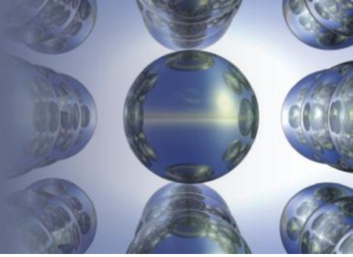
$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2 \qquad (12.4)$$

  - The **integrated second-order rate law** has the form

$$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0} \qquad (12.5)$$

Characteristics of Equation (12.5)

- A plot of 1/[A] versus *t* will produce a straight line with a slope equal to *k*
- The equation shows how [A] depends on time and can be used to calculate [A] at any time *t*, provided *k* and $[A]_0$ are known



Half-Life for a Second-Order Reaction

- When one half-life of the second-order reaction has elapsed ($t = t_{1/2}$), by definition,

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{2}$$

  - Equation (12.5) becomes

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

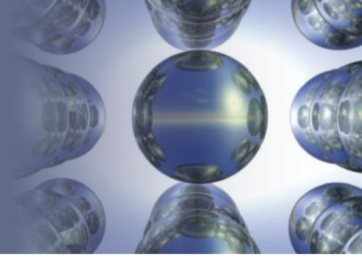
Half-Life for a Second-Order Reaction (Continued)

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

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

- Solving for $t_{1/2}$ gives the expression for the half-life of a second-order reaction

$$\mathrm{t}_{1/2} = \frac{1}{k[\mathrm{A}]_0} \qquad (12.6)$$



Example 12.5 - Determining Rate Laws

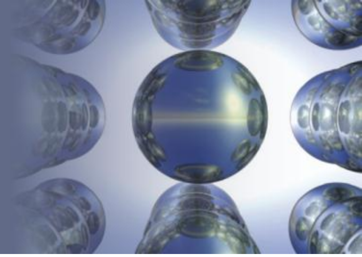
- Butadiene reacts to form its dimer according to the equation

$$2C_4H_6(g) \rightarrow C_8H_{12}(g)$$

$[C_4H_6]$ (mol/L)	Time (±1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

Example 12.5 - Determining Rate Laws (Continued)

a. Is this reaction a first order or second order?
b. What is the value of the rate constant for the reaction?
c. What is the half-life for the reaction under the initial conditions of this experiment?



Example 12.5 - Solution (a)

- To decide whether the rate law for this reaction is first order or second order, we must see whether the plot of ln[C_4H_6] versus time is a straight line (first order) or the plot of 1/[C_4H_6] versus time is a straight line (second order)

Example 12.5 - Solution (a) (Continued 1)

- The data necessary to make these plots are as follows:

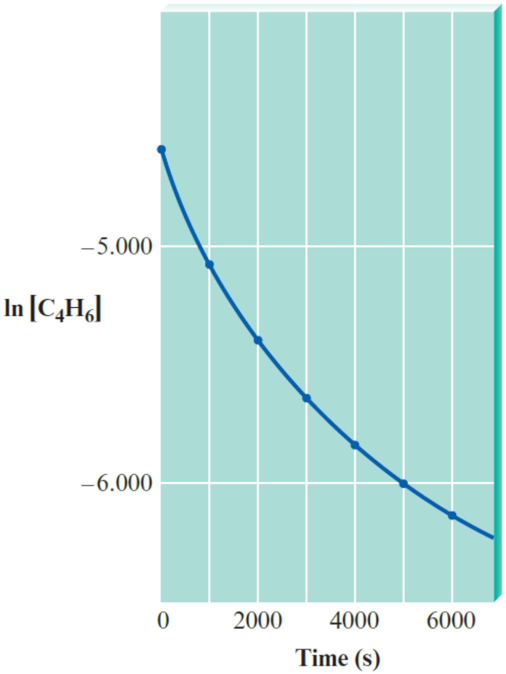
t (s)	$\frac{1}{[C_4H_6]}$	$\ln[C_4H_6]$
0	100	−4.605
1000	160	−5.075
1800	210	−5.348
2800	270	−5.599
3600	320	−5.767
4400	370	−5.915
5200	415	−6.028
6200	481	−6.175

Example 12.5 - Solution (a) (Continued 2)

- The reaction is second order
- The rate law for this reaction is:

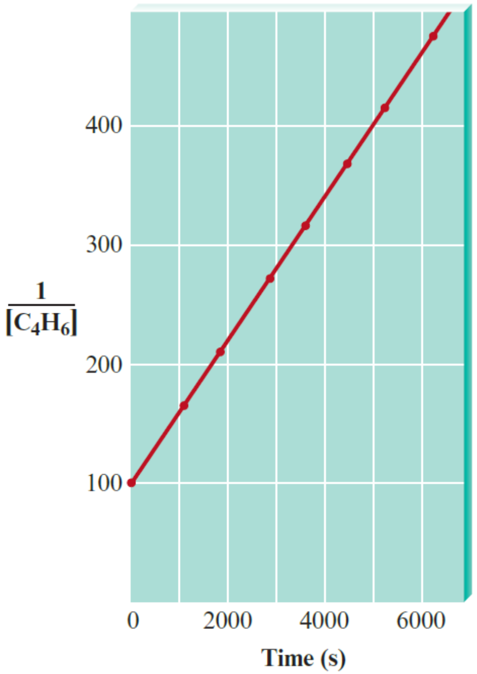
$$\text{Rate} = -\frac{\Delta[C_4H_6]}{\Delta t}$$

$$= k[C_4H_6]^2$$



a

A plot of ln[C_4H_6] versus *t*



b

A plot of 1/[C_4H_6] versus *t*

Example 12.5 - Solution (b)

- For a second-order reaction, a plot of $1/[C_4H_6]$ versus *t* produces a straight line of slope *k*
    - In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[C_4H_6]$ and $x = t$
    - Slope of the line can be expressed as follows:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{\Delta\left(\dfrac{1}{[C_4H_6]}\right)}{\Delta t}$$

Example 12.5 - Solution (b) (Continued)

- Using the points at *t* = 0 and *t* = 6200, we can find the rate constant for the reaction

$$k = \text{slope} = \frac{(481 - 100)\ \text{L/mol}}{(6200 - 0)\ \text{s}} = \frac{381}{6200}\ \text{L/mol}\cdot\text{s}$$

$$= 6.14 \times 10^{-2}\ \text{L/mol}\cdot\text{s}$$

Example 12.5 - Solution (c)

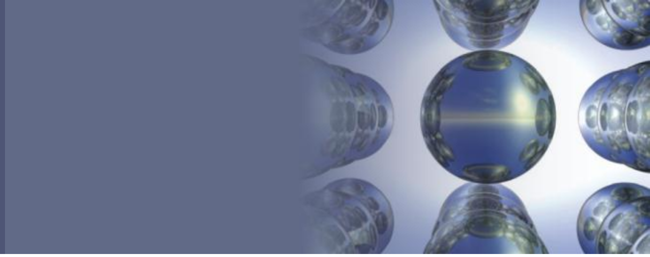
- The expression for the half-life of a second-order reaction is

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

  - In this case $k = 6.14 \times 10^{-2}$ L/mol · s (from part b) and $[\mathrm{A}]_0 = [\mathrm{C_4H_6}]_0 = 0.01000\ M$ (the concentration at $t = 0$)

$$t_{1/2} = \frac{1}{(6.14\times10^{-2}\ \mathrm{L/mol\cdot s})\,(1.000\times10^{-2}\ \mathrm{mol/L})} = 1.63\times10^{3}\,\mathrm{s}$$

