

12 Chemical Kinetics

Objectives:

- Understand reaction rates, how to use and derive rate laws, and how to use the integrated rate laws.
- Understand the basics of collision theory, and how the Arrhenius equation relates temperature to rate.
- Understand how to determine the consistency of a reaction mechanism and the role of catalysts in reactions.



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Reaction Rates

Factors That Influence Reaction Rate

- 1. The nature of the reactants:** some reagents naturally react faster than others.
- 2. Concentration:** molecules must come in contact with each other in order to react.
Rate \propto collision frequency \propto concentration
- 3. Physical state:** molecules must mix in order to collide and react with each other.
 - When reactants are in the same phase (a *homogeneous reaction*), thermal motion easily brings them into contact.
 - When reactants are in different phases (a *heterogeneous reaction*), contact only occurs at the surface, so a more finely divided reactant, with a larger surface area (a mist or a powder vs liquids or large chunks) will react faster.

Chemical Kinetics

- There are several fundamental questions chemists ask about all chemical reactions:
 - What happens? (*Stoichiometry* [Ch. 3 & 9])
 - What will the reactant and product concentrations be at the “end” of the reaction? (*Equilibrium* [Ch. 13-16])
 - Is the reaction spontaneous, and is energy released or absorbed? (*Thermodynamics* [Ch. 6 & 17])
 - How fast does it happen? (*Kinetics* [Ch. 12])
- **Chemical kinetics** is the study of **reaction rates**, the changes in concentration of reactants and products as a function of time.
- Reaction rates give us clues about the **mechanism** of the reaction — the series of individual steps comprising the overall observed reaction.

Speed of Reactions

- The speed of some reactions depends on the conditions:
 - liquid gasoline + O₂: relatively slow reaction
 - vaporized gasoline + O₂: fast rxn
 - digestion: slow reaction
 - sugar + KClO₃: fast reaction [[movie](#)]

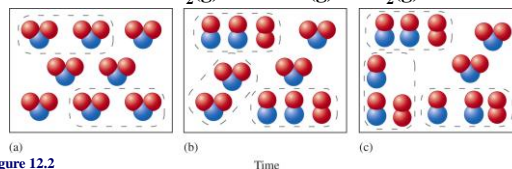


Figure 12.2

Factors That Influence Reaction Rate

- 4. Temperature:** molecules must collide with enough energy in order to react. Raising the temperature increases the reaction rate by increasing the frequency and energy of the collisions.
Rate \propto collision energy \propto temperature
- 5. Catalysts:** catalysts increase the rate of chemical reactions without themselves being changed.

Reaction Rates

- [A] = concentration of species A (usually in mol/L).

$$\text{Rate} = \frac{\text{change in concentration}}{\text{change in time}} = \frac{[A]_2 - [A]_1}{t_2 - t_1} = \frac{\Delta[A]}{\Delta t}$$

- For the reaction



the rate of disappearance of NO_2 can be written as

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{[\text{NO}_2]_2 - [\text{NO}_2]_1}{t_2 - t_1}$$

and the rate of appearance of NO is:

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

Change in Concentration Over Time

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ (at 300°C)

Time (± 1 s)	Concentration (mol/L)		
	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

- The product $[\text{NO}]$ increases at the same rate that the $[\text{NO}_2]$ decreases; the $[\text{O}_2]$ increases at half the rate that the $[\text{NO}_2]$ decreases.

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Change in Concentration Over Time

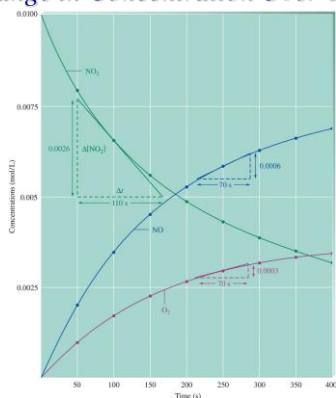


Figure 12.1

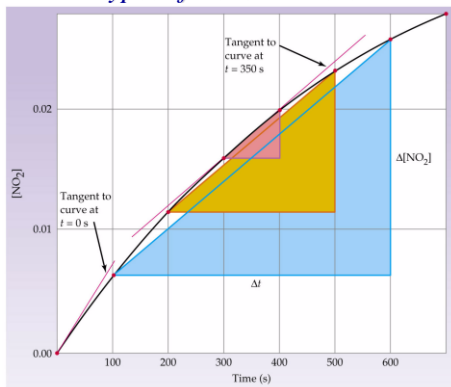
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Types of Reaction Rates

- The **reaction rate** can be defined as either the increase in the concentration of a product per unit time or as the decrease in the concentration of a reactant per unit time. [Note that the reaction rates change over time, slowing down as the reaction proceeds.]
- The units of reaction rate are *moles per liter per second* ($\text{mol L}^{-1} \text{s}^{-1}$, $\text{mol/L}\cdot\text{s}$, or M/s)
- The rate over the entire period of time is the **average rate** of the reaction.
- The **instantaneous rate** is the rate at a particular instant (the slope of a line tangent to the curve).
- Often, we use the **initial rate** — the rate of the reaction at the moment the reagents are mixed.

