John E. McMurry • Robert C. Fay

CHEMISTRY

Fifth Edition

Chapter 12

Chemical Kinetics

Lecture Notes

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Reaction Rates

Chemical Kinetics: The area of chemistry concerned with reaction rates and the sequence of steps by which reactions occur.

Reaction Rate: Either the *increase* in the concentration of a product per unit time or the *decrease* in the concentration of a reactant per unit time.

Reaction Rates

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

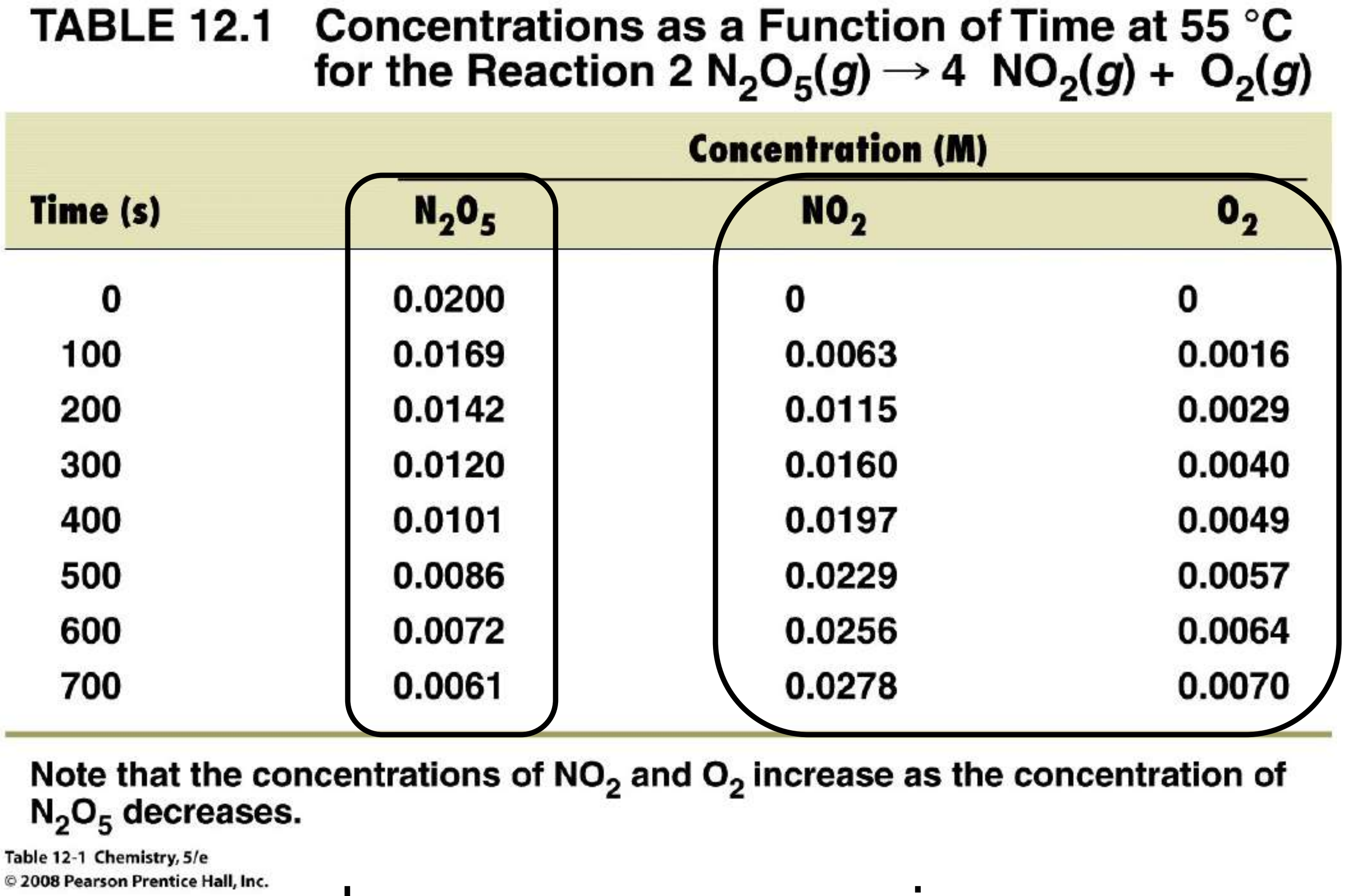


TABLE 12.1 Concentrations as a Function of Time at 55 °C for the Reaction $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

	Concentration (M)		
Time (s)	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

Note that the concentrations of NO_2 and O_2 increase as the concentration of N_2O_5 decreases.

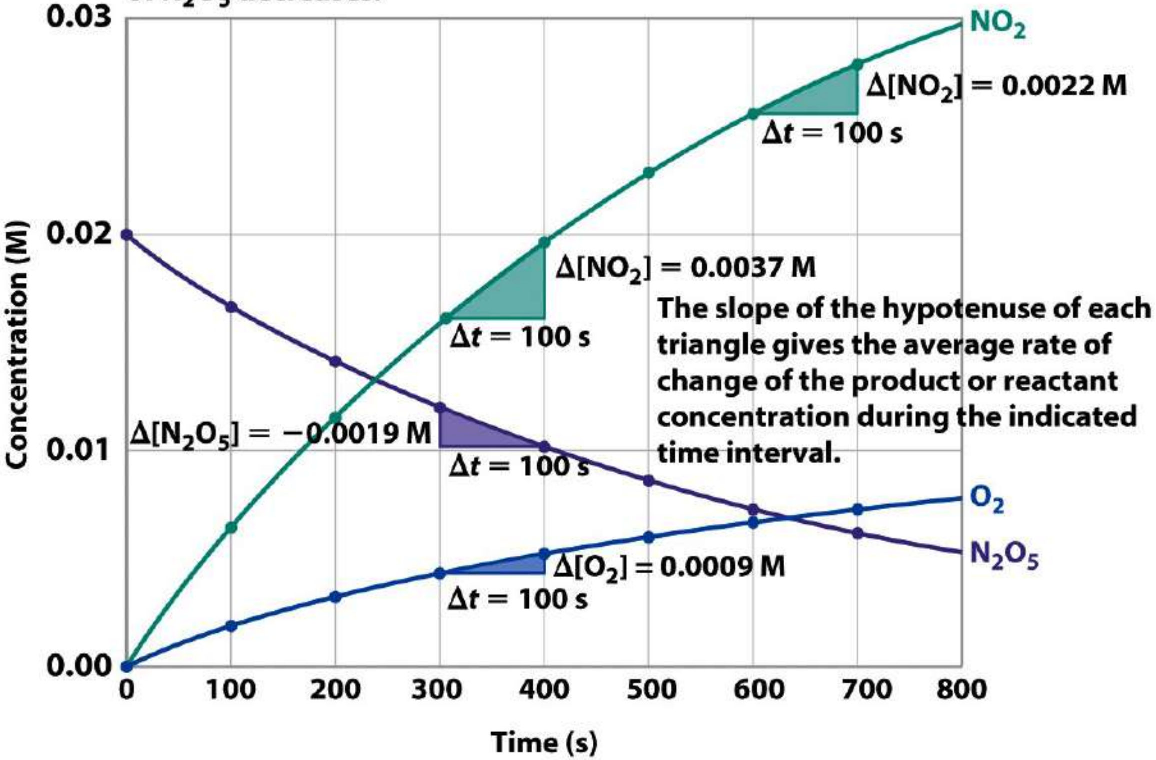
Table 12-1 Chemistry, 5/e

decrease increase

Reaction Rates

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

The concentrations of O_2 and NO_2 increase as the concentration of N_2O_5 decreases.



The slope of the hypotenuse of each triangle gives the average rate of change of the product or reactant concentration during the indicated time interval.

The rate of formation of O_2 is one-fourth the rate of formation of NO_2 and one half the rate of decomposition of N_2O_5.

Figure 12-1 Chemistry, 5/e

Reaction Rates

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

Rate of decomposition of N_2O_5:

$$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{-(0.0101\text{ M} - 0.0120\text{ M})}{(400\text{ s} - 300\text{ s})}$$

$$= 1.9 \times 10^{-5}\,\frac{\text{M}}{\text{s}}$$

Reaction Rates

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

General rate of reaction:

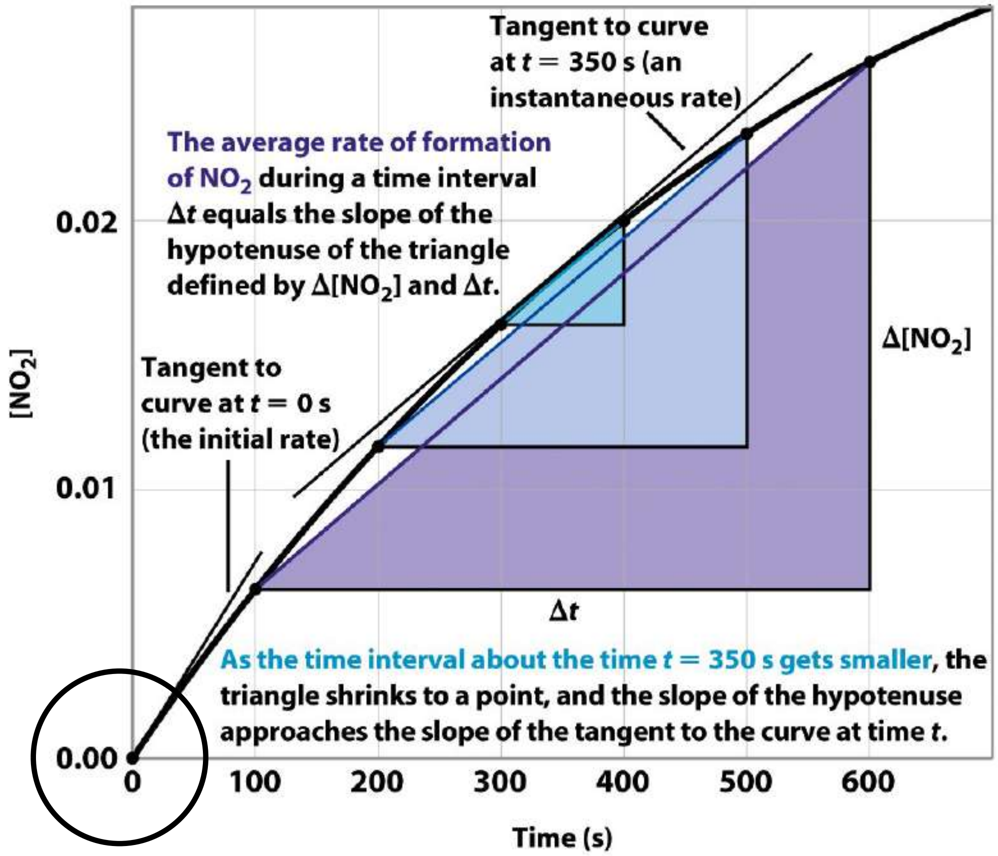
$$\text{rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow d\,\mathrm{D} + e\,\mathrm{E}$$

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

Reaction Rates

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


Tangent to curve at $t = 350$ s (an instantaneous rate)

The average rate of formation of NO_2 during a time interval Δt equals the slope of the hypotenuse of the triangle defined by $\Delta[NO_2]$ and Δt.

Tangent to curve at $t = 0$ s (the initial rate)

As the time interval about the time $t = 350$ s gets smaller, the triangle shrinks to a point, and the slope of the hypotenuse approaches the slope of the tangent to the curve at time t.

The slope of the tangent at time t is defined as the instantaneous rate at that particular time. The initial rate is the slope of the tangent to the curve at $t = 0$.

Figure 12-2 Chemistry 5/e

Rate Laws and Reaction Order

Rate Law: An equation that shows the dependence of the reaction rate on the concentration of each reactant.

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

$$\text{rate} \propto [A]^m[B]^n$$

$$\text{rate} = k[A]^m[B]^n$$

k is the **rate constant**

Rate Laws and Reaction Order

The values of the exponents in the rate law **must be determined by experiment**; they cannot be deduced from the stoichiometry of the reaction.