    - The initial concentration of C_4H_6 is halved in 1630 s



Half-Life for a First-Order Reaction versus Half-Life of a Second-Order Reaction

- $t_{1/2}$
  - First-order reaction - $t_{1/2}$ depends on k
  - Second-order reaction - $t_{1/2}$ depends on k and $[A]_0$
- Half-life
  - First-order reaction - A constant time is required to reduce the concentration of the reactant by half
  - Second-order reaction - Each successive half-life is double the preceding one

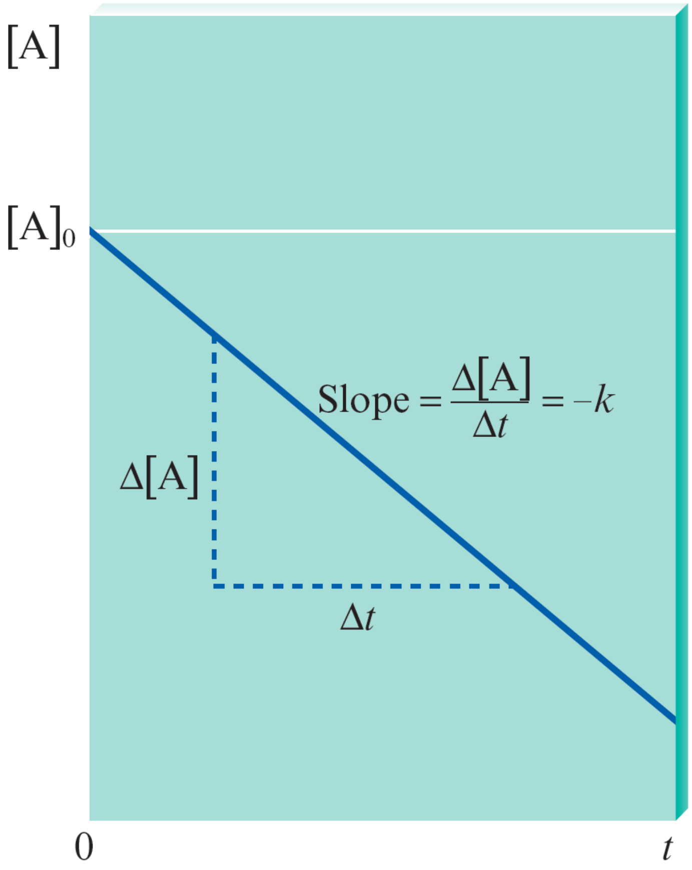
Zero-Order Rate Laws

- Rate law for a **zero-order reaction**

  $$\text{Rate} = k[\text{A}]^0 = k(1) = k$$

  - The rate is constant
- **Integrated rate law for a zero-order reaction**

  $$[\text{A}] = -kt + [\text{A}]_0 \qquad (12.7)$$



Zero-Order Rate Laws (Continued)

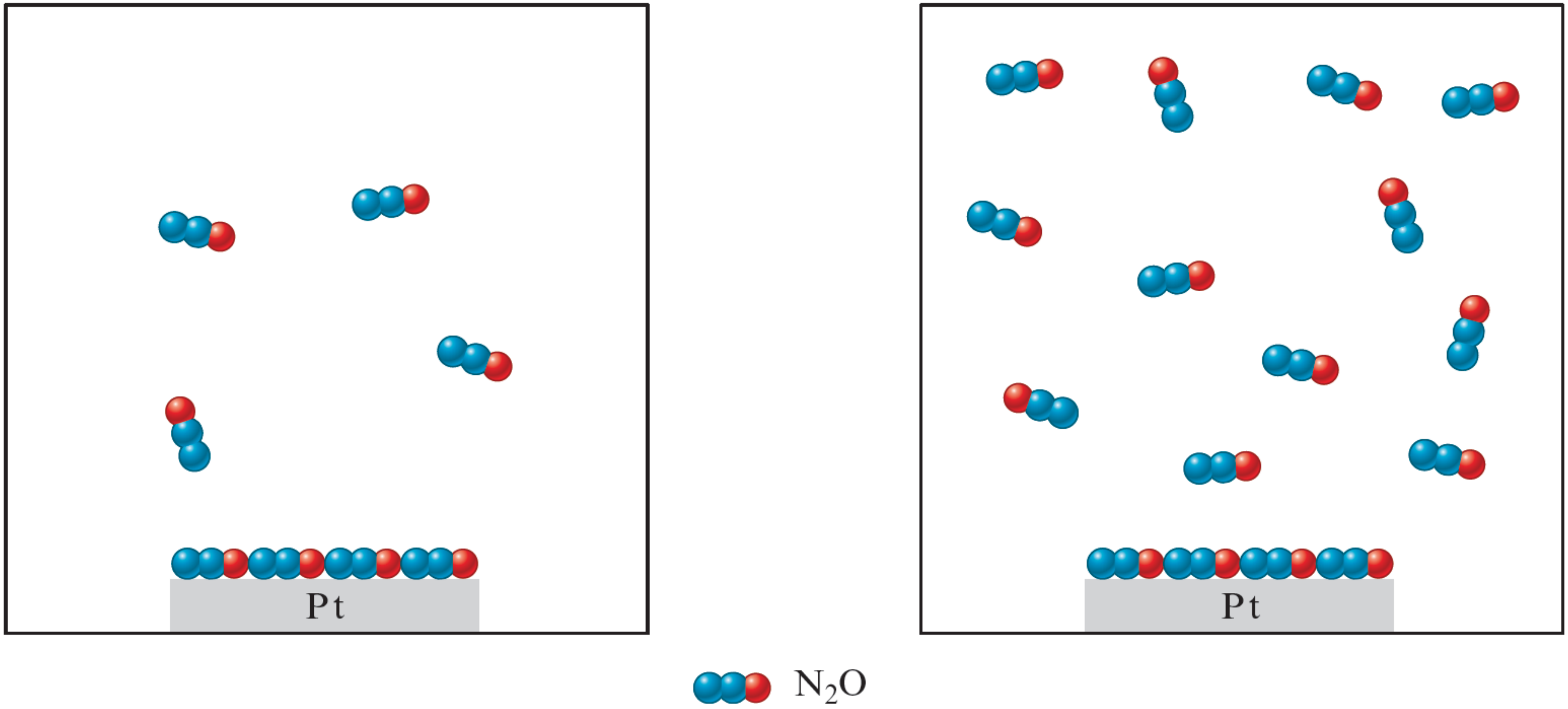
- The expression for the half-life of a zero-order reaction can be obtained from the integrated rate law
  - By definition, $[A] = [A]_0/2$ when $t = t_{1/2}$

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0 \qquad \text{or} \qquad kt_{1/2} = \frac{[A]_0}{2k}$$

  - Solving for $t_{1/2}$ gives

$$t_{1/2} = \frac{[A]_0}{2k} \qquad (12.8)$$

Figure 12.7 - The Decomposition of Nitrous Oxide on a Platinum Surface



Critical Thinking

- Consider the simple reaction aA→ products
  - You run this reaction and wish to determine its order
  - What if you made a graph of reaction rate versus time?
    - Could you use this to determine the order?
    - Sketch the three plots of rate versus time for the reaction if it is zero, first, or second order
    - Sketch these plots on the same graph, compare them, and defend your answer

Integrated Rate Laws for Reactions with More Than One Reactant

- Consider the following reaction

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$$

  - The rate law is

$$\text{Rate} = -\frac{\Delta[BrO_3^-]}{\Delta t} = k[BrO_3^-][Br^-][H^+]^2$$

  - Assume that the reaction occurs under the following conditions:
    - $[BrO_3^-]_0 = 1.0 \times 10^{-3}\ M$
    - $[Br^-]_0 = 1.0\ M$
    - $[H^+]_0 = 1.0\ M$

Integrated Rate Laws for Reactions with More than One Reactant (Continued 1)