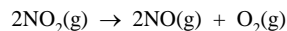
Types of Reaction Rates



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Examples: Reaction Rates

- From the data on slide 8, calculate the rate of disappearance of NO_2 in the reaction



at the following time intervals:

- between 0 and 10 seconds.

$$\begin{aligned} \text{Rate} &= -\Delta[\text{NO}_2] / \Delta t \\ &= -(0.0079 \text{ M} - 0.0100 \text{ M}) / (50 \text{ s} - 0 \text{ s}) \\ &= -(-0.0021 \text{ M} / 50 \text{ s}) = 4.2 \times 10^{-5} \text{ M s}^{-1} \end{aligned}$$

- between 90 and 100 seconds.

$$\begin{aligned} \text{Rate} &= -(0.0031 \text{ M} - 0.0034 \text{ M}) / (400 \text{ s} - 350 \text{ s}) \\ &= -(-0.0003 \text{ M} / 50 \text{ s}) = 6 \times 10^{-6} \text{ M s}^{-1} \end{aligned}$$

- the average rate of the reaction.

$$\begin{aligned} \text{Rate} &= -(0.0031 \text{ M} - 0.0100 \text{ M}) / (400 \text{ s} - 0 \text{ s}) \\ &= -(-0.0069 \text{ M} / 400 \text{ s}) = 1.7 \times 10^{-5} \text{ M s}^{-1} \end{aligned}$$

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General Reaction Rates

- For a reaction of the form



- for a reactant A:

$$\text{Rate of reaction} = -\frac{[A]_2 - [A]_1}{t_2 - t_1} = -\frac{\Delta[A]}{\Delta t}$$

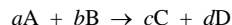
- for a product B:

$$\text{Rate of reaction} = \frac{[B]_2 - [B]_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

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General Reaction Rates

- For a reaction of the form



the rate is related to reactant and product concentrations as follows:

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

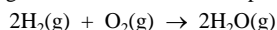
or

$$\text{Rate} = -\frac{1}{a} \text{rate}_A = -\frac{1}{b} \text{rate}_B = \frac{1}{c} \text{rate}_C = \frac{1}{d} \text{rate}_D$$

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Examples: Reaction Rates

2. Because of its non-polluting product gases, hydrogen gas is used for fuel in the Space Shuttle:



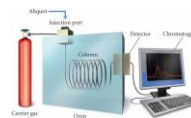
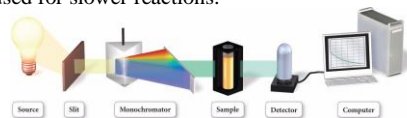
- (a) Express the rate of this reaction in terms of changes in $[\text{H}_2]$, $[\text{O}_2]$, and $[\text{H}_2\text{O}]$ with time. (b) When $[\text{O}_2]$ is decreasing at $0.23 \text{ mol L}^{-1} \text{ s}^{-1}$, at what rate is $[\text{H}_2\text{O}]$ increasing?

Answer: $0.46 \text{ mol L}^{-1} \text{ s}^{-1}$

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Measuring Reaction Rates

- At least one of the reactant or product concentrations must be measured as a function of time.
- Spectroscopy can be used to study reaction rates over extremely small timescales, which is especially good for fast reactions; gas chromatography can be used for slower reactions.

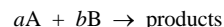


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Rate Laws

The Rate Law and Its Components

- The **rate law** for a reaction expresses the rate as a function of reactant concentrations. For a reaction of the form



the rate law has the form:

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

- k is a proportionality constant called the **rate constant**, with units that when multiplied by $[A]^m [B]^n$ produce units of $\text{M} \cdot \text{time}^{-1}$ for the rate.

- The exponents are used to describe the **order of the reaction** with respect to each reactant:

0 zero order	2 second order
1 first order	3 third order

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The Rate Law and Its Components

- The **overall order of a reaction** is the sum of all the exponents (overall order = $m + n$)
- There is **no** relationship between the exponents of a rate law and the coefficients of the balanced reaction! **The exponents must be determined by experiment!**
- This is so important I'll say it three times:

THE EXPONENTS OF THE RATE LAW MUST BE DETERMINED BY EXPERIMENT !!!

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Rate Laws and Reaction Orders

- Zero-order:** For $n=0$, the rate of the reaction is independent of the concentration of the reactant:

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

- For a zero-order reaction, the concentration decreases linearly with time.
- Doubling $[A]$ does not change the rate.