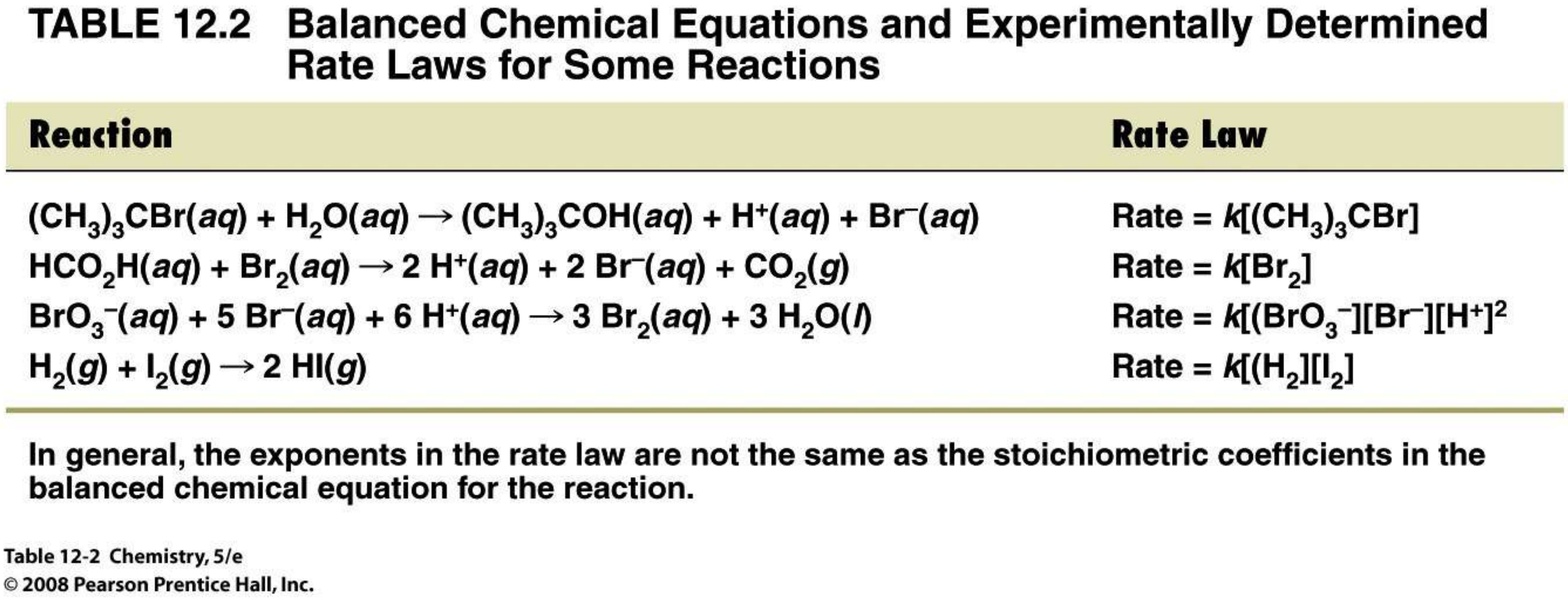


TABLE 12.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions

Reaction	Rate Law
$(CH_3)_3CBr(aq) + H_2O(aq) \rightarrow (CH_3)_3COH(aq) + H^+(aq) + Br^-(aq)$	Rate = $k[(CH_3)_3CBr]$
$HCO_2H(aq) + Br_2(aq) \rightarrow 2\ H^+(aq) + 2\ Br^-(aq) + CO_2(g)$	Rate = $k[Br_2]$
$BrO_3^-(aq) + 5\ Br^-(aq) + 6\ H^+(aq) \rightarrow 3\ Br_2(aq) + 3\ H_2O(l)$	Rate = $k[(BrO_3^-][Br^-][H^+]^2$
$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$	Rate = $k[(H_2][I_2]$

In general, the exponents in the rate law are not the same as the stoichiometric coefficients in the balanced chemical equation for the reaction.

Table 12-2 Chemistry, 5/e

Experimental Determination of a Rate Law

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

$$\text{rate} = k[NO]^m[O_2]^n$$

Compare the initial rates to the changes in initial concentrations.

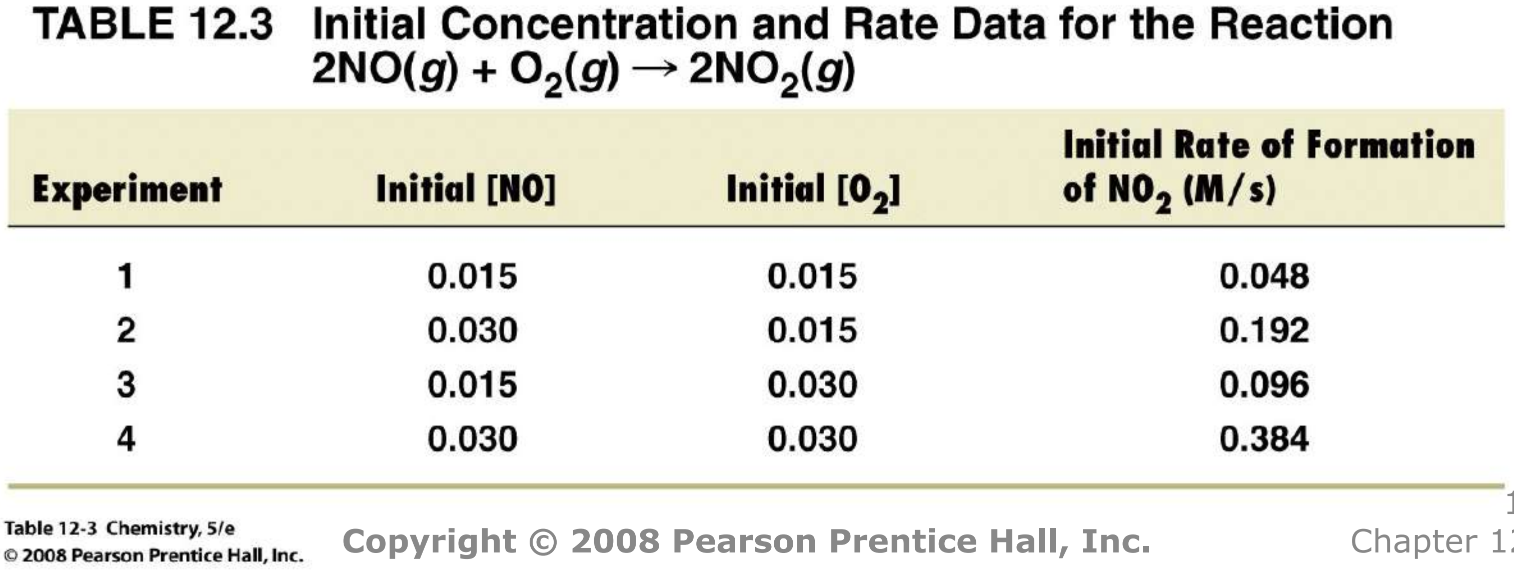


TABLE 12.3 Initial Concentration and Rate Data for the Reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Experiment	Initial [NO]	Initial [O_2]	Initial Rate of Formation of NO_2 (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

Table 12-3 Chemistry, 5/e
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Experimental Determination of a Rate Law

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

$$\text{rate} = k[NO]^2\,[O_2]^n$$

The concentration of NO **doubles**, the concentration of O_2 remains constant, and the rate **quadruples**.

$$2^m = 4 \qquad m = 2$$

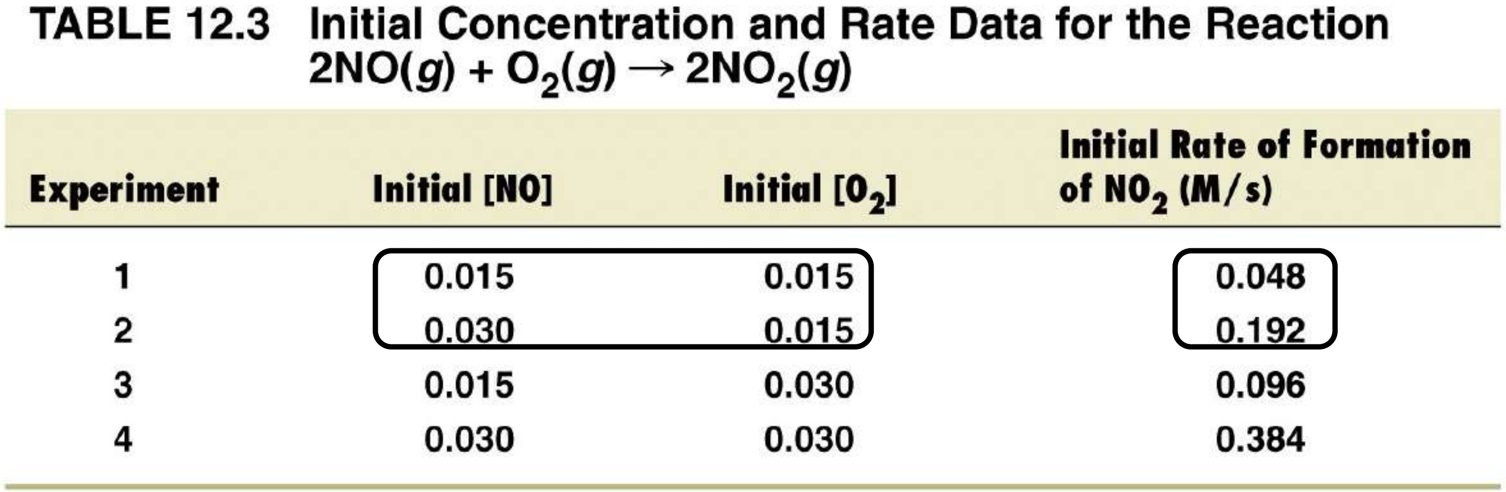

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Table 12-3 Chemistry, 5/e
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Experimental Determination of a Rate Law

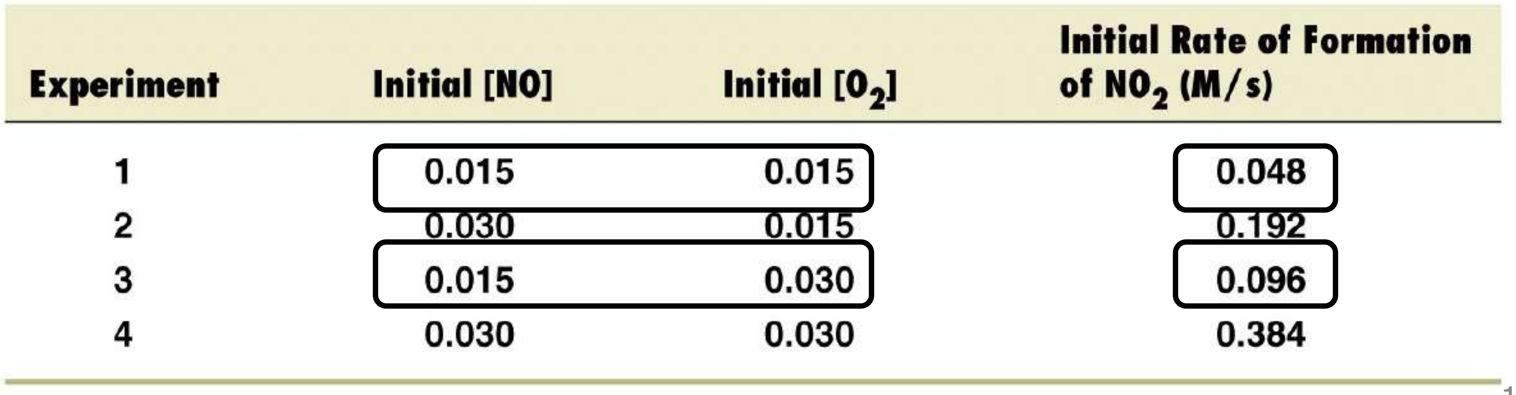
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$\text{rate} = k[NO]^2 [O_2]$$

The concentration of O_2 **doubles**, the concentration of NO remains constant, and the rate **doubles**.

$$2^n = 2 \qquad n = 1$$

TABLE 12.3 Initial Concentration and Rate Data for the Reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$



Experiment	Initial [NO]	Initial $[O_2]$	Initial Rate of Formation of NO_2 (M/s)
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Table 12-3 Chemistry, 5/e

Experimental Determination of a Rate Law

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

$$\text{rate} = k[NO]^2\,[O_2]$$

Reaction Order With Respect to a Reactant

- NO:second-order
- O_2:first-order

Overall Reaction Order

- 2 + 1 = 3 (third-order)

Experimental Determination of a Rate Law

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

$$\text{rate} = k[NO]^2\,[O_2]$$

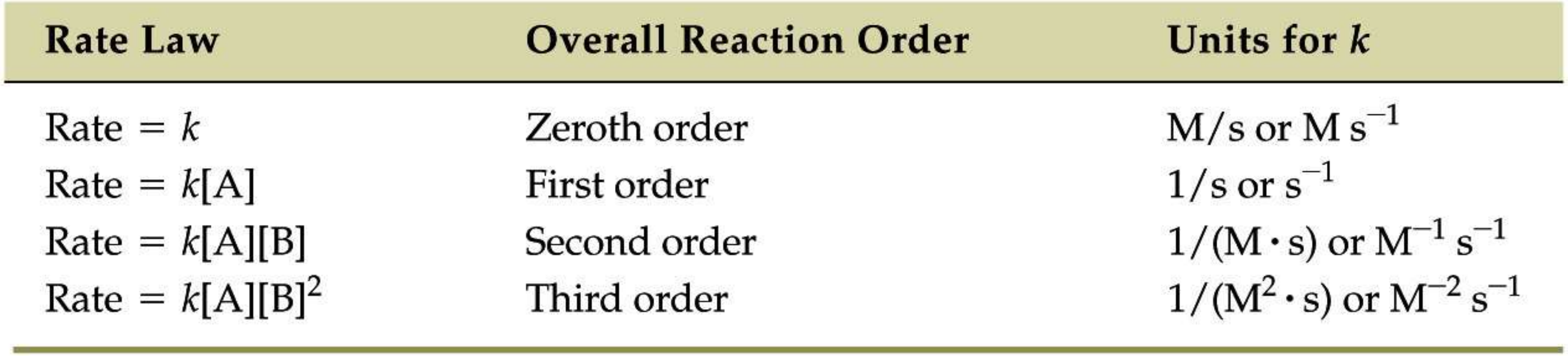
Units for this third-order reaction:

$$k = \frac{\text{rate}}{[NO]^2\,[O_2]} = \frac{\frac{M}{s}}{(M^2)\,(M)} = \frac{1}{M^2\,s}$$

Experimental Determination of a Rate Law

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

$$\text{rate} = k[NO]^2[O_2]$$



Rate Law	**Overall Reaction Order**	**Units for *k***
Rate = k	Zeroth order	M/s or M s^{-1}
Rate = $k[A]$	First order	1/s or s^{-1}
Rate = $k[A][B]$	Second order	$1/(M \cdot s)$ or $M^{-1}\ s^{-1}$
Rate = $k[A][B]^2$	Third order	$1/(M^2 \cdot s)$ or $M^{-2}\ s^{-1}$

Integrated Rate Law for a First-Order Reaction

$$A \longrightarrow \text{product(s)}$$

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

Calculus can be used to derive an **integrated** rate law.