- As the reaction proceeds, $[BrO_3^-]$ decreases significantly
  - $[Br^-]$ and $[H^+]$ remain approximately constant
  - Thus, $[Br^-] = [Br^-]_0$ and $[H^+] = [H^+]_0$
- The rate law can be rewritten as

$$\text{Rate} = k[Br^-]_0[H^+]_0^{\,2}[BrO_3^-] = k'[BrO_3^-]$$

  - Since $[Br^-]_0$ and $[H^+]_0$ are constant,

$$k' = k[Br^-]_0[H^+]_0^{\,2}$$

Integrated Rate Laws for Reactions with More than One Reactant (Continued 2)

- The rate law, rate = $k'[\mathrm{BrO_3}^-]$, is first order
    - Known as **pseudo-first-order rate law**
- Since $[\mathrm{Br}^-]_0$ and $[\mathrm{H}^+]$ are known, the value of *k* can be calculated from the equation

$$k' = k[\mathrm{Br}^-]_0[\mathrm{H}^+]_0^{\,2}$$

    - Rearranging the equation gives

$$k = \frac{k'}{[\mathrm{Br}^-]_0[\mathrm{H}^+]_0^{\,2}}$$

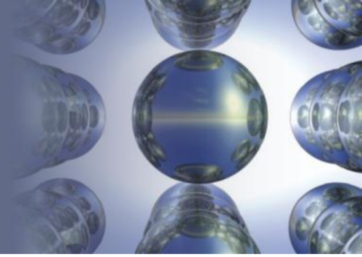


Table 12.6 - Summary of the Kinetics for Reactions of Type aA ⟶ Products That Are Zero-, First-, and Second-Order

	Order		
	Zero	**First**	**Second**
Rate law	Rate $= k$	Rate $= k[\text{A}]$	Rate $= k[\text{A}]^2$
Integrated rate law	$[\text{A}] = -kt + [\text{A}]_0$	$\ln[\text{A}] = -kt + \ln[\text{A}]_0$	$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$
Plot needed to give a straight line	$[\text{A}]$ versus t	$\ln[\text{A}]$ versus t	$\frac{1}{[\text{A}]}$ versus t
Relationship of rate constant to the slope of straight line	Slope $= -k$	Slope $= -k$	Slope $= k$
Half-Life	$t_{1/2} = \frac{[\text{A}]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[\text{A}]_0}$

Reaction Mechanism

- Most chemical reactions occur by a series of steps
- Example - The reaction between nitrogen dioxide and carbon monoxide involves the following steps:

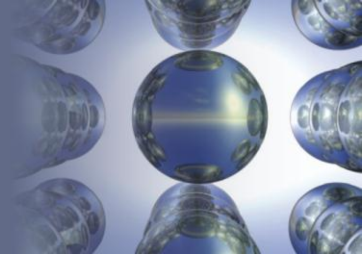
$$\mathrm{NO_2}(\mathrm{g}) + \mathrm{NO_2}(g) \xrightarrow{k_1} \mathrm{NO_3}(g) + \mathrm{NO}(g)$$

$$\mathrm{NO_3}(g) + \mathrm{CO}(g) \xrightarrow{k_2} \mathrm{NO_2}(g) + \mathrm{CO_2}(g)$$

  - Where k_1 and k_2 are the rate constants of the individual reactions

Reaction Mechanism (Continued)

- In the reaction, NO_3 is an intermediate
  - **Intermediate**: Species that is formed and consumed during the reaction but is neither a reactant nor a product
- Each of the reactions is called an elementary step
  - **Elementary step**: A reaction whose rate law can be written from its molecularity



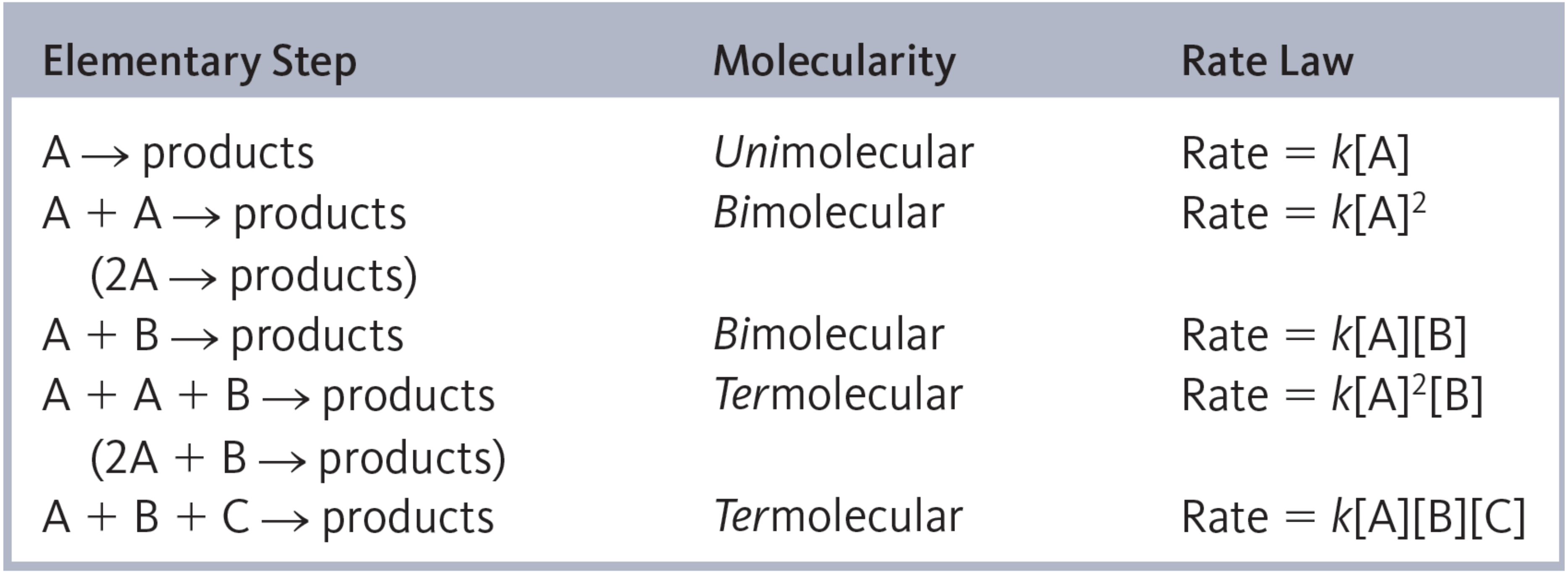
Molecularity

- Number of species that must collide to produce the reaction represented by an elementary step
    - **Unimolecular**: Reaction that involves one molecule
    - **Bimolecular**: Reaction that involves the collision of two species
    - **Termolecular**: Reaction that involves the collision of three species

Requirements of a Reaction Mechanism

- The sum of the elementary steps must give the overall balanced equation for the reaction
- The mechanism must agree with the experimentally determined rate law

Table 12.7 - Examples of Elementary Steps



Elementary Step	Molecularity	Rate Law
A → products	*Uni*molecular	Rate = $k[A]$
A + A → products (2A → products)	*Bi*molecular	Rate = $k[A]^2$
A + B → products	*Bi*molecular	Rate = $k[A][B]$
A + A + B → products (2A + B → products)	*Ter*molecular	Rate = $k[A]^2[B]$
A + B + C → products	*Ter*molecular	Rate = $k[A][B][C]$

Example 12.6 - Reaction Mechanisms

- The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

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

- Experimentally determined rate law is

$$\text{Rate} = k[NO_2][F_2]$$

Example 12.6 - Reaction Mechanisms (Continued)

- Suggested mechanism for this reaction is

$$\mathrm{NO_2 + F_2 \xrightarrow{k_1} NO_2F + F} \quad \text{(slow)}$$

$$\mathrm{F + NO_2 \xrightarrow{k_2} NO_2F} \quad \text{(fast)}$$

  - Is this an acceptable mechanism?
    - Does it satisfy the two requirements?