- First-order:** For $n=1$, the rate is directly proportional to the concentration of the reactant:

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

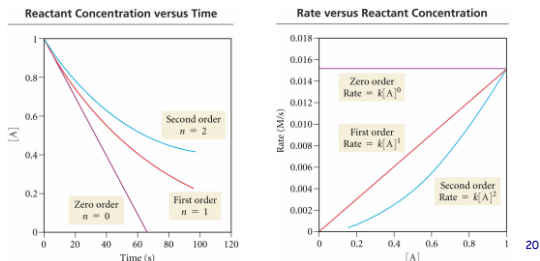
- For a first-order reaction, the rate slows down as the reaction proceeds.
- Doubling $[A]$ increases the rate by a factor of 2.

Rate Laws and Reaction Orders

- For a reaction of the form

$$\text{Rate} = k [A]^n$$

the way in which $[A]$ changes with time and with concentration for $n=0, 1$, and 2 is shown below:



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Rate Laws and Reaction Orders

- Second-order:** For $n=2$, the rate is proportional to the square of the concentration of the reactant:

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

- A second-order reaction is even more sensitive to the reactant concentration.
- Doubling $[A]$ increases the rate by a factor of 4.

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Examples: Reaction Rates

- For each of the following reactions, determine the order with respect to each reactant and the overall order from the rate law.
 - $\text{NO(g)} + \text{O}_3\text{(g)} \rightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$
Rate = $k [\text{NO}][\text{O}_3]$
 - $(\text{CH}_3)_3\text{CBr(l)} + \text{H}_2\text{O(l)} \rightarrow (\text{CH}_3)_3\text{COH(l)} + \text{HBr(aq)}$
Rate = $k [(\text{CH}_3)_3\text{CBr}]$
 - $\text{H}_2\text{O}_2\text{(aq)} + 3\text{I}^-\text{(aq)} + 2\text{H}^+\text{(aq)} \rightarrow \text{I}_3^-\text{(aq)} + 2\text{H}_2\text{O(l)}$
Rate = $k [\text{H}_2\text{O}_2][\text{I}^-]$
 - $\text{CHCl}_3\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{CCl}_4\text{(g)} + \text{HCl(g)}$
Rate = $k [\text{CHCl}_3][\text{Cl}_2]^{1/2}$

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Reaction Orders — Method of Initial Rates

- There are two ways to determine the orders in a rate law. In the **method of initial rates**, we run a series of experiments with different concentrations of the reactants, and determine the initial rate in each reaction. The experiments are designed so that only one concentration is changed at a time.

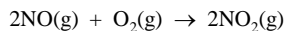


Expt.	Initial Concentrations, M		Initial Rate of Formation of Products (M s ⁻¹)
	[A]	[B]	
1	0.10	0.10	0.20
2	0.20	0.10	0.40
3	0.30	0.10	0.60
4	0.30	0.20	2.40
5	0.30	0.30	5.40

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

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Method of Initial Rates — Example



$$\text{Rate} = k [\text{NO}]^m [\text{O}_2]^n$$

Expt.	Initial Concentrations, M		Initial Rate of Formation of NO_2 (M s^{-1})
	[NO]	[O ₂]	
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
5	0.30	0.30	5.40

- Once we have the form of the rate law, we can plug in the data from any experiment and solve for k to determine the value and units for the rate constant.

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Reaction Orders and Units for Rate Constants

Conc. change	Rate change	Exp.	Conc. change	Rate change	Exp.
2×	no change	0	2×	4 (= 2 ²)	2
3×	no change	0	3×	9 (= 3 ²)	2
4×	no change	0	4×	16 (= 4 ²)	2
2×	2 (= 2 ¹)	1	2×	8 (= 2 ³)	3
3×	3 (= 3 ¹)	1	3×	27 (= 3 ³)	3
4×	4 (= 4 ¹)	1	4×	64 (= 4 ³)	3

Rate Law	Overall Order	Units for k
Rate = k	Zeroth order	M s^{-1} ($\text{mol L}^{-1} \text{s}^{-1}$)
Rate = $k [\text{A}]$	First order	s^{-1}
Rate = $k [\text{A}]^2$	Second order	$\text{M}^{-1} \text{s}^{-1}$ ($\text{L mol}^{-1} \text{s}^{-1}$)
Rate = $k [\text{A}] [\text{B}]$	Second order	$\text{M}^{-1} \text{s}^{-1}$ ($\text{L mol}^{-1} \text{s}^{-1}$)
Rate = $k [\text{A}]^3$	Third order	$\text{M}^{-2} \text{s}^{-1}$ ($\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$)
Rate = $k [\text{A}] [\text{B}]^2$	Third order	$\text{M}^{-2} \text{s}^{-1}$ ($\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$)
Rate = $k [\text{A}]^2 [\text{B}]$	Third order	$\text{M}^{-2} \text{s}^{-1}$ ($\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$)

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Examples: Determining Rate Laws

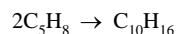
2. Initial rate data for the decomposition of gaseous N_2O_5 at 55 °C are shown in the table below. What is the rate law and the value of the rate constant?