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \begin{cases} [A]_t \text{concentration of A at time } t \\ [A]_0 \text{initial concentration of A} \end{cases}$$

Using: $\ln\left(\frac{x}{y}\right) = \ln(x) - \ln(y)$

$$\boxed{\begin{array}{c} \mathbf{\ln[A]_{\mathit{t}} = -k\mathit{t} + \ln[A]_0} \\ y \quad = mx + b \end{array}}$$

Integrated Rate Law for a First-Order Reaction

$$\mathbf{ln[A]}_{\boldsymbol{t}} = -k\boldsymbol{t} + \ln[\mathrm{A}]_0$$

$$y \quad = mx + b$$

A plot of **ln[A]** versus **time** gives a straight-line fit and the **slope** will be ***-k***.

Integrated Rate Law for a First-Order Reaction

$$\mathbf{\ln[A]}_{\boldsymbol{t}} = -k\boldsymbol{t} + \ln[A]_0$$

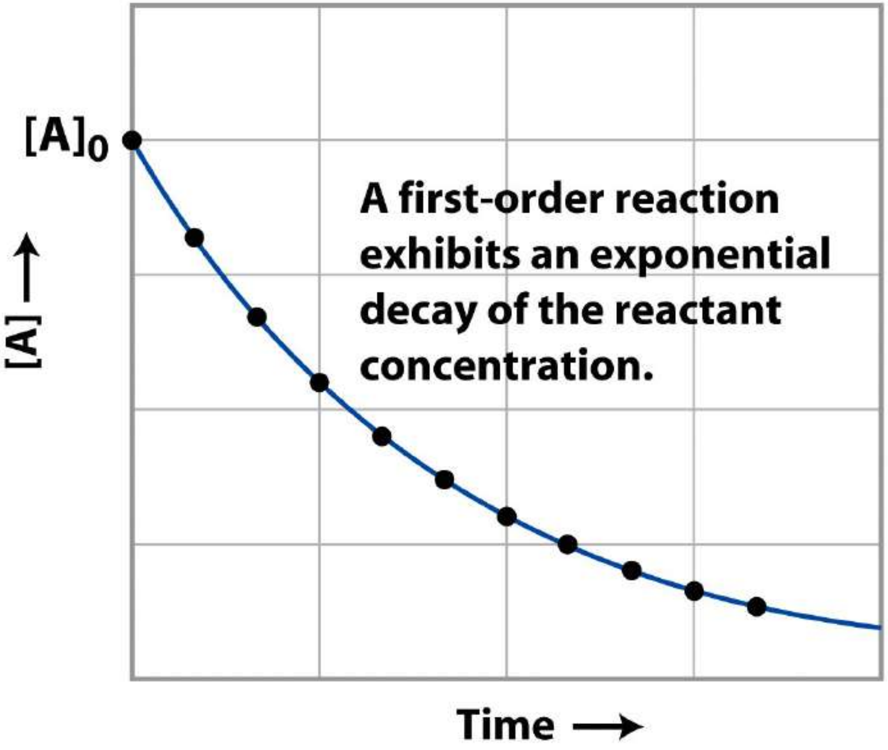


Figure 12-6a Chemistry, 5/e

This is a plot of **[A]** versus **time**.

The best-fit is a *curve* and not a *line*.

Integrated Rate Law for a First-Order Reaction

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

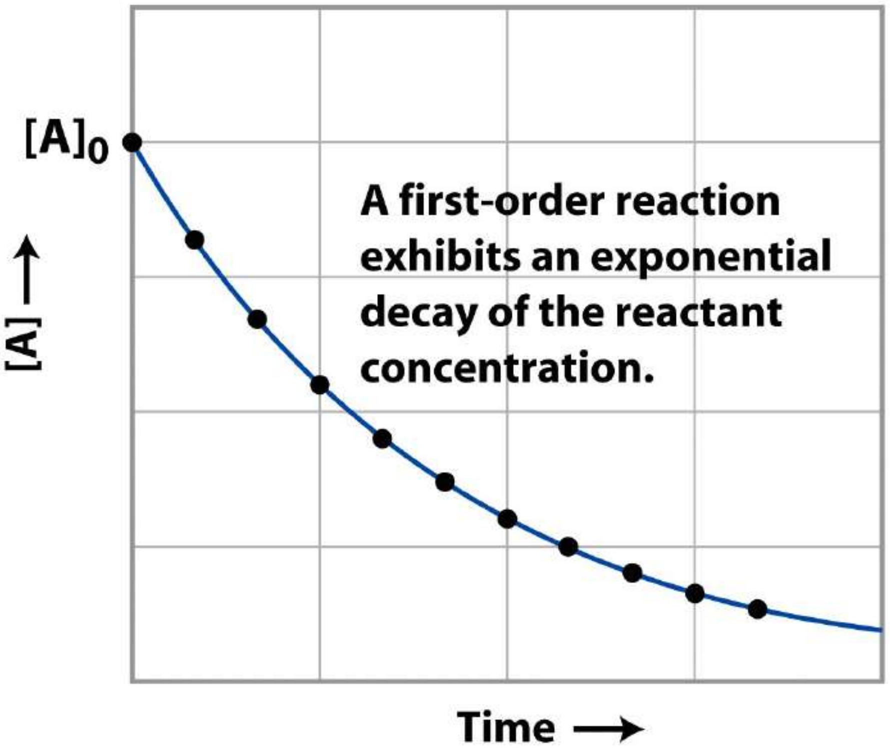


Figure 12-6a Chemistry, 5/e

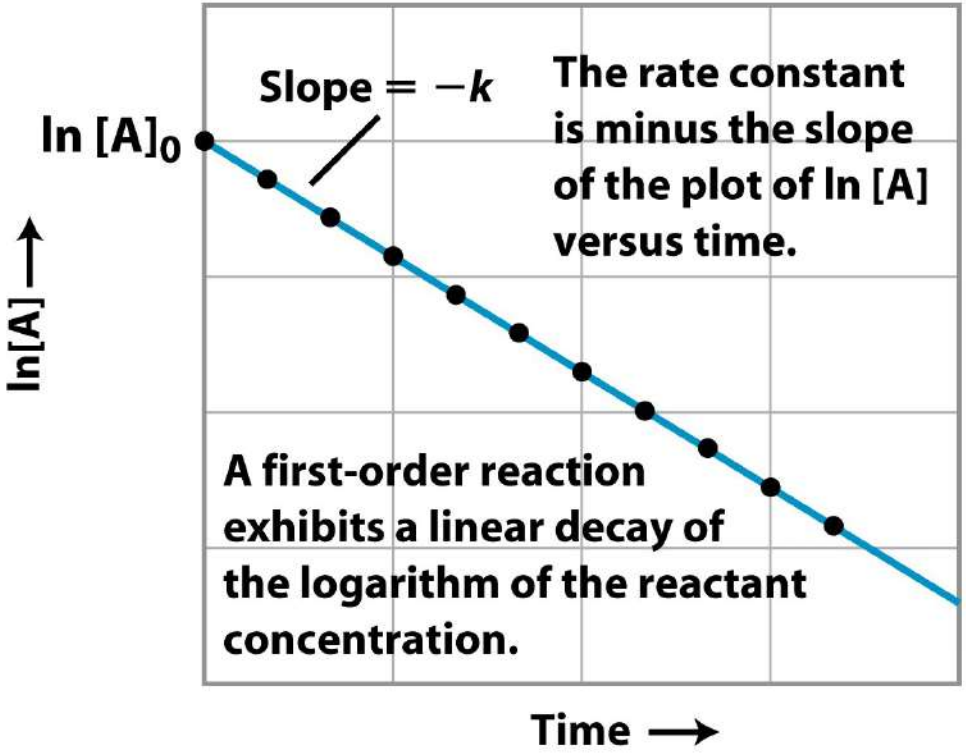
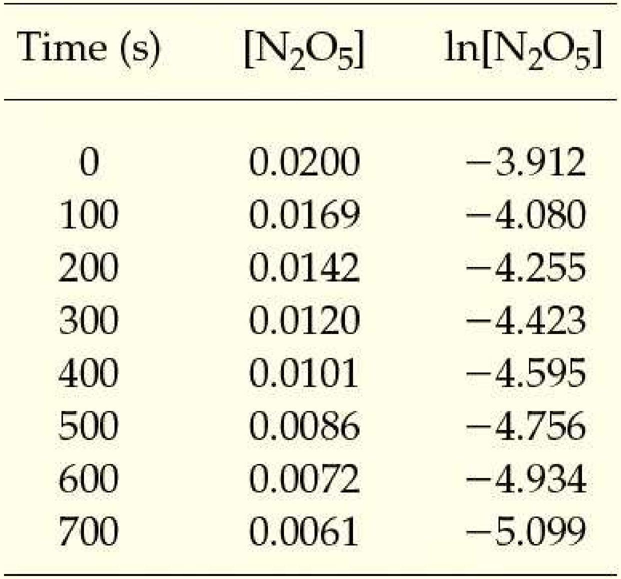


Figure 12-6b Chemistry, 5/e

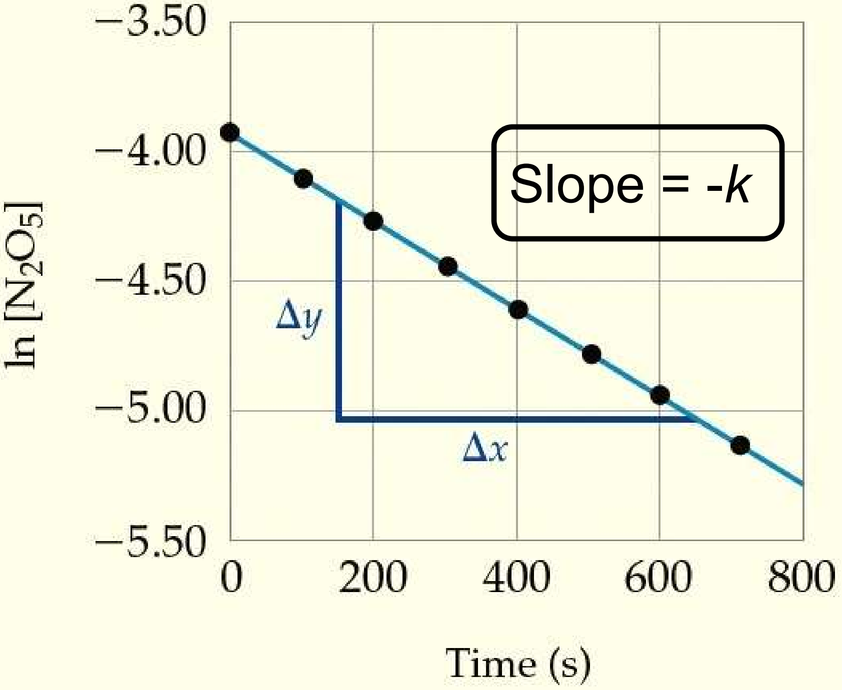
Integrated Rate Law for a First-Order Reaction

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

$$\text{rate} = k[N_2O_5]$$



Time (s)	$[N_2O_5]$	$\ln[N_2O_5]$
0	0.0200	−3.912
100	0.0169	−4.080
200	0.0142	−4.255
300	0.0120	−4.423
400	0.0101	−4.595
500	0.0086	−4.756
600	0.0072	−4.934
700	0.0061	−5.099



Slope = -*k*

Example 12-6 part 2 Chemistry, 5/e
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Integrated Rate Law for a First-Order Reaction