Example 12.6 - Solution

- First requirement for an acceptable mechanism
  - The sum of the steps should give the balanced equation

$$NO_2 + F_2 \longrightarrow NO_2F + F$$

$$F + NO_2 \longrightarrow NO_2F$$

$$\overline{2NO_2 + F_2 + \cancel{F} \longrightarrow 2NO_2F + \cancel{F}}$$

$$\text{Overall reaction: } 2NO_2 + F_2 \longrightarrow 2NO_2F$$

  - The first requirement is met

Example 12.6 - Solution (Continued)

- Second requirement
    - The mechanism must agree with the experimentally determined rate law
        - The overall reaction rate must be that of the first step
        - The first step is bimolecular, so the rate law is

$$\text{Rate} = k_1[NO_2][F_2]$$

        - The second requirement is met
- The mechanism is acceptable as both requirements are satisfied

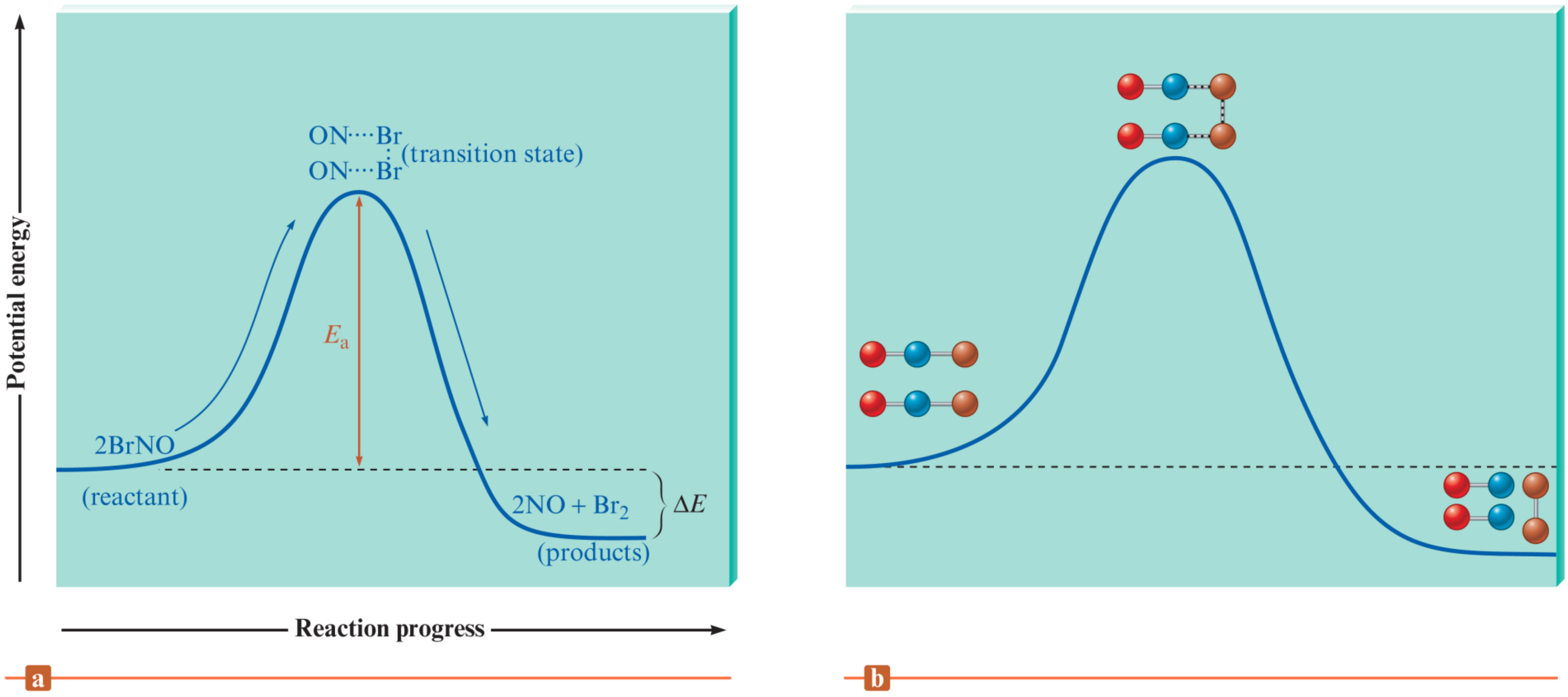
Collision Model

- States that a reaction requires the collision of molecules
  - **Activation energy**: Threshold energy that must be overcome to produce a chemical reaction

$$2\mathrm{BrNO}(g) \longrightarrow 2\mathrm{NO}(g) + \mathrm{Br}_2(g)$$

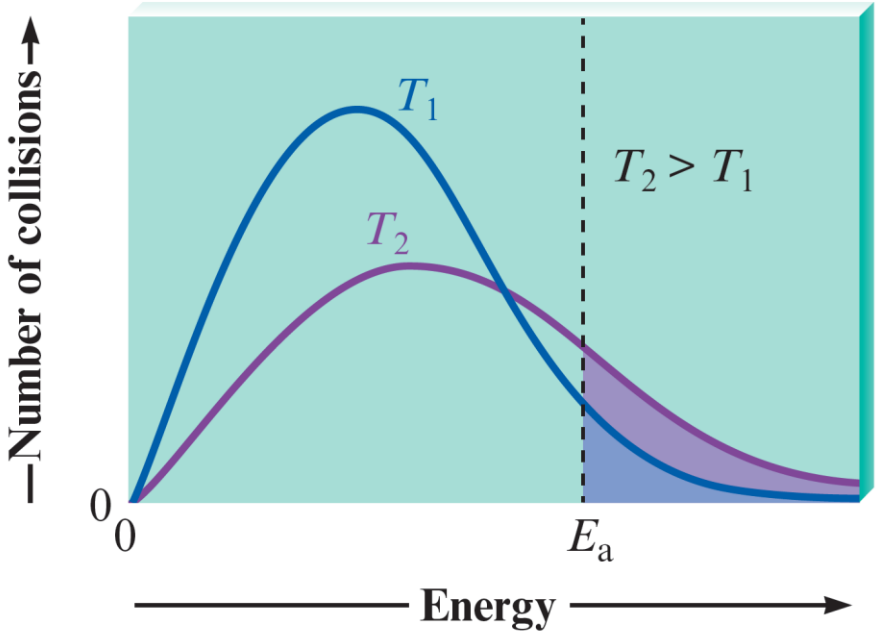
  - The energy comes from the kinetic energies possessed by the reacting molecules before the collision
    - Kinetic energy is changed into potential energy as the molecules are distorted during a collision to break bonds and rearrange the atoms into product molecules