Expt.	Initial [N ₂ O ₅]	Initial Rate of Decomposition of N ₂ O ₅ (M s^{-1})
1	0.015	0.048
2	0.030	0.192

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Examples: Determining Rate Laws

3. Isoprene (C_5H_8) forms a dimer called dipentene ($\text{C}_{10}\text{H}_{16}$).



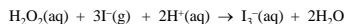
What is the rate law for this reaction given the following data for the initial rate of formation of dipentene? What is the value of the rate constant?

Expt.	Initial [C ₅ H ₈]	Initial Rate of Formation of C ₁₀ H ₁₆ (M s^{-1})
1	0.50	1.98
2	1.50	17.8

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Examples: Determining Rate Laws

4. The oxidation of iodide ion by hydrogen peroxide in an acidic solution is described by the equation



The rate of formation of the red-colored triiodide ion, $\Delta[\text{I}_3^-]/\Delta t$, can be determined by measuring the rate of appearance of the color. Following are initial rate data at 25 °C.

- What is the rate law for the formation of I_3^- ?
- What is the value of the rate constant?
- What is the rate of formation of I_3^- when the concentrations are $[\text{H}_2\text{O}_2] = 0.300 \text{ M}$ and $[\text{I}^-] = 0.400 \text{ M}$?

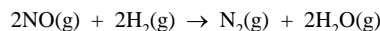
Expt.	Initial [H ₂ O ₂]	Initial [I ⁻]	Initial [H ⁺]	Initial Rate of Formation of I ₃ ⁻ (M/s)
1	0.010	0.010	0.00050	1.15 × 10 ⁻⁶
2	0.020	0.010	0.00050	2.30 × 10 ⁻⁶
3	0.010	0.020	0.00050	2.30 × 10 ⁻⁶
4	0.010	0.010	0.00100	1.15 × 10 ⁻⁶



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Examples: Determining Rate Laws

5. The following data were measured for the reduction of nitric oxide with hydrogen. What is the rate law for the reaction? What is the value of the rate constant?

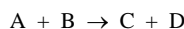


Expt.	Initial Concentrations, M		Initial Rate of Formation of H ₂ O (M s^{-1})
	[NO]	[H ₂]	
1	0.10	0.10	1.23 × 10 ⁻³
2	0.10	0.20	2.46 × 10 ⁻³
3	0.20	0.10	4.92 × 10 ⁻³

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Examples: Determining Rate Laws

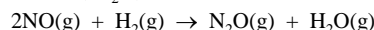
6. Given the following data for the reaction below, what is the rate law for the reaction? What is the value of the rate constant?



Expt.	Initial Concentrations, M		Initial Rate of Formation of C (M s ⁻¹)
	[A]	[B]	
1	0.40	0.30	1.0 10 ⁻⁴
2	0.80	0.30	4.0 10 ⁻⁴
3	0.80	0.60	1.6 10 ⁻³

Examples: Determining Rate Laws

7. Nitric oxide, NO, reacts with hydrogen to give nitrous oxide, N₂O, and water:



Given the following data, what is the rate law for the reaction? What is the value of the rate constant?

Expt.	Initial Concentrations, M		Initial Rate of Decomposition of NO (M s ⁻¹)
	[NO]	[H ₂]	
1	6.4 10 ⁻³	2.2 10 ⁻³	2.6 10 ⁻⁵
2	12.8 10 ⁻³	2.2 10 ⁻³	1.0 10 ⁻⁴
3	6.4 10 ⁻³	4.5 10 ⁻³	5.1 10 ⁻⁵

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Integrated Rate Laws — First Order Reactions

- The rate laws we've seen so far only relate the rate to the reactant concentrations at a *particular* time.
- The **integrated rate laws** take into account the passage of time in a chemical reaction.
- For a general **first-order reaction**,



the **integrated rate law** is:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad [A]_t = [A]_0 e^{-kt}$$

where [A]_t is the concentration at time *t* during the reaction, and [A]₀ is the initial concentration.

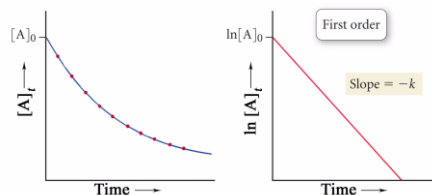
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Integrated Rate Laws — First Order Reactions

- Rearranging the first-order integrated rate law, we obtain an equation which has the form of an equation of a line:

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

- A graph of **ln[A]_t** (y-axis) vs. **time** (x-axis) will give a straight line (with a slope of *-k*) for a first-order reaction, but not for a second-order reaction.



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Everything You Always Wanted To Know About Logarithms (But Were Afraid To Ask)

- Logarithm** — an exponent indicating the power to which a base must be raised in order to obtain a given number.
- In **common logarithms** (log N), the base is 10.