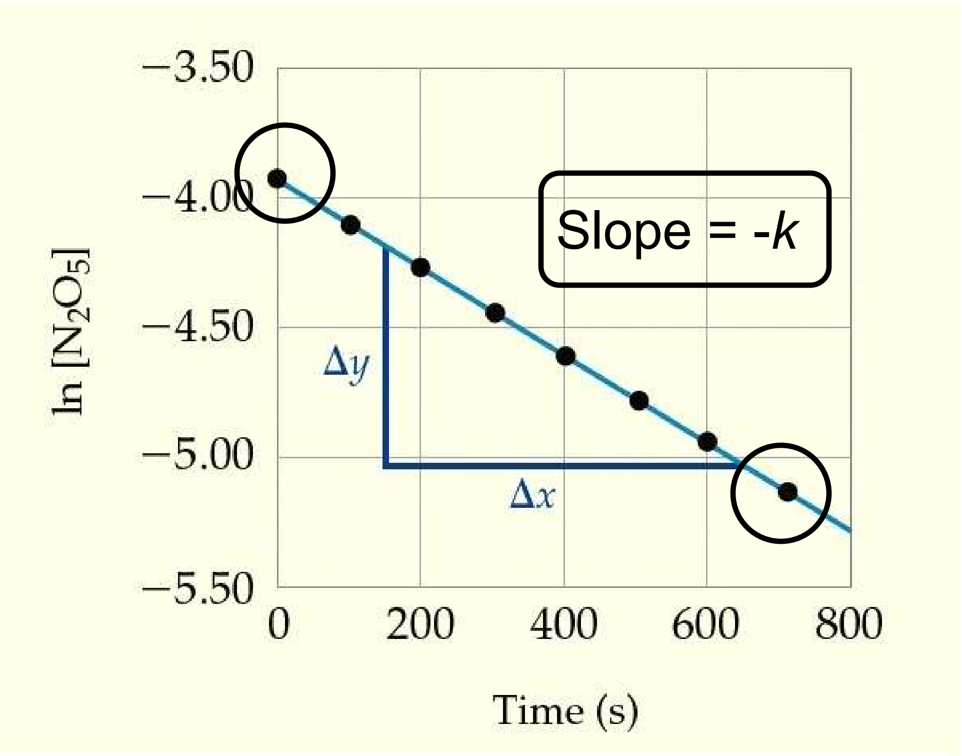
$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{rate} = k[N_2O_5]$$

Calculate the slope:

$$\frac{-5.099 - (-3.912)}{(700 - 0)\ \text{s}} = -0.0017\,\frac{1}{\text{s}}$$

$$k = 0.00170\,\frac{1}{\text{s}}$$



Example 12-6 part 2 Chemistry, 5/e
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Half-Life for a First-Order Reaction

Half-Life: The time required for the reactant concentration to drop to one-half of its initial value.

$$A \longrightarrow \text{product(s)}$$

$$\text{rate} = k[A]$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \left\{ \begin{array}{l} t = t_{1/2} \\ [A]_{t_{1/2}} = \dfrac{[A]_0}{2} \end{array} \right.$$

$$\boxed{\ln\left(\frac{1}{2}\right) = -kt_{1/2} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k}}$$

Half-Life for a First-Order Reaction

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

For a first-order reaction, the half-life is independent of the initial concentration.

Each successive half-life is an equal period of time.

Each successive half-life is an equal period of time in which the reactant concentration decreases by a factor of 2.

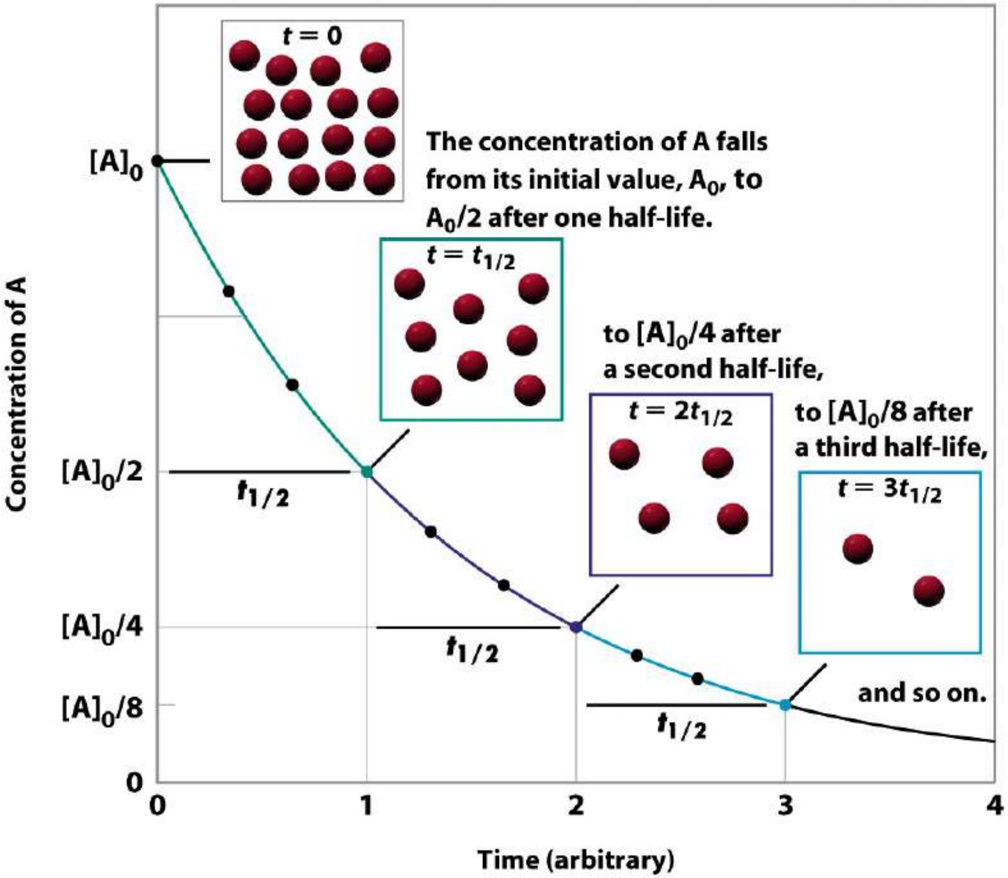


Figure 12-7 Chemistry, 5/e

Second-Order Reactions

$$A \longrightarrow \text{product(s)}$$

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

Calculus can be used to derive an **integrated** rate law.

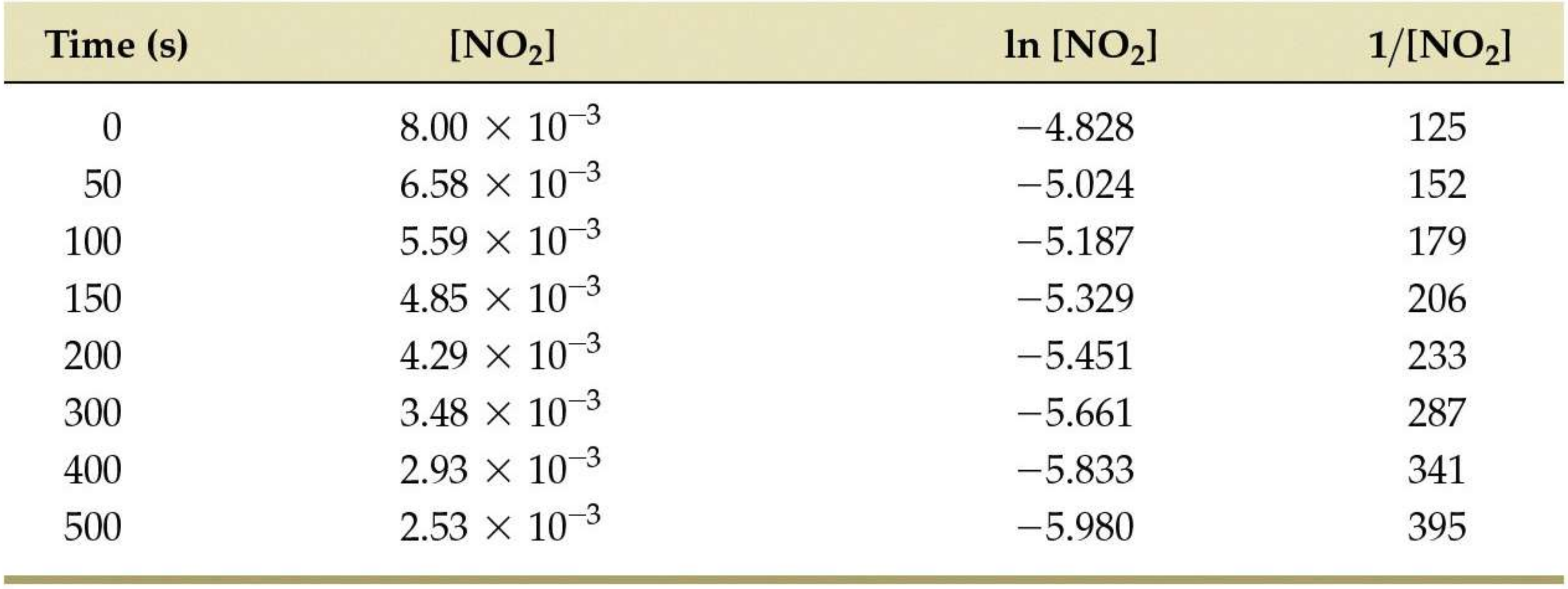
$$\boxed{\begin{array}{c} \dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0} \\ y = mx + b \end{array}}$$

$[A]_t$ concentration of A at time t

$[A]_0$ initial concentration of A

Second-Order Reactions

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



Time (s)	$[NO_2]$	$\ln [NO_2]$	$1/[NO_2]$
0	8.00×10^{-3}	−4.828	125
50	6.58×10^{-3}	−5.024	152
100	5.59×10^{-3}	−5.187	179
150	4.85×10^{-3}	−5.329	206
200	4.29×10^{-3}	−5.451	233
300	3.48×10^{-3}	−5.661	287
400	2.93×10^{-3}	−5.833	341
500	2.53×10^{-3}	−5.980	395

Example 12-8 part 2 Chemistry, 5/e
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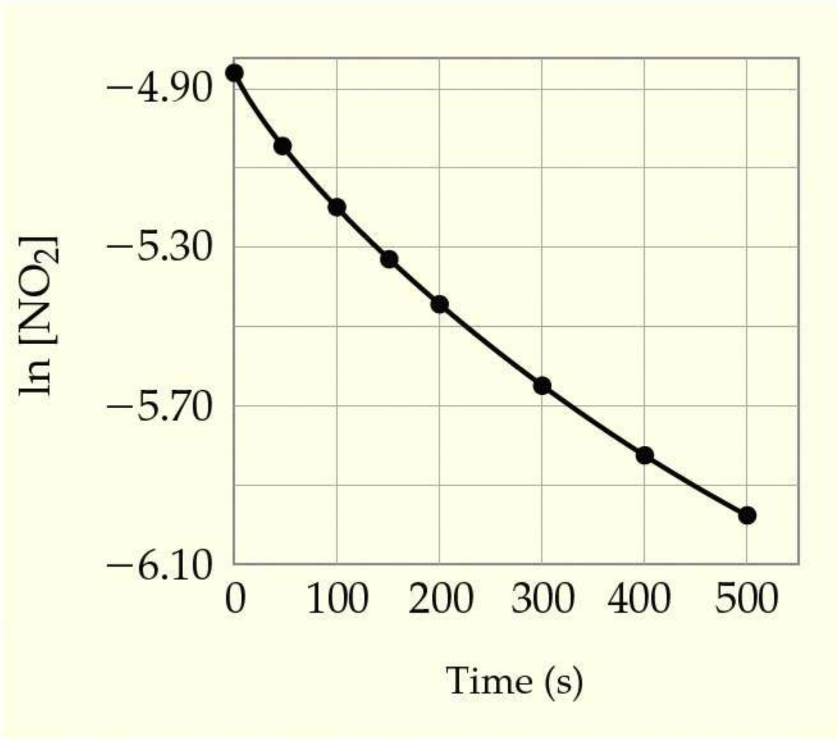
Second-Order Reactions

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



Example 12-8 part 3 Chemistry, 5/e

Plotting **ln[NO_2]** versus **time** gives a curve and not a straight-line fit.

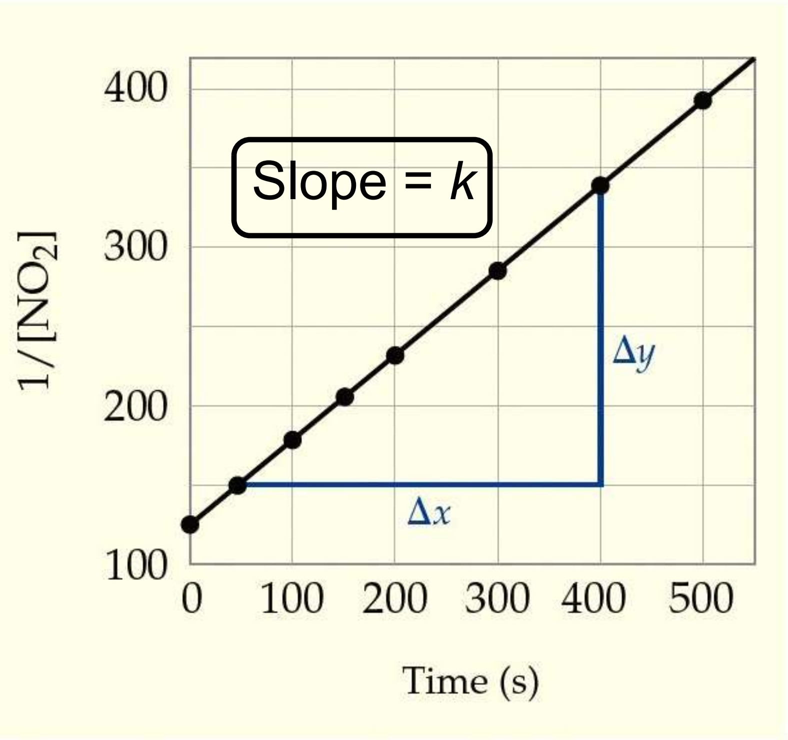
Therefore, this is **not** a first-order reaction.