Figure 12.10 - Activated Complex/Transition State



Relation between Effective Collisions and Temperature

- The fraction of effective collisions increases exponentially with temperature

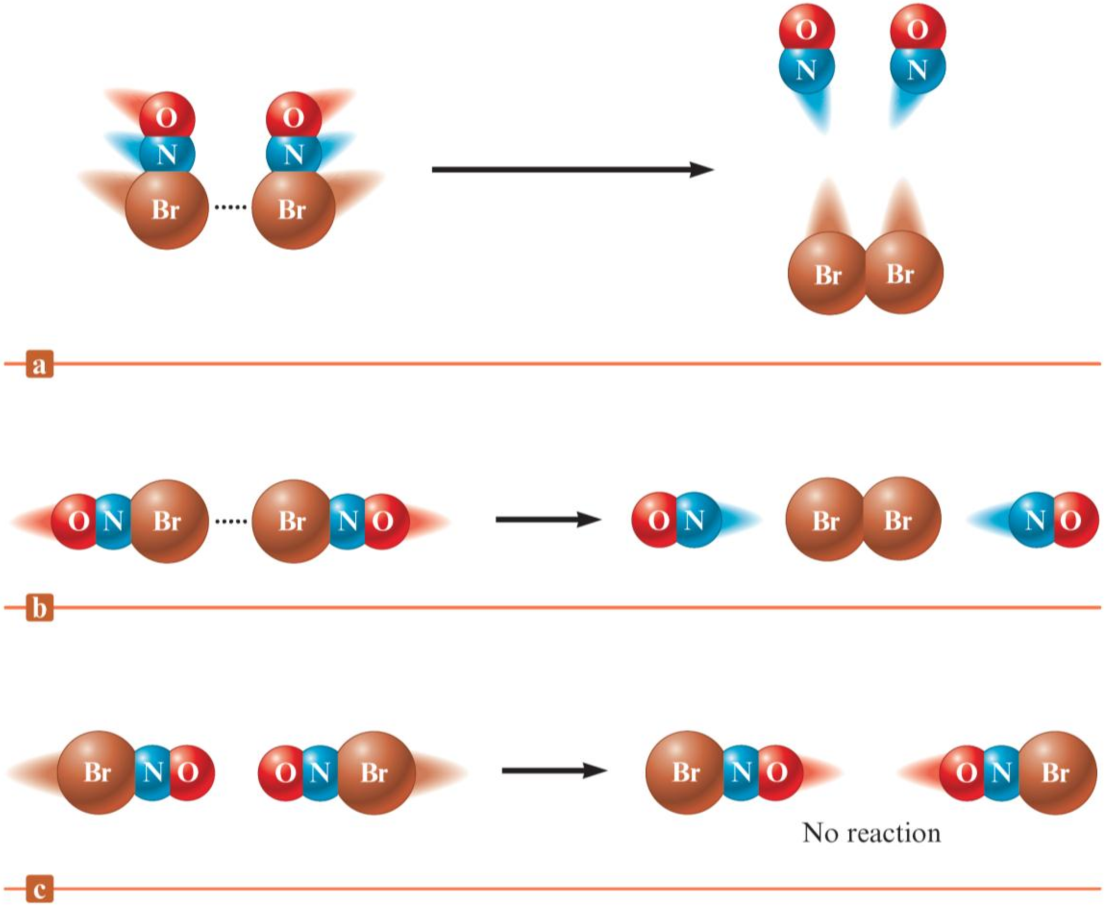


Relation between Activation Energy and Number of Collisions

$$\text{Number of collisions with the activation energy} = (\text{total number of collisions})e^{-E_a/RT}$$

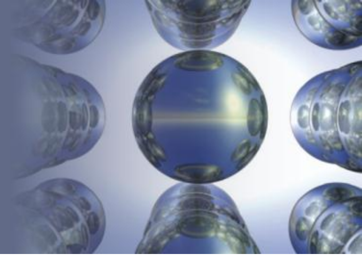
- E_a - Activation energy
- R - Universal gas constant
- T - Temperature in Kelvin
- $e^{-E_a/RT}$ - Fraction of collisions with energy E_a or greater at temperature T

Figure 12.12 - Molecular Orientations



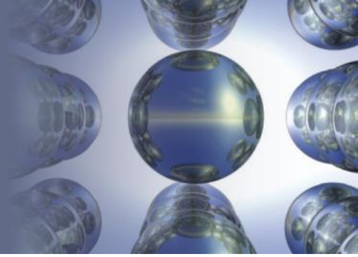
Requirements to be Satisfied for Reactants to Collide Successfully

- The collision energy must equal or exceed the activation energy
- The relative orientation of the reactants must allow the formation of any new bonds necessary to produce products



Rate Constant in Molecular Collision

- Represented as $k = zpe^{-E_a/RT}$
  - z - Collision frequency
  - p - **Steric factor**
    - Always lesser than 1
    - Reflects the fraction of collisions with effective orientations
  - $e^{-E_a/RT}$ - Fraction of collisions with sufficient energy to produce a reaction



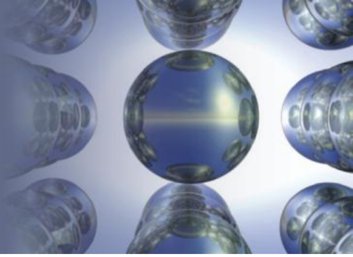
Arrhenius Equation

- A modification of the rate constant equation for collision of molecules

$$k = Ae^{-E_a/RT} \qquad (12.9)$$

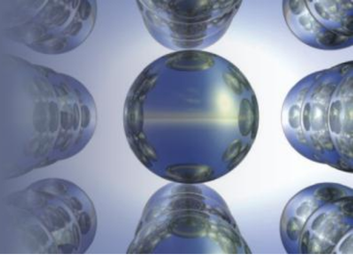
  - A - **Frequency factor** for the reaction
  - Taking the natural logarithm of each side gives

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \qquad (12.10)$$



Arrhenius Equation (Continued)

- Equation (12.10) is a linear equation of the type $y = mx + b$
  - $y = \ln(k)$
  - $m = -E_a/R$ = slope
  - $x = 1/T$
  - $b = \ln(A)$ = intercept



Critical Thinking

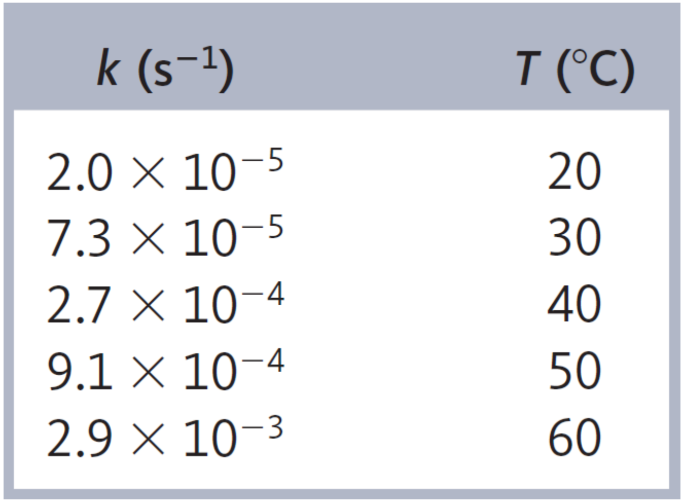
- There are many conditions that need to be met to result in a chemical reaction between molecules
  - What if all collisions between molecules resulted in a chemical reaction?
    - How would life be different?

Interactive Example 12.7 - Determining Activation Energy I

- The following reaction was studied at several temperatures

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

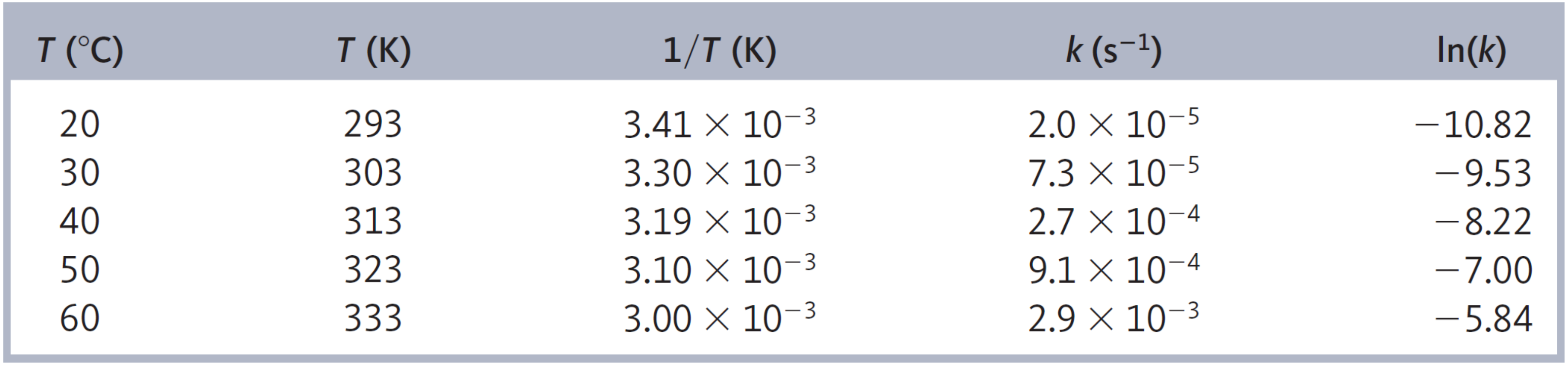
  - Values of *k* were obtained
  - Calculate the value of E_a for this reaction



k (s^{-1})	T (°C)
2.0×10^{-5}	20
7.3×10^{-5}	30
2.7×10^{-4}	40
9.1×10^{-4}	50
2.9×10^{-3}	60