$N = 10^x$	$\log N = x$
$100 = 10^2$	$\log 100 = 2$
$10 = 10^1$	$\log 10 = 1$
$5 = 10^{0.698}$	$\log 5 = 0.698$
$1 = 10^0$	$\log 1 = 0$
$0.01 = 10^{-2}$	$\log 0.01 = -2$
$0.0001 = 10^{-4}$	$\log 0.0001 = -4$

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Everything You Always Wanted To Know About Logarithms (But Were Afraid To Ask)

- Natural logarithms** (ln N or log_e N) follow the same idea, except that the base is the irrational number *e*, 2.7182818...

$N = \exp(x) = e^x$	$\ln N = x$
$100 = \exp(4.605) = e^{4.605}$	$\ln 100 = 4.605$
$10 = \exp(2.303) = e^{2.303}$	$\ln 10 = 2.303$
$1 = \exp(0) = e^0$	$\ln 1 = 0$
$0.1 = \exp(-2.303) = e^{-2.303}$	$\ln 0.1 = -2.303$
$0.01 = \exp(-4.605) = e^{-4.605}$	$\ln 0.01 = -4.605$

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Everything You Always Wanted To Know About Logarithms (But Were Afraid To Ask)

- Common logarithms may be converted to natural logarithms using the following equation:

$$(2.303)(\log N) = \ln N$$

- Some useful algebraic rules for manipulating logarithms:

$$\ln(A \times B) = \ln A + \ln B$$

$$\ln(A / B) = \ln A - \ln B$$

$$\ln(A + B) \neq \ln A + \ln B$$

$$\ln x^n = n \ln x$$

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Half-Life of a First Order Reaction

- The **half-life** ($t_{1/2}$) of a reaction is the time required for the reactant concentration to drop to one-half of its initial value.

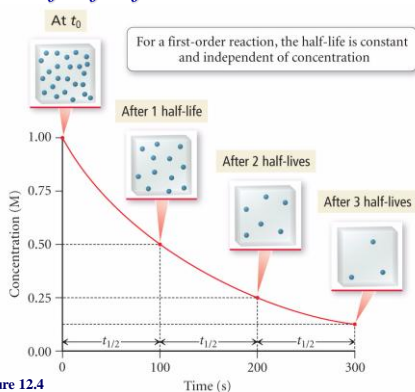
$$\text{Half-life of a first order reaction: } t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

- Notice that for a first order reaction, the half-life is constant, depending *only* on the value of the rate constant, and not the reaction concentration.
- Reactions that are not first order have half-lives that *do* depend on the initial concentration.
- Radioactive decay is a common first-order process; the half-life of radioactive particles is used in *radiometric dating*.



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Half-Life of a First Order Reaction

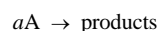


sim. to Figure 12.4

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Integrated Rate Laws — Second Order Reactions

- For a general **second-order reaction**,



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

the **integrated rate law** is:

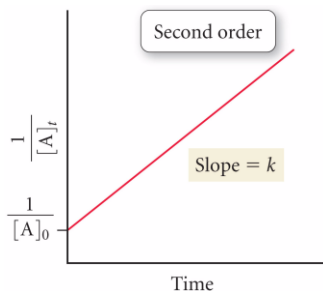
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where $[A]_t$ is the concentration at time t during the reaction, and $[A]_0$ is the initial concentration.

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Integrated Rate Laws — Second Order Reactions

- Since this has the form of an equation of a line, a graph of $1/[A]_t$ (y-axis) vs. **time** (x-axis) will give a straight line for a second-order reaction, but not for a first-order reaction.

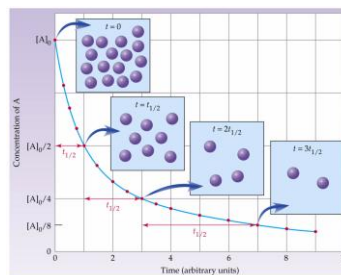


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Half-Life of a Second Order Reaction

- For a second-order reaction, the half-life is given by the following equation:

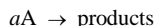
$$\text{Half-life of a second order reaction: } t_{1/2} = \frac{1}{k[A]_0}$$



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Zeroth-Order Reactions

- For a general **zeroth-order reaction**,



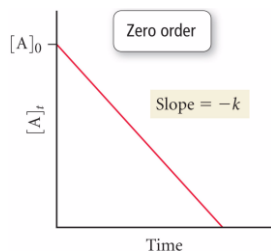
$$\text{Rate} = k[A]^0 = k$$

the **integrated rate law** is:

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

and the **half-life** is

$$\text{Zeroth-order reactions: } t_{1/2} = \frac{[A]_0}{2k}$$



Summary of Integrated Rate Laws

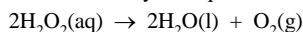
TABLE 12.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow \text{Products}$ That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
Rate Law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-Life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

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Examples: Integrated Rate Laws

8. The decomposition of hydrogen peroxide under basic conditions is described by the equation



The reaction is first order in H_2O_2 , $k = 1.8 \times 10^{-5} \text{ s}^{-1}$ at 20°C , and the initial concentration of H_2O_2 is 0.30 M .