Second-Order Reactions

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

Plotting $\frac{1}{[NO_2]}$ versus **time** gives a straight-line fit.

Therefore, this is a second-order reaction.



Example 12-8 part 3 Chemistry, 5/e
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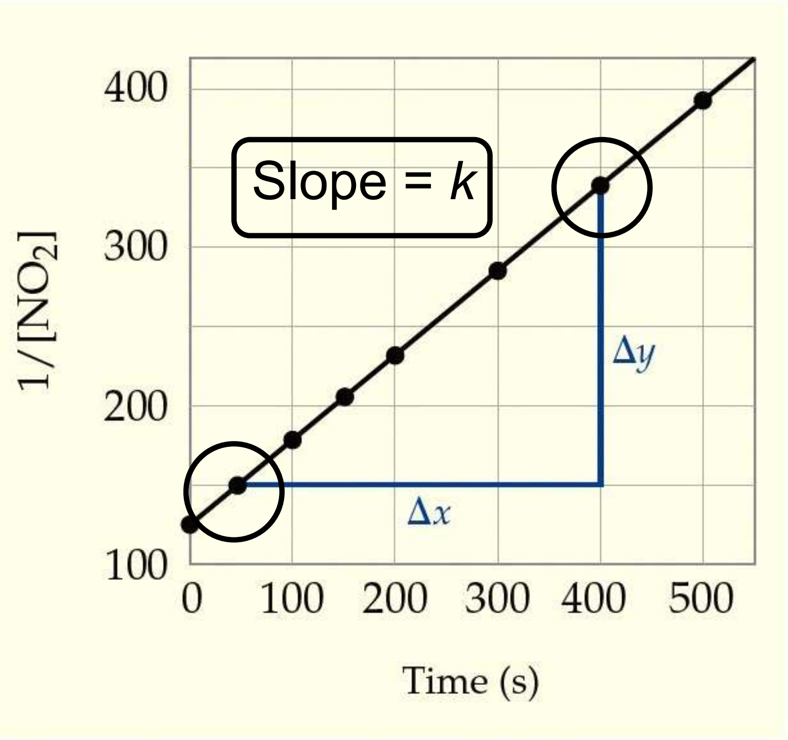
Second-Order Reactions

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

Calculate the slope:

$$\frac{(395 - 125)\dfrac{1}{M}}{(500 - 0)\ s} = 0.540\ \frac{1}{M\ s}$$

$$k = 0.540\ \frac{1}{M\ s}$$



Example 12-8 part 3 Chemistry, 5/e
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Second-Order Reactions

Half-life for a second-order reaction

$$A \longrightarrow \text{product(s)}$$

$$\text{rate} = k[A]^2$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad \left\{ \begin{array}{l} t = t_{1/2} \\ [A]_{t_{1/2}} = \dfrac{[A]_0}{2} \end{array} \right.$$

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

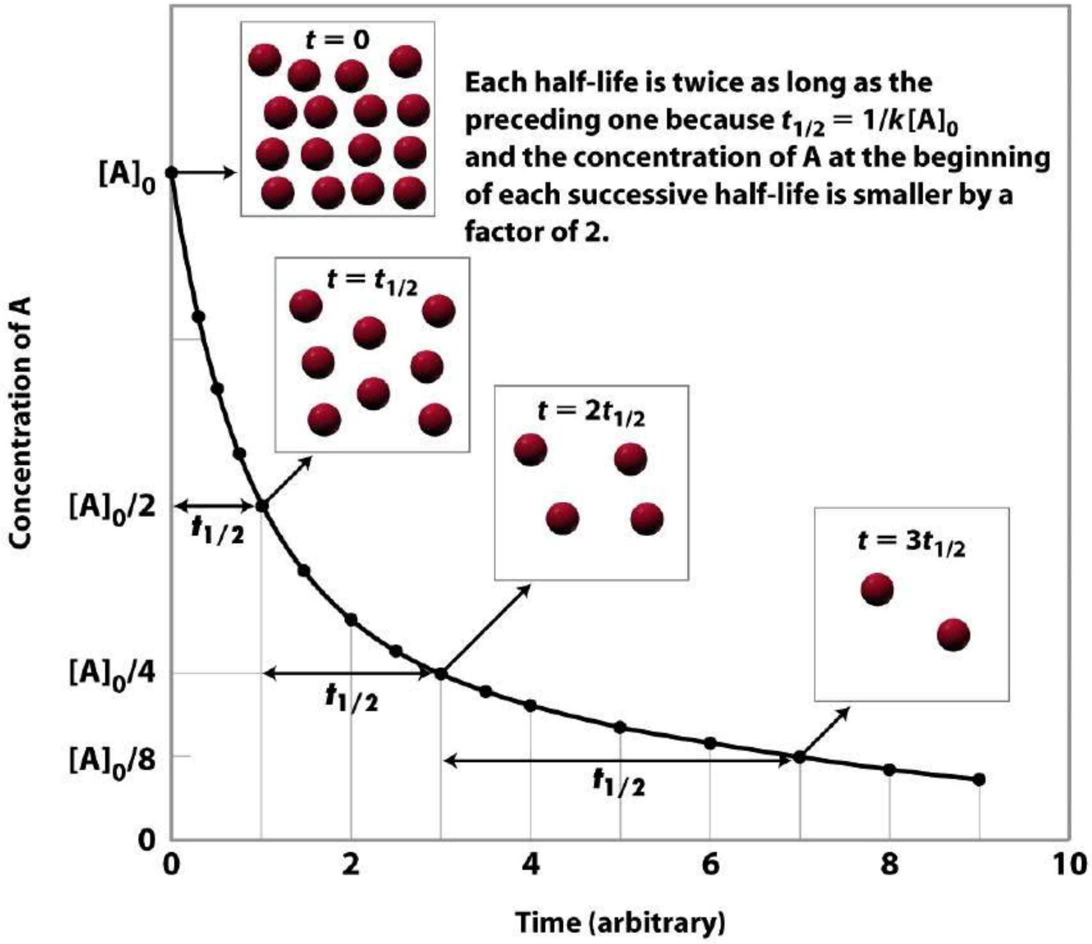
$$\boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

Second-Order Reactions

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

For a second-order reaction, the half-life is dependent on the initial concentration.

Each successive half-life is twice as long as the preceding one.



Each half-life is twice as long as the preceding one because $t_{1/2} = 1/k[A]_0$ and the concentration of A at the beginning of each successive half-life is smaller by a factor of 2.

Figure 12-8 Chemistry, 5/e
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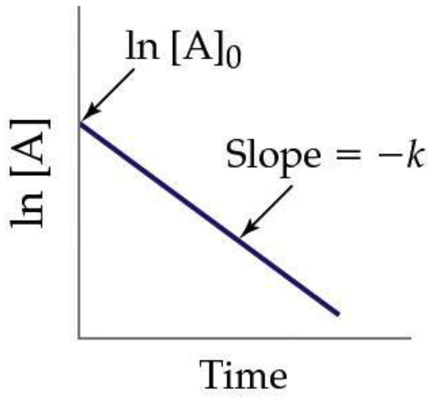
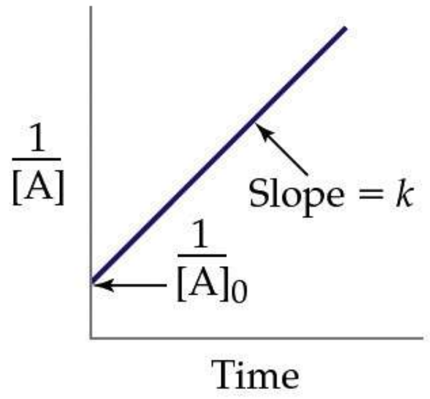
TABLE 12.4 Characteristics of First- and Second-Order Reactions of the Type A → Products

	First-Order	Second-Order
Rate law	$-\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$	$-\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$
Concetration–time equation	$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$
Linear graph	$\ln[\text{A}]$ versus t	$\frac{1}{[\text{A}]}$ versus t
		
Graphical determination of k	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[\text{A}]_0}$ (not constant)

Zeroth-Order Reactions

For a zeroth-order reaction, the rate is independent of the concentration of the reactant.

$$A \longrightarrow \text{product(s)}$$

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

Calculus can be used to derive an **integrated** rate law.

$$\boxed{[A]_t = -kt + [A]_0}$$

$[A]_t$ concentration of A at time *t*

$[A]_0$ initial concentration of A

$$y = mx + b$$

Zeroth-Order Reactions

A plot of **[A]** versus **time** gives a straight-line fit and the **slope** will be ***-k***.

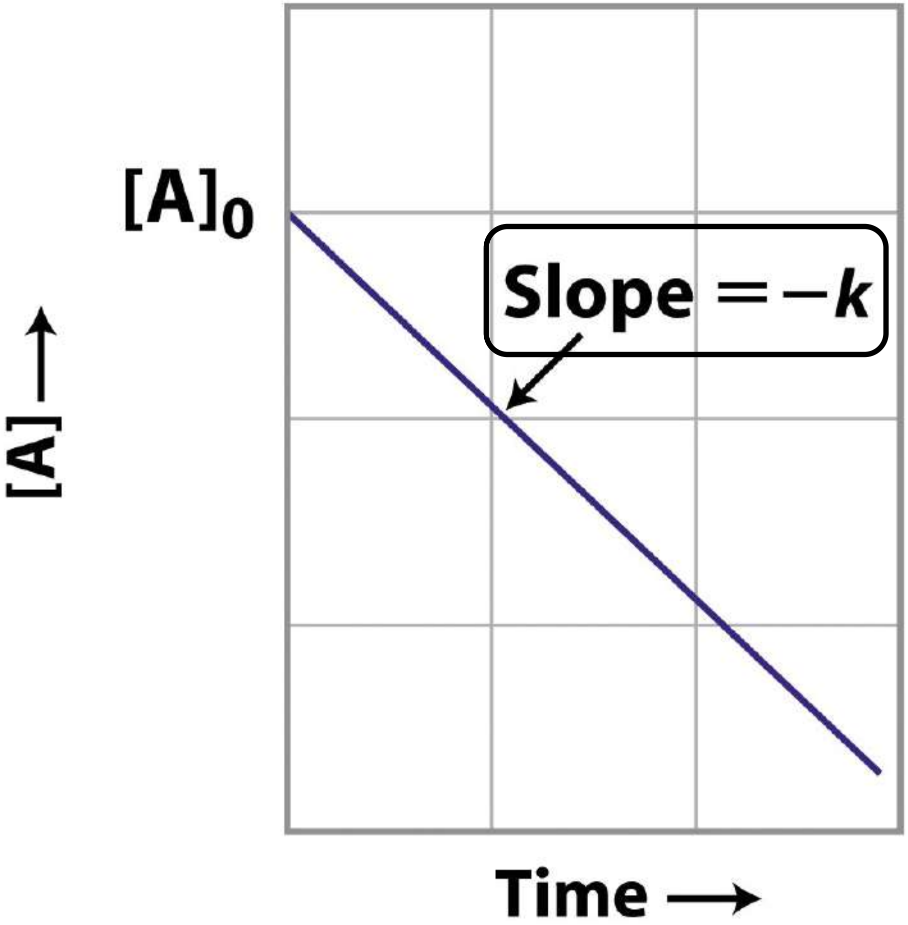


Figure 12-9 Chemistry, 5/e
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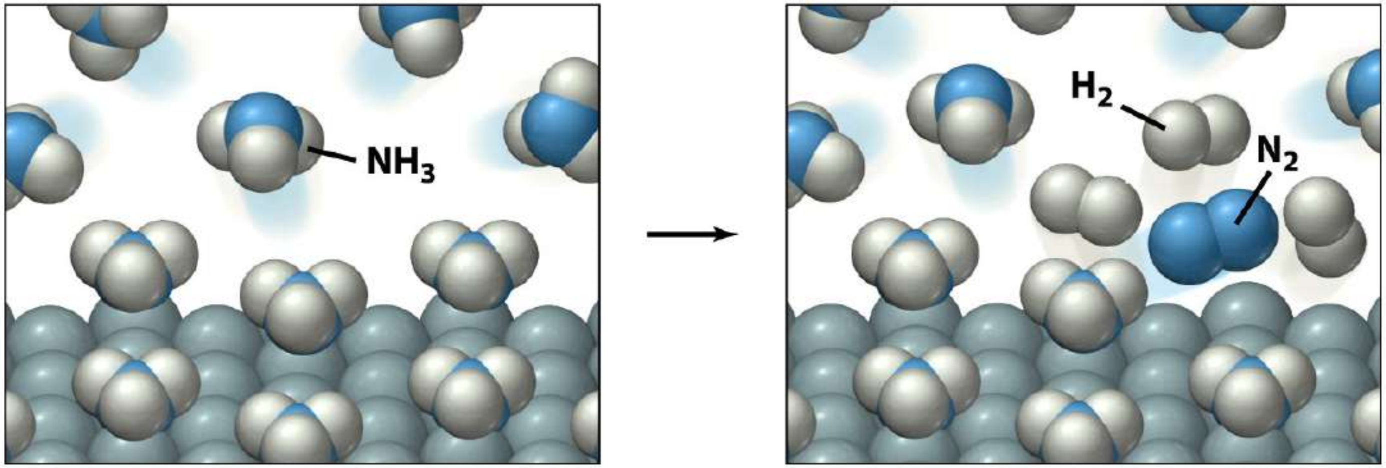
Zeroth-Order Reactions

$$\text{rate} = k[\text{NH}_3]^0 = k$$



Most of the NH_3 molecules are in the gas phase above the surface and are unable to react.