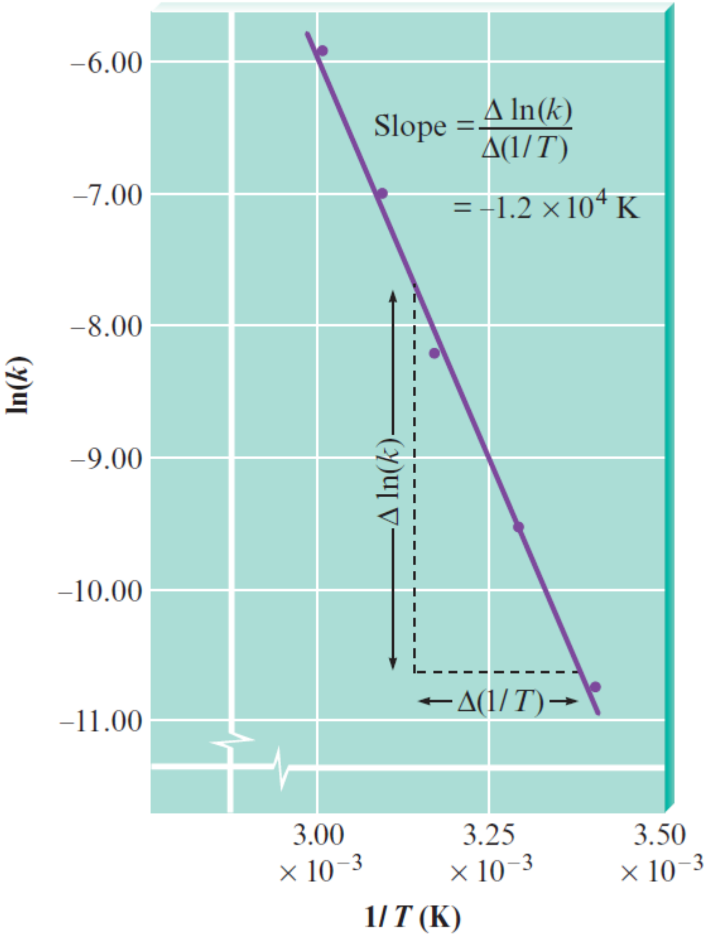
Interactive Example 12.7 - Solution

- Calculate the values of ln(k) and 1/T and construct a plot



T (°C)	T (K)	1/T (K)	k (s^{-1})	ln(k)
20	293	3.41×10^{-3}	2.0×10^{-5}	−10.82
30	303	3.30×10^{-3}	7.3×10^{-5}	−9.53
40	313	3.19×10^{-3}	2.7×10^{-4}	−8.22
50	323	3.10×10^{-3}	9.1×10^{-4}	−7.00
60	333	3.00×10^{-3}	2.9×10^{-3}	−5.84

Interactive Example 12.7 - Solution (Continued 1)



Interactive Example 12.7 - Solution (Continued 2)

- Based on the plot

$$\text{Slope} = \frac{\Delta \ln(k)}{\Delta\left(\frac{1}{T}\right)} = -1.2 \times 10^{4}\ \text{K}$$

- Determine the value of E_a by solving the following equation

$$\text{Slope} = \frac{-E_a}{R}$$

Interactive Example 12.7 - Solution (Continued 3)

- The value of the activation energy is

$$E_a = –R(\text{slope}) = –(8.3145\ \text{J/K} \cdot \text{mol})(–1.2 \times 10^4\ \text{K})$$

$$= 1.0 \times 10^5\ \text{J/mol}$$

Alternative Method to Determine E_a

- At temperature T_1, where the rate constant is k_1

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$$

- At temperature T_2, where the rate constant is k_2

$$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

Alternative Method to Determine E_a (Continued)

- Subtracting the first equation from the second gives

$$\ln(k_2) - \ln(k_1) = \left[-\frac{E_a}{RT_2} + \ln(A)\right] - \left[-\frac{E_a}{RT_1} + \ln(A)\right]$$

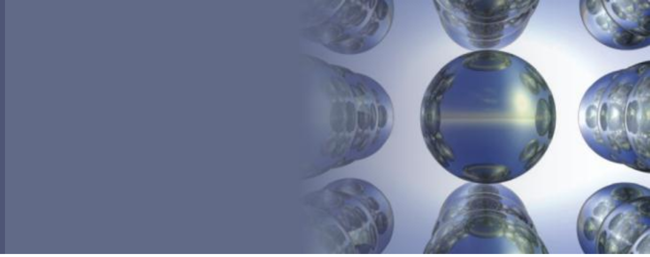
$$= -\frac{E_a}{RT_2} + -\frac{E_a}{RT_1}$$

  - And

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (12.11)$$

Critical Thinking

- Most modern refrigerators have an internal temperature of 45° F
    - What if refrigerators were set at 55° F in the factory?
        - How would this affect our lives?



Interactive Example 12.8 - Determining Activation Energy II

- The gas-phase reaction between methane and diatomic sulfur is given by the equation

$$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$$

  - At 550° C the rate constant for this reaction is 1.1 L/mol · s
  - At 625° C the rate constant is 6.4 L/mol · s
  - Using these values, calculate E_a for this reaction

Interactive Example 12.8 - Solution

- Information available

k (L/mol · s)	T (°C)	T (K)
$1.1 = k_1$	550	$823 = T_1$
$6.4 = k_2$	625	$898 = T_2$

Interactive Example 12.8 - Solution (Continued)

- Substitute the values into Equation (12.11)

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145\ \mathrm{J/K\cdot mol}}\left(\frac{1}{823\ \mathrm{K}} - \frac{1}{898\ \mathrm{K}}\right)$$

Solving for E_a gives

$$E_a = \frac{(8.3145\ \mathrm{J/K\cdot mol})\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823\ \mathrm{K}} - \frac{1}{898\ \mathrm{K}}\right)}$$

$$= 1.4\times10^5\ \mathrm{J/mol}$$

Catalyst

- A substance that speeds up a reaction without being consumed itself
- Provides a new pathway with a lower activation energy for the reaction