- What is the concentration of H_2O_2 after 4.00 h ?
- How long will it take for the H_2O_2 concentration to drop to 0.12 M ?
- How long will it take for 90% of the H_2O_2 to decompose?

Answer: (a) 0.23 M , (b) 14 h , (c) 36 h

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Examples: Integrated Rate Laws

9. Cyclobutane (C_4H_8) decomposes at 1000°C to two molecules of ethylene (C_2H_4) with a first-order rate constant, 87 s^{-1} . If the initial concentration of cyclobutane is 2.00 M , what is the concentration after 0.010 s ? What fraction of cyclobutane has decomposed in this time?

Answer: 0.84 M ; 58% decomposed

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Examples: Integrated Rate Laws

10. Dinitrogen pentoxide, N_2O_5 , decomposes in the gas phase by a first-order reaction into N_2O_4 and O_2 . At 45°C , the rate constant for the reaction in carbon tetrachloride is $6.22 \times 10^{-4} \text{ s}^{-1}$. If the initial concentration of the N_2O_5 in the solution is 0.100 M , how many minutes will it take for the concentration to drop to 0.0100 M ?

Answer: 61.7 min

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Examples: Integrated Rate Laws

11. Hydrogen iodide decomposes slowly to H_2 and I_2 at 600K . The reaction is second order in HI and the rate constant $k = 9.70 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$. If the initial concentration of HI is 0.100 M :

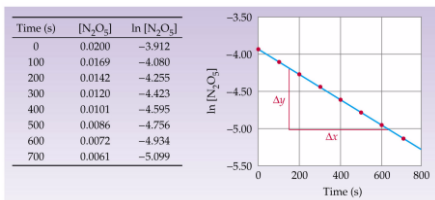
- What is the molarity after a reaction time of 6.00 days ?
- What is the half-life of the reaction?

Answer: (a) 0.0665 M , (b) 11.9 days

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Examples: Integrated Rate Laws

12. Experimental concentration-vs.-time data for the decomposition of gaseous N_2O_5 at 55 °C are listed in the following table and plotted as shown. Use those data to confirm that the decomposition of N_2O_5 is a first-order reaction. What is the value of the rate constant for the consumption of N_2O_5 ?

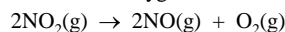


Answer: (b) $1.7 \times 10^{-3} \text{ s}^{-1}$

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Examples: Integrated Rate Laws

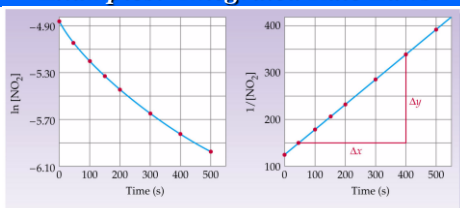
13. At 300 °C, nitrogen dioxide decomposes to nitric oxide and molecular oxygen:



Concentration-time data for the reaction of NO_2 are shown below; and graphs of $\ln[\text{NO}_2]$ vs time and $1/[\text{NO}_2]$ vs. time are shown on the next slide:

Time (s)	$[\text{NO}_2]$	$\ln [\text{NO}_2]$	$1/[\text{NO}_2]$
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

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Examples: Integrated Rate Laws

- Is the reaction first order or second order?
- What is the value of the rate constant?
- What is the concentration of NO_2 at $t = 20.0 \text{ min}$?
- What is the half-life when $[\text{NO}_2]_0 = 6.00 \times 10^{-3} \text{ M}$?
- What is the half-life when $[\text{NO}_2]_0 = 3.00 \times 10^{-3} \text{ M}$?

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Examples: Half-Lives

14. Cyclopropane, a cyclic hydrocarbon, rearranges to form propene at 1000°C with a rate constant of 9.2 s^{-1} (first order). How long does it take for the initial concentration of cyclopropane to decrease by one-half?

Answer: **0.075 s**

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Examples: Half-Lives

15. The half-life of radioactive iodine-131 is 8.0 days. What fraction of the initial iodine-131 would be present in a patient after 24 days if none of it were eliminated through natural body processes?

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Examples: Half-Lives

16. The reaction



has the rate law $k[\text{HI}]^2$ with $k = 0.079 \text{ L mol}^{-1} \text{ s}^{-1}$ at 508°C . What is the half-life for this reaction at this temperature when the initial concentration of HI is 0.050 M ?

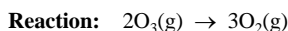
Answer: **253 s = 4.22 min**

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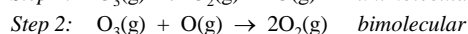
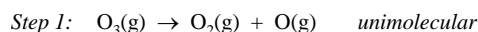
Reaction Mechanisms

Elementary Reactions

- A **reaction mechanism** is a sequence of molecular events, or reaction steps, that defines the overall reaction pathway from reactants to products.
- A single step in a mechanism is called an **elementary reaction**, which describes a single molecular event, such as two particles colliding or one particle breaking apart.
- The number of reactant particles involved in an elementary reaction is the **molecularity** of that step.