As NH_3 molecules on the surface decompose, they are replaced by molecules from the gas phase, so the number of NH_3 molecules on the surface remains constant.

Because only the NH_3 molecules on the surface react under these conditions, the reaction rate is independent of the total concentration of NH_3.

Figure 12-10 Chemistry, 5/e
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Reaction Mechanisms

Reaction Mechanism: A sequence of reaction steps that describes the pathway from reactants to products.

Elementary Reaction (step): A single step in a reaction mechanism.

Reaction Mechanisms

Experimental evidence suggests that the reaction between NO_2 and CO takes place by a two-step mechanism:

$NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ **elementary reaction**

$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ **elementary reaction**

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ **overall reaction**

An **elementary reaction** describes an individual molecular event.

The **overall reaction** describes the reaction stoichiometry and is a summation of the elementary reactions.

Reaction Mechanisms

$$NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$$

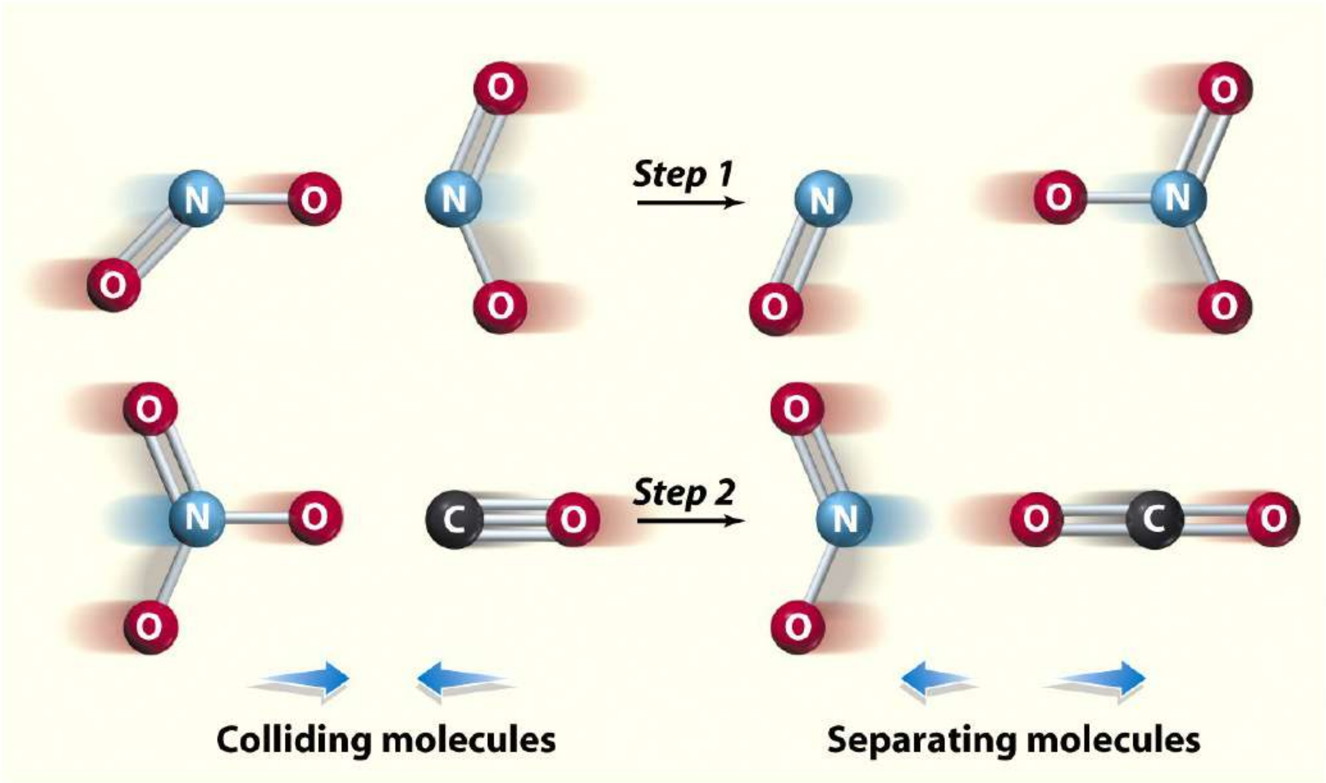


Figure 12-11 Chemistry, 5/e

$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$$

Reaction Mechanisms

Experimental evidence suggests that the reaction between NO_2 and CO takes place by a two-step mechanism:

$NO_2(g) + NO_2(g) \longrightarrow NO(g) + \boxed{NO_3(g)}$ elementary reaction

$\boxed{NO_3(g)} + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ elementary reaction

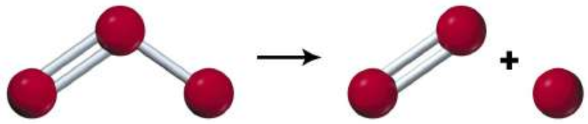
$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ overall reaction

A **reactive intermediate** is formed in one step and consumed in a subsequent step.

Reaction Mechanisms-Molecularity

Molecularity: A classification of an elementary reaction based on the number of molecules (or atoms) on the reactant side of the chemical equation.

unimolecular reaction: $O_3^*(g) \longrightarrow O_2(g) + O(g)$



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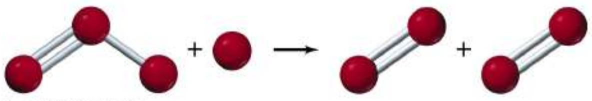
bimolecular reaction: $O_3(g) + O(g) \longrightarrow 2\ O_2(g)$



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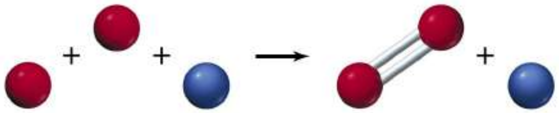
termolecular reaction: $O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g)$



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Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an **elementary reaction is an individual molecular event.**

unimolecular reaction: $O_3^*(g) \longrightarrow O_2(g) + O(g)$

rate = $k[O_3]$

bimolecular reaction: $O_3(g) + O(g) \longrightarrow 2\ O_2(g)$

rate = $k[O_3][O_2]$

termolecular reaction: $O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g)$

rate = $k[O]^2[M]$

Rate Laws for Elementary Reactions

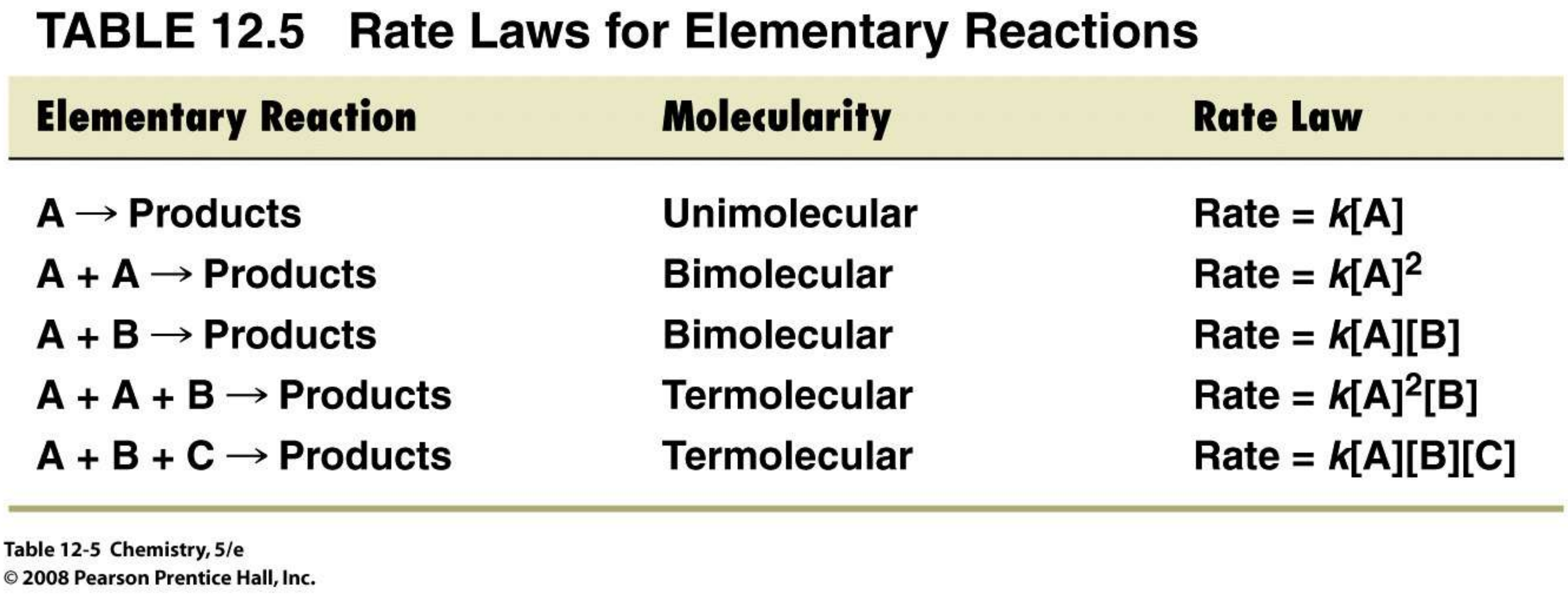


TABLE 12.5 Rate Laws for Elementary Reactions

Elementary Reaction	Molecularity	Rate Law
A → Products	Unimolecular	Rate = $k[A]$
A + A → Products	Bimolecular	Rate = $k[A]^2$
A + B → Products	Bimolecular	Rate = $k[A][B]$
A + A + B → Products	Termolecular	Rate = $k[A]^2[B]$
A + B + C → Products	Termolecular	Rate = $k[A][B][C]$

Table 12-5 Chemistry, 5/e

Rate Laws for Overall Reactions

Rate-Determining Step: The slow step in a reaction mechanism since it acts as a bottleneck and limits the rate at which reactants can be converted to products.

Rate Laws for Overall Reactions

Initial Slow Step

$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO(g) + NO_3(g)$ **slow step**

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

---

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ overall reaction

Based on the slow step: **rate = $\boldsymbol{k_1[NO_2]^2}$**

Rate Laws for Overall Reactions

Initial Fast Step

$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$ fast step, reversible

$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$ **slow step**

$N_2O(g) + H_2(g) \xrightarrow{k_3} N_2(g) + H_2O(g)$ fast step

---

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

Based on the slow step: **rate = $k_2[N_2O_2][H_2]$**

Rate Laws for Overall Reactions

$$\text{rate} = k_2[N_2O_2][H_2]$$

intermediate

First step: $\text{Rate}_{\text{forward}} = k_1[NO]^2$ $\text{Rate}_{\text{reverse}} = k_{-1}[N_2O_2]$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