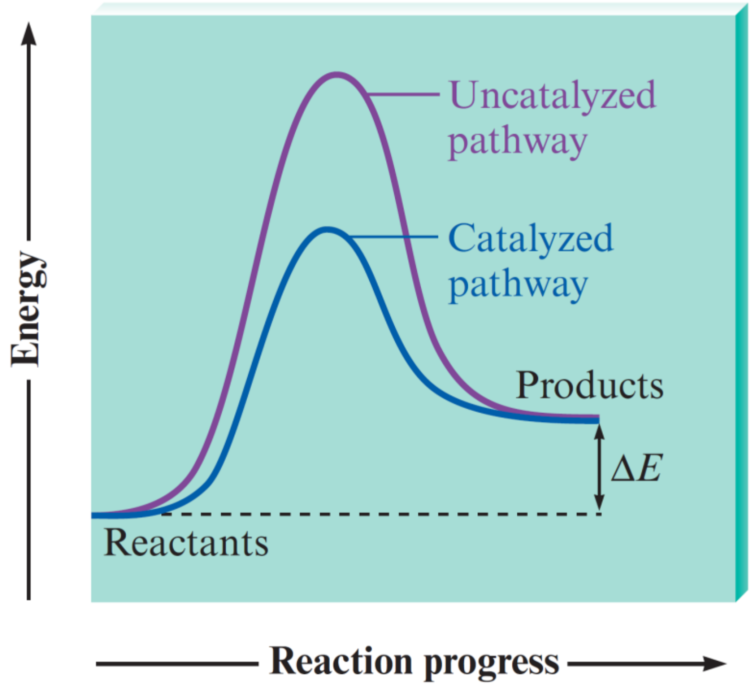
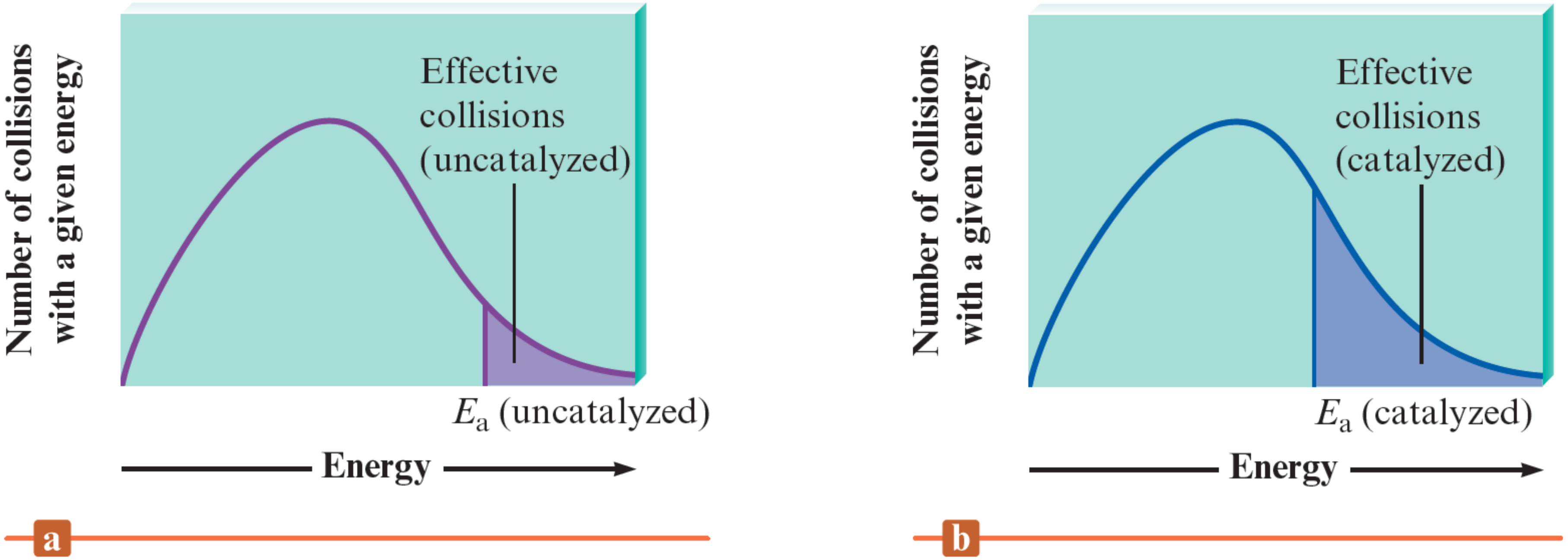
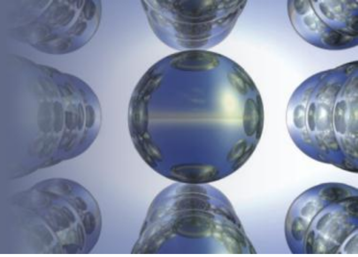


Figure 12.14 - Effect of a Catalyst on the Number of Reaction-Producing Collisions

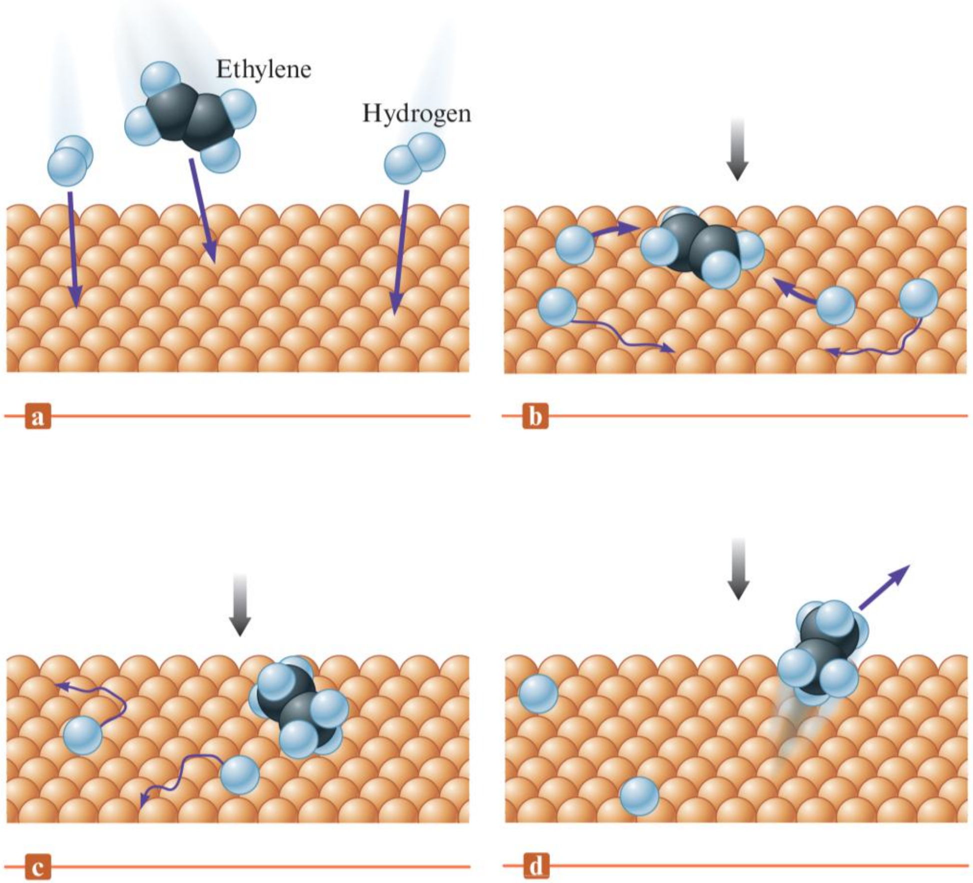


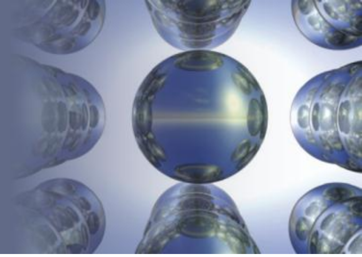


Heterogeneous Catalysis

- Mostly involves gaseous reactants being adsorbed on the surface of a solid catalyst
  - **Adsorption**: Collection of one substance on the surface of another substance