Mechanism:



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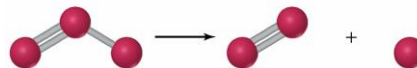
56

Elementary Reactions and Overall Reactions

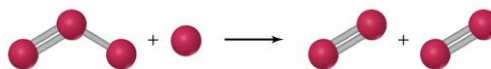
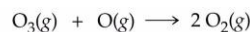
- Keep in mind the difference between an *elementary reaction* and the *overall reaction*:
 - An elementary reaction describes a **single molecular event** that involves breaking or making chemical bonds.
 - The overall reaction describes the **reaction stoichiometry**, but does not necessarily provide any information about *how* the reaction occurs.
- The elementary steps must add up to the overall equation.

Elementary Reactions — Ozone Example

- Step 1 is a **unimolecular reaction**, involving *one* reactant molecule:



- Step 2 is a **bimolecular reaction**, involving a collision between *two* reactant molecules:

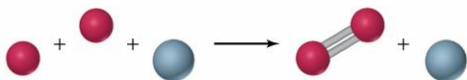
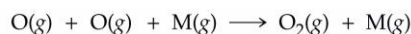


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Elementary Reactions — Ozone Example

- In this example, O is a **reaction intermediate**, which is formed and consumed during the reaction. Notice that it cancels out when the equations are added together, and does not appear in the overall reaction.
- Some **termolecular reactions**, involving the collisions of *three* separate species, are known, but these kinds of collisions are highly improbable. Higher molecularities are not known.



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Examples: Elementary Reactions

- The following two-step mechanism has been proposed for the gas-phase decomposition of nitrous oxide (N_2O):



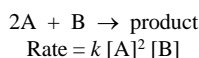
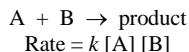
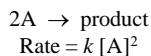
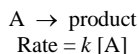
- Write the equation for the overall reaction.
- Identify any reaction intermediates.
- What is the molecularity of the elementary rxns.?
- What is the molecularity of the overall reaction?

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Rate Laws of Elementary Reactions

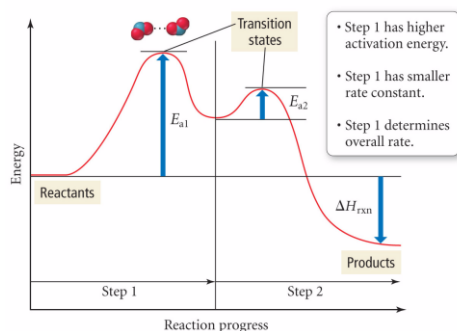
- For an elementary reaction, the stoichiometric coefficients are equal to the reaction orders in the rate law.

This is true **ONLY** for elementary reactions!



Rate-Determining Steps

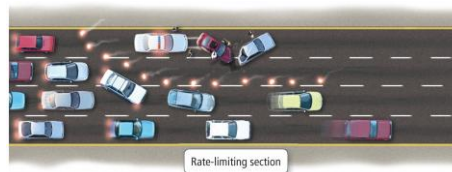
Because E_{a1} for step 1 $>$ E_{a2} for step 2, step 1 has the smaller rate constant and is rate-limiting.



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Rate-Determining Steps

- Usually one step in a mechanism is much slower than the other steps, and acts as a “bottleneck” for the reaction; the rate of this step limits how fast the overall reaction can occur, and is known as the **rate-determining step**.
- The rate law for the rate-determining step represents the rate law for the overall reaction.



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Rate Laws for Overall Reactions

- The observed rate law for an overall reaction depends on the reaction mechanism.
- If the overall reaction occurs in a single elementary step, the experimental rate law is the same as the rate law for the elementary reaction.
- Mechanisms are experimentally determined, usually from circumstantial evidence, and are often difficult to verify.
 - We can never prove, just from the data, that a particular mechanism is correct.
 - We can, however, find out whether a proposed mechanism is consistent with the evidence, and modify or discard the mechanism if necessary.

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Rate Laws for Overall Reactions

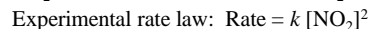
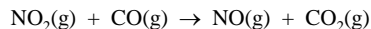
- The elementary steps in the mechanism must sum to the overall reaction.
 - All reaction intermediate must cancel out.
 - Catalysts (more later) cancel out as well.
- The rate law predicted by the mechanism must be consistent with the experimentally observed rate law.
 - That is, the rate law for the slow, rate determining, step in the mechanism must match the experimental rate law.

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Examples: Reaction Mechanisms

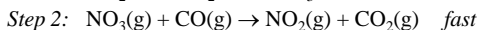
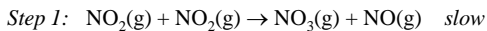
2. Reaction Mechanisms with a Slow Initial Step.

Is the proposed mechanism below consistent with the experimental rate law for this reaction?



This reaction cannot be elementary. Why not?