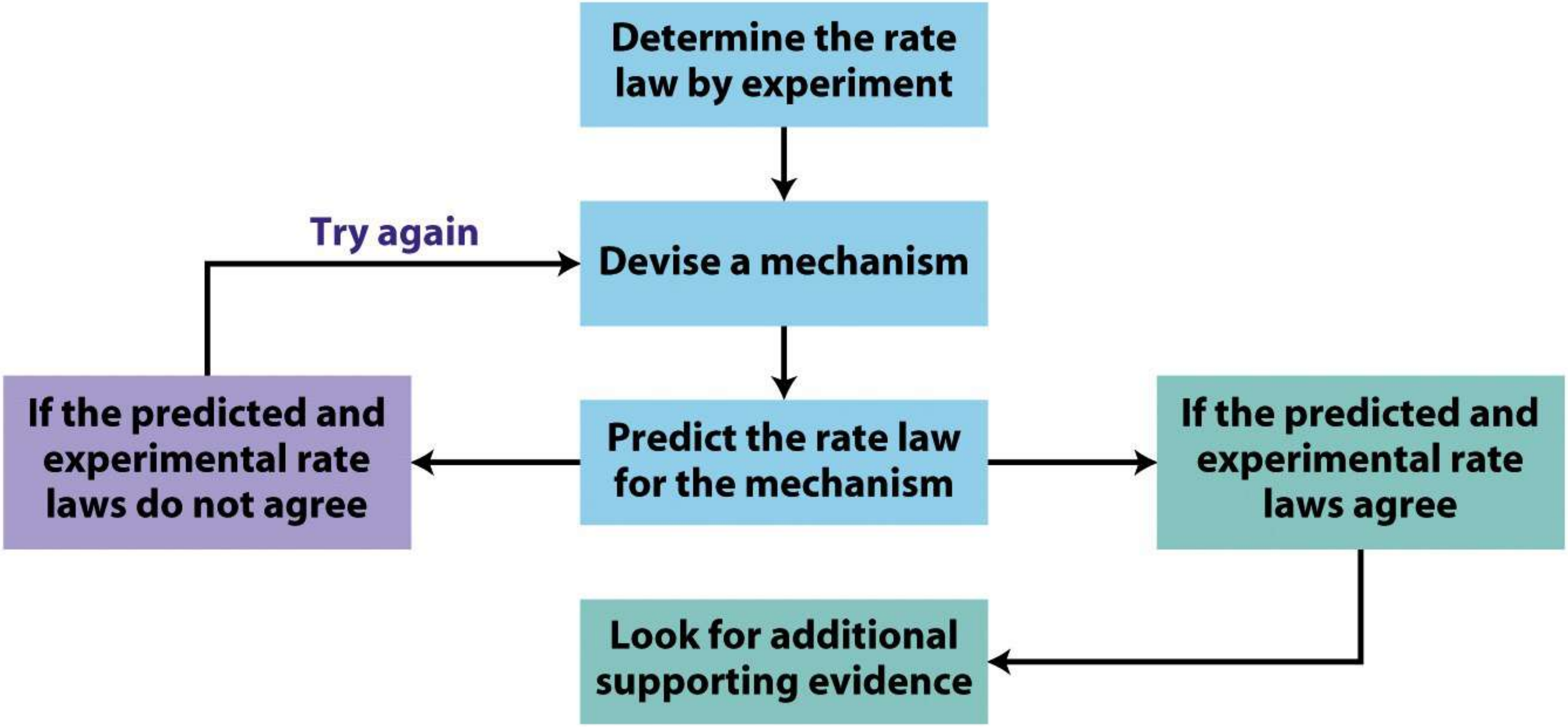
$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

Slow step: $\text{rate} = k_2[N_2O_2][H_2]$

$$\boxed{\text{rate} = k_2\frac{k_1}{k_{-1}}[NO]^2[H_2]}$$

Rate Laws for Overall Reactions

Procedure for Studying Reaction Mechanisms



Determine the rate law by experiment

Try again

Devise a mechanism

If the predicted and experimental rate laws do not agree

Predict the rate law for the mechanism

If the predicted and experimental rate laws agree

Look for additional supporting evidence

Figure 12-13 Chemistry, 5/e

The Arrhenius Equation

Typically, as the temperature increases, the rate of reaction increases.

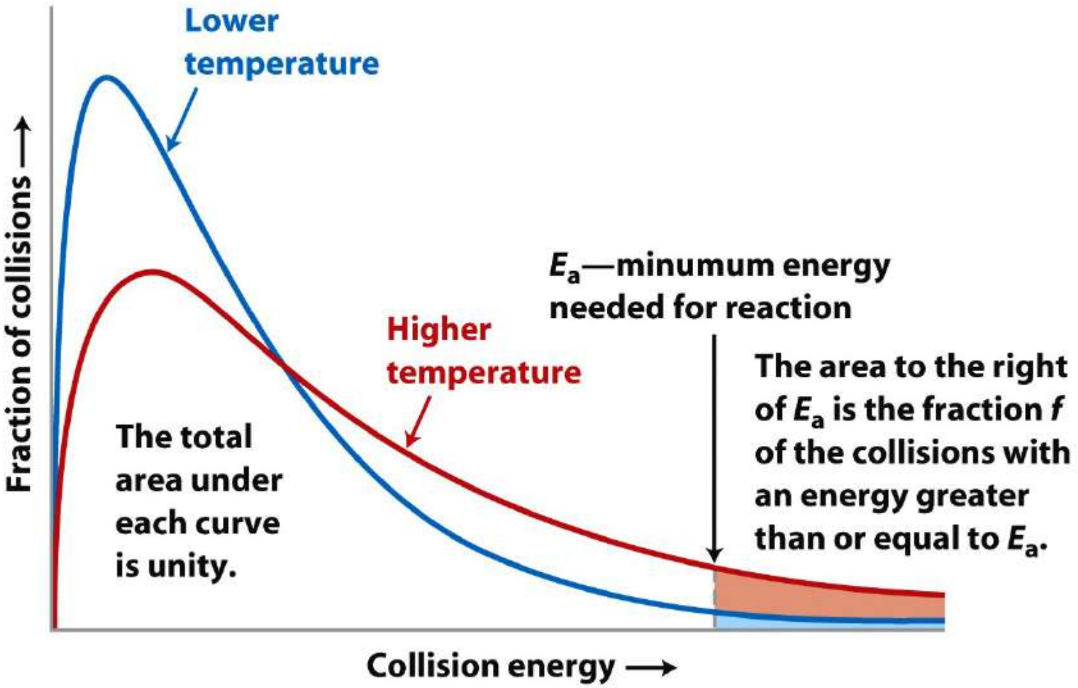
$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{rate} = \boldsymbol{k}[N_2O_5]$$

The **rate constant** is dependent on temperature.

The Arrhenius Equation

Collision Theory: As the average kinetic energy increases, the average molecular speed increases, and thus the collision rate increases.

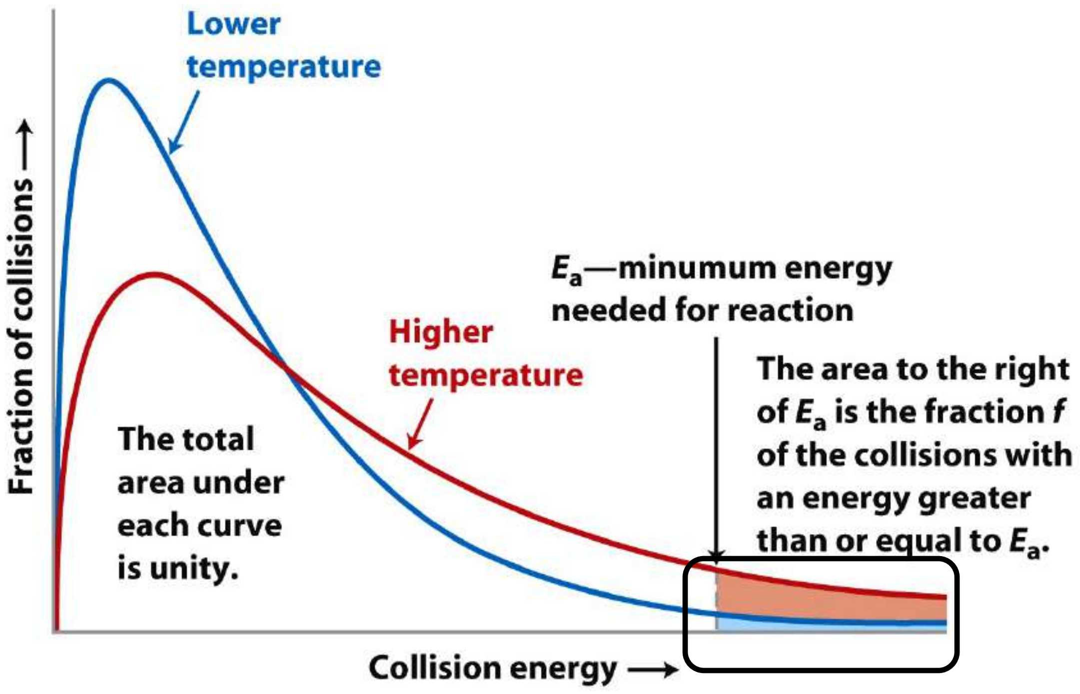


The fraction of collisions that are sufficiently energetic to result in reaction increases exponentially with increasing temperature.

Figure 12-16 Chemistry, 5/e

The Arrhenius Equation

Activation Energy (E_a): The minimum energy needed for reaction. As the temperature increases, the fraction of collisions with sufficient energy to react increases.



The fraction of collisions that are sufficiently energetic to result in reaction increases exponentially with increasing temperature.

Figure 12-16 Chemistry, 5/e
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The Arrhenius Equation

Transition State: The configuration of atoms at the maximum in the potential energy profile. This is also called the activated complex.

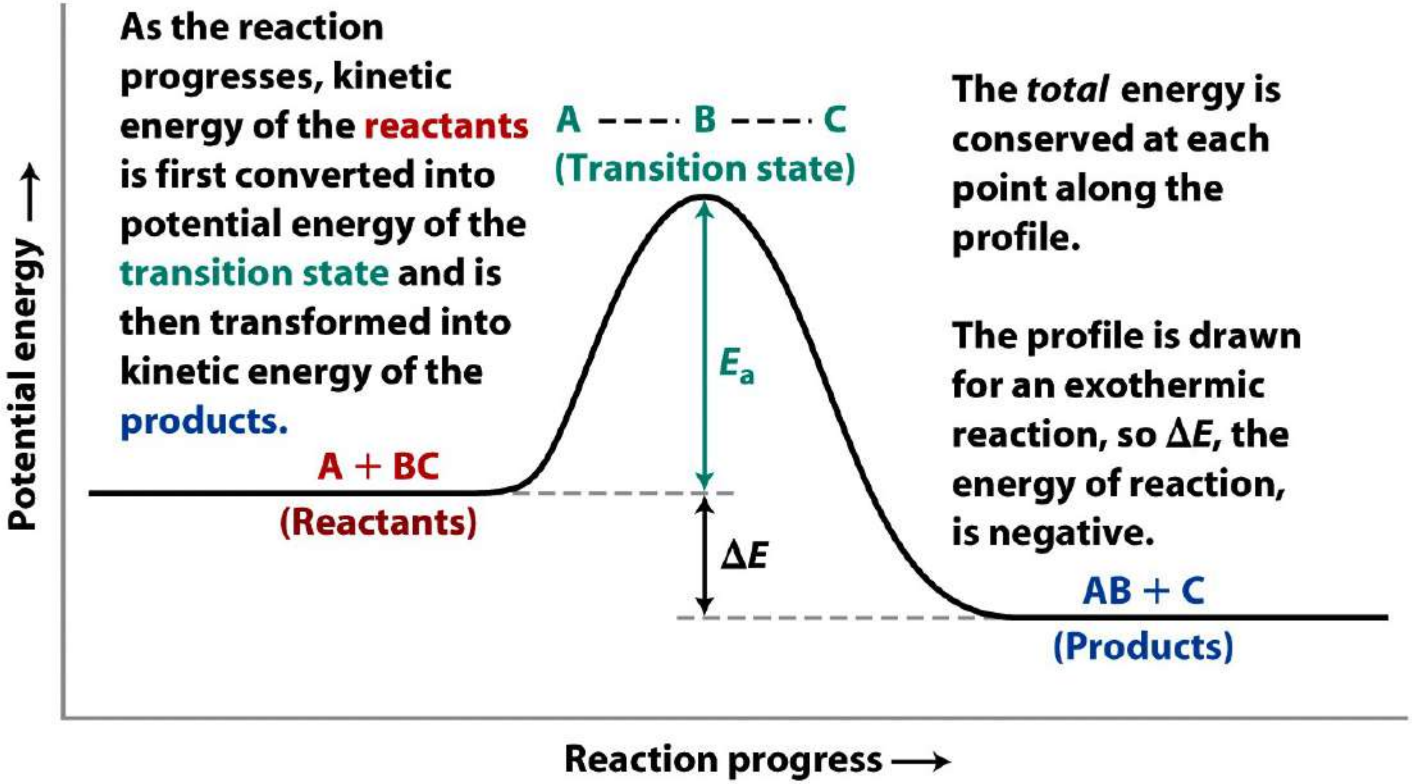

Figure 12-15 Chemistry, 5/e
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The Arrhenius Equation

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

k rate constant

A collision frequency factor

E_a activation energy

R gas constant

T temperature (K)

Using the Arrhenius Equation

$$\ln(k) = \ln(A) + \ln(e^{-E_a/RT})$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \xrightarrow[\text{rearrange the equation}]{} \boxed{\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)}$$