Figure 12.15 - Heterogeneous Catalysis of the Hydrogenation of Ethylene

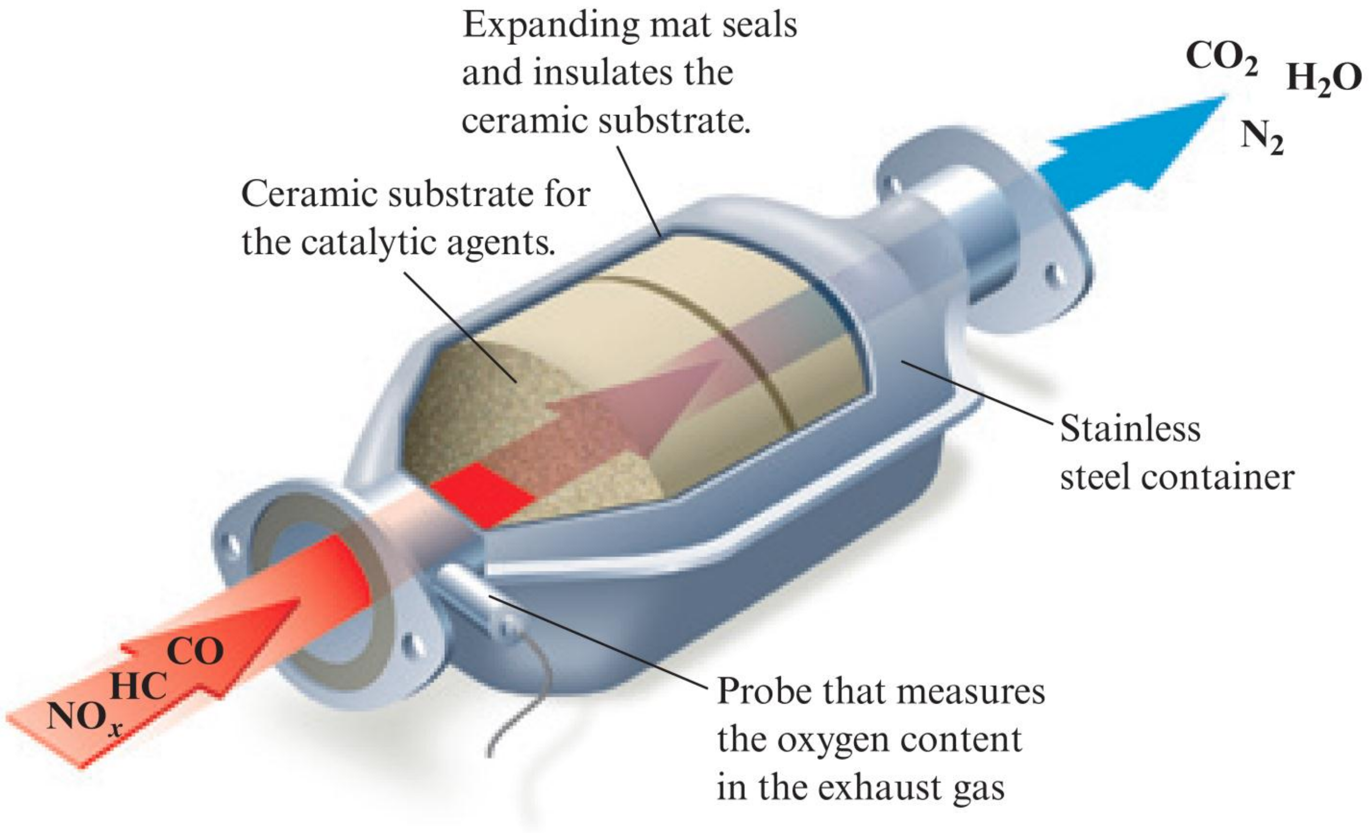




Oxidation of Gaseous Sulfur Dioxide to Gaseous Sulfur Trioxide

- Dust particles and water droplets catalyze the reaction between SO_2 and O_2 in the air
- Negative aspects
  - Toxic air pollutants are formed
  - Acid rain is produced
- Positive aspects
  - Used in the manufacture of sulfuric acid
  - Utilized in the catalytic converters in automobile exhaust systems

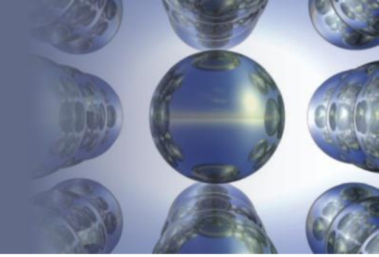
Figure 12.16 - Use of Heterogeneous Catalysis in Exhaust Systems



Homogeneous Catalysis

- Exists in the same phase as the reacting molecules
- Consider the catalytic behavior of nitric oxide toward ozone
    - NO catalyzes ozone production in the troposphere
    - In the lower atmosphere, NO is produced in any high-temperature combustion process in the presence of N_2

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$



Homogeneous Catalysis (Continued 1)

- Significant amounts of NO escape into the atmosphere to react with O_2

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

- NO_2 absorbs light and decomposes as follows

$$2NO_2(g) \xrightarrow{\text{Light}} NO(g) + O_2(g)$$

- The oxygen atoms are very reactive and can combine to form ozone

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

- Ozone is a powerful oxidizing agent that can react with other air pollutants to form toxic substances

Homogeneous Catalysis (Continued 2)

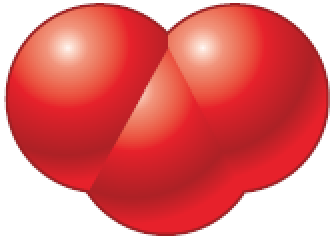
- Summarizing the reactions

$$\mathrm{NO}(g) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{NO}_2(\mathrm{g})$$

$$\mathrm{NO}_2(g) \xrightarrow{\text{Light}} \mathrm{NO}(g) + \mathrm{O}(g)$$

$$\underline{\mathrm{O}_2(g) + \mathrm{O}(g) \longrightarrow \mathrm{O}_3\ (g)}$$

$$\frac{3}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{O}_3(g)$$



Ozone

Homogeneous Catalysis (Continued 3)

- In the upper atmosphere, the presence of nitric oxide leads to the depletion of ozone

$$\begin{array}{l} NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \\ \underline{O(g) + NO_2(g) \longrightarrow NO(g) + O_2(g)} \\ O(g) + O_3(g) \longrightarrow 2O_2(g) \end{array}$$

  - Depletion of the ozone layer increases the earth's exposure to ultraviolet radiation from the sun

Freons

- Group of stable, noncorrosive compounds that cause ozone layer depletion
  - Formerly used as refrigerants and as propellants in aerosol cans
  - Freon-12 (CCl_2F_2) migrates into the upper atmosphere and decomposes in the presence of high-energy light

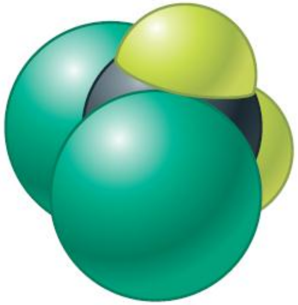
$$CCl_2F_2(g) \xrightarrow{\text{Light}} CClF_2(g) + Cl(g)$$

Freons (Continued)

- Chlorine atoms released during the decomposition of Freons catalyze the decomposition of ozone

$$\begin{array}{l} \mathrm{Cl}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{ClO}(g) + \mathrm{O_2}(g) \\ \underline{\mathrm{O}(g) + \mathrm{ClO}(g) \longrightarrow \mathrm{Cl}(g) + \mathrm{O_2}(\mathrm{g})} \\ \mathrm{O}(g) + \mathrm{O_3}(g) \longrightarrow 2\mathrm{O_2}(g) \end{array}$$

- Banned by international agreement due to environmental concerns
  - Substitute compounds are now being used



Freon-12