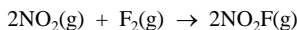
Proposed Mechanism:



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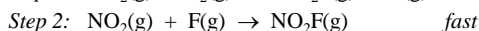
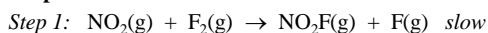
Examples: Reaction Mechanisms**3. Reaction Mechanisms with a Slow Initial Step.**

Is the proposed mechanism below consistent with the experimental rate law for this reaction?



Experimental rate law: $\text{Rate} = k [\text{NO}_2] [\text{F}_2]$

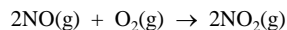
This reaction cannot be elementary. Why not? (There are two reasons.)

Proposed Mechanism:

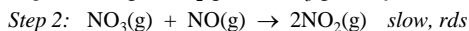
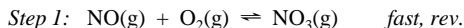
67

Examples: Reaction Mechanisms**4. Reaction Mechanisms with a Fast Initial Step.**

Is the proposed mechanism below consistent with the experimental rate law for this reaction?



Experimental rate law: $\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$

Proposed Mechanism:

[A fast initial step reaches equilibrium, with the slow step acting as a bottleneck, so we must do a little algebraic manipulation of the rate law to see that it is consistent.]

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A Model for Chemical Kinetics:

The Arrhenius Equation

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Temperature and the Rate Constant

- The rates of chemical reactions are sensitive to temperature: most reactions slow down at lower temperatures and speed up at higher temperatures.
 - This temperature dependence is contained in the rate constant, k .

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

- Increasing the value of k increases the rate of the reaction. For many reactions, every increase in temperature by 10°C doubles the reaction rate.
- The temperature dependence of k is given by the **Arrhenius equation**:

$$k = Ae^{-\frac{E_a}{RT}}$$

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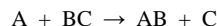
Collision Theory

- Collision theory** views the reaction rate as the result of particles colliding with a certain frequency and minimum energy.
 - Particles must collide in order to react, but most collisions do not result in a reaction, either because the particles do not hit each other hard enough, or they are turned the wrong way, etc.
 - As the number of colliding reactants increases, the chances of two reactants colliding also increases. Thus, increasing concentration increases the rate of the reaction.
 - Anything that increases the number of effective collisions increases the rate.

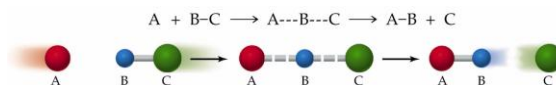
71

Collision Theory

- For a general reaction



as A and BC collide, their electron clouds repel each other. The energy needed to overcome this repulsion comes from the kinetic energy of the particles, and is converted to the potential energy of the $A\cdots B\cdots C$ complex.



- The energy needed to overcome the repulsions between the reactants is the **activation energy**, E_a .

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Potential Energy Diagram Showing E_a

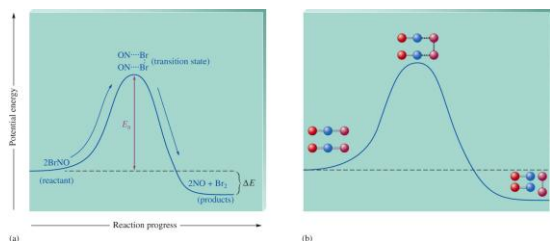


Figure 12.10

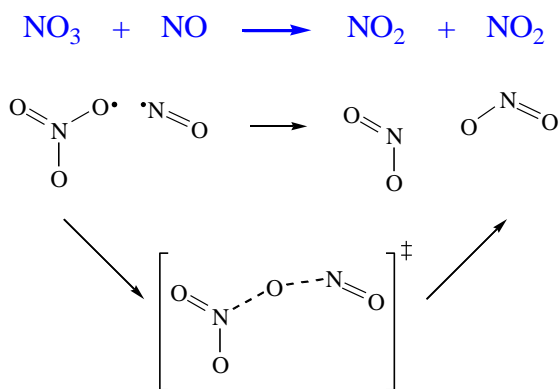
73

Activation Energy, E_a

- The height of the barrier is the **activation energy**, E_a , and the configuration of the atoms at the maximum potential energy in Figure 13.12 is the **transition state** or *activated complex* (\ddagger).
 - If the reactant particles collide with an energy less than E_a , they bounce apart.
 - If the collision energy is greater than E_a (and orientation is right), there is enough energy to overcome the repulsions, and they react.
 - In the transition state, the reactant bonds are in the process of breaking, and the product bonds are in the process of forming.
 - The higher E_a is, the slower the reaction will be.



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Factors that Influence Effective Collisions

- Not every collision between reactant molecules leads to the formation of a product molecule. The number of **effective collisions**, which actually lead to the formation of a product molecule, depends on three factors:
 - the **exponential factor**, f — the fraction with enough energy to react (related to the activation energy).
 - the **collision frequency**, Z — the number of collisions per unit of