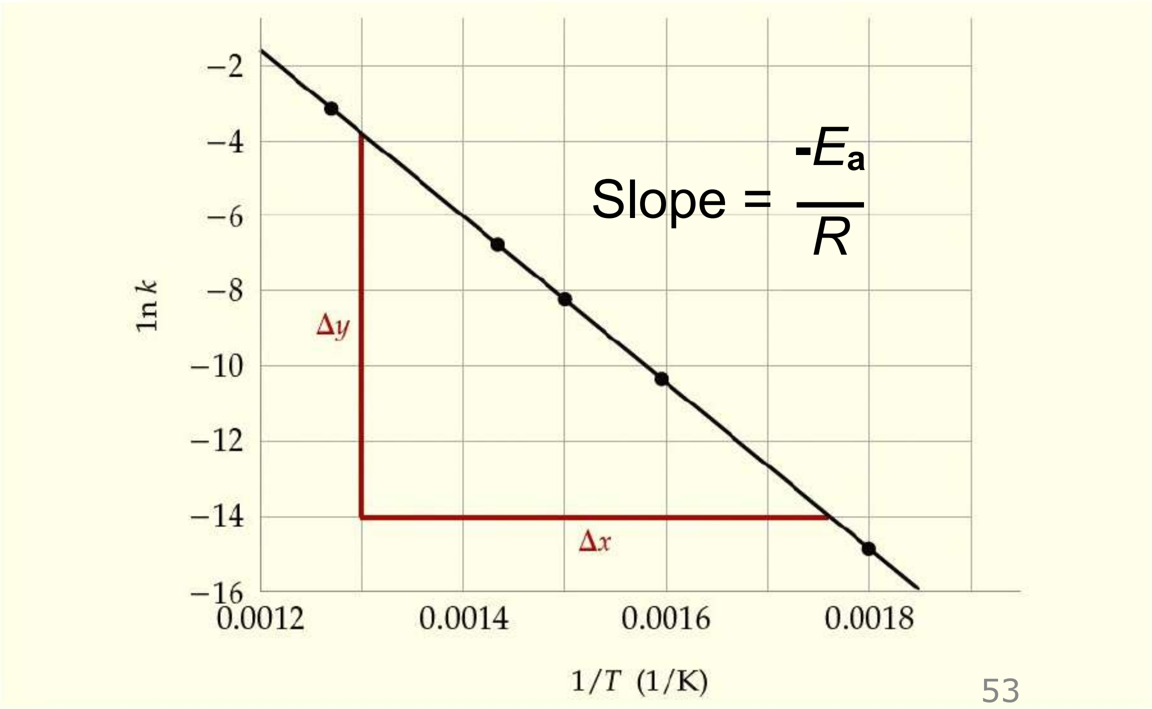
$$y \quad = \quad mx \quad + \quad b$$

Using the Arrhenius Equation

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

t (°C)	T (K)	k ($M^{-1}\,s^{-1}$)	$1/T$ (1/K)	$\ln k$
283	556	3.52×10^{-7}	0.001 80	−14.860
356	629	3.02×10^{-5}	0.001 59	−10.408
393	666	2.19×10^{-4}	0.001 50	−8.426
427	700	1.16×10^{-3}	0.001 43	−6.759
508	781	3.95×10^{-2}	0.001 28	−3.231

Plot **ln(*k*)** versus $\frac{\mathbf{1}}{\boldsymbol{T}}$



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

Catalysis

Catalyst: A substance that increases the rate of a reaction without itself being consumed in the reaction. A catalyst is used in one step and regenerated in a later step.

$$\begin{array}{ll} H_2O_2(aq) + \boxed{I^{1-}(aq)} \longrightarrow H_2O(l) + IO^{1-}(aq) & \text{rate-determining step} \\ H_2O_2(aq) + IO^{1-}(aq) \longrightarrow H_2O(l) + O_2(g) + \boxed{I^{1-}(aq)} & \text{fast step} \\ \hline 2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g) & \text{overall reaction} \end{array}$$

Catalysis

Since the catalyst is involved in the **rate determining step**, it often appears in the rate law.

$$\text{rate} = k[\mathrm{H_2O_2}][\mathrm{I^{1-}}]$$

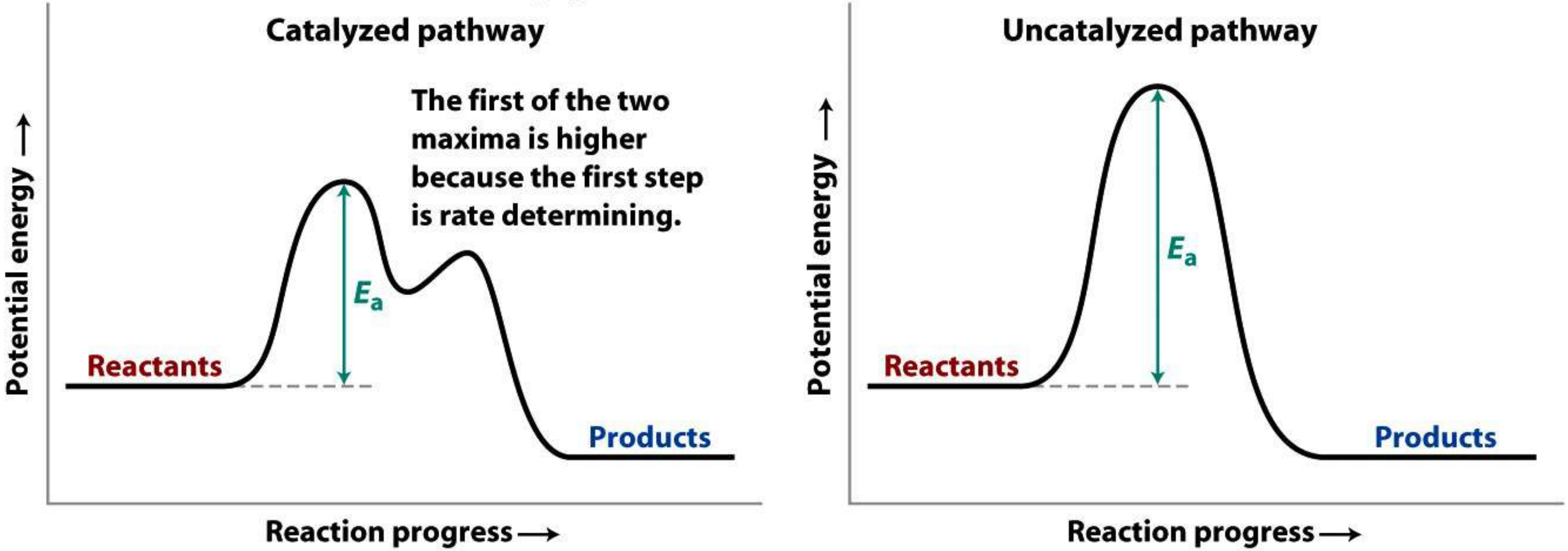
$\mathrm{H_2O_2}(aq) + \boxed{\mathrm{I^{1-}}(aq)} \longrightarrow \mathrm{H_2O}(l) + \mathrm{IO^{1-}}(aq)$ **rate-determining step**

$\mathrm{H_2O_2}(aq) + \mathrm{IO^{1-}}(aq) \longrightarrow \mathrm{H_2O}(l) + \mathrm{O_2}(g) + \boxed{\mathrm{I^{1-}}(aq)}$ fast step

---

$2\mathrm{H_2O_2}(aq) \longrightarrow 2\mathrm{H_2O}(l) + \mathrm{O_2}(g)$ overall reaction

Catalysis



The shape of the barrier for the catalyzed pathway applies to the decomposition of H_2O_2.

The first of the two maxima is higher because the first step is rate determining.

The activation energy E_a is lower for the catalyzed pathway.

Figure 12-18 Chemistry, 5/e

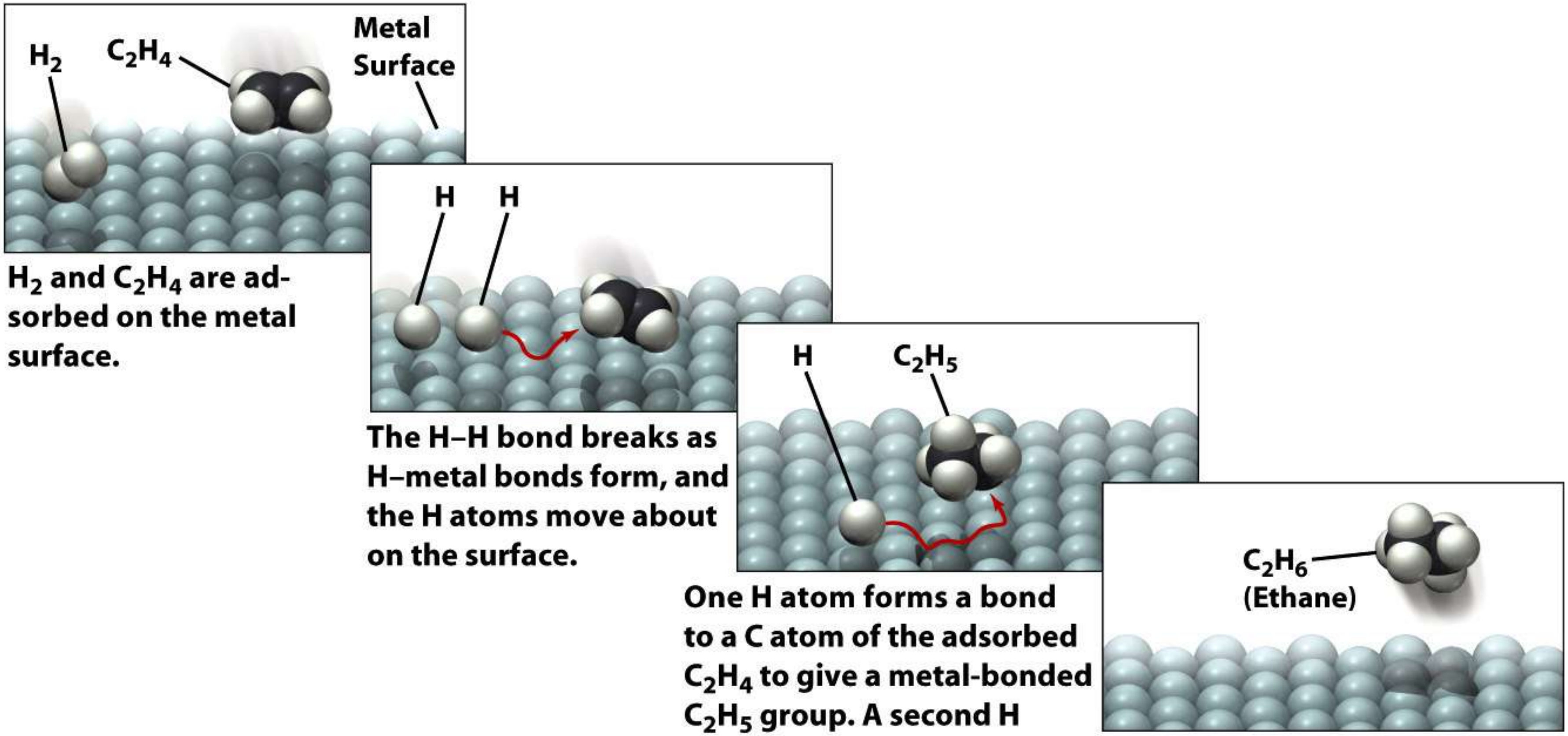
Note that the presence of a catalyst does not affect the energy difference between the reactants and the products

Homogeneous and Heterogeneous Catalysts

Homogeneous Catalyst: A catalyst that exists in the same phase as the reactants.

Heterogeneous Catalyst: A catalyst that exists in a different phase from that of the reactants.

Homogeneous and Heterogeneous Catalysts



H_2 and C_2H_4 are adsorbed on the metal surface.

The H–H bond breaks as H–metal bonds form, and the H atoms move about on the surface.

One H atom forms a bond to a C atom of the adsorbed C_2H_4 to give a metal-bonded C_2H_5 group. A second H atom bonds to the C_2H_5 group.

The resulting C_2H_6 molecule is desorbed from the surface.

Figure 12-19 Chemistry, 5/e
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Homogeneous and Heterogeneous Catalysts

TABLE 12.6 Some Heterogeneous Catalysts Used in Commercially Important Reactions

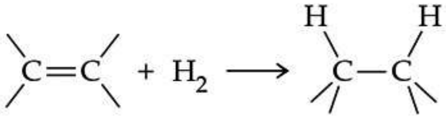
Reaction	Catalyst	Commercial Process	End Product: Commercial Uses
$2\,SO_2 + O_2 \rightarrow 2\,SO_3$	Pt or V_2O_5	Intermediate step in the contact process for synthesis of sulfuric acid	H_2SO_4: Manufacture of fertilizers, chemicals; oil refining
$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$	Pt and Rh	First step in the Ostwald process for synthesis of nitric acid	HNO_3: Manufacture of explosives, fertilizers, plastics, dyes, lacquers
$N_2 + 3\,H_2 \rightarrow 2\,NH_3$	Fe, K_2O, and Al_2O_3	Haber process for synthesis of ammonia	NH_3: Manufacture of fertilizers, nitric acid
$H_2O + CH_4 \rightarrow CO + 3\,H_2$	Ni	Steam–hydrocarbon re-forming process for synthesis of hydrogen	H_2: Manufacture of ammonia, methanol
$CO + H_2O \rightarrow CO_2 + H_2$	ZnO and CuO	Water-gas shift reaction to improve yield in the synthesis of H_2	H_2: Manufacture of ammonia, methanol
$CO + 2\,H_2 \rightarrow CH_3OH$	ZnO and Cr_2O_3	Industrial synthesis of methanol	CH_3OH: Manufacture of plastics, adhesives, gasoline additives; industrial solvent
	Ni, Pd, or Pt	Catalytic hydrogenation of compounds with C=C bonds, as in conversion of unsaturated vegetable oils to solid fats	Food products: margarine, shortening

Table 12-6 Chemistry, 5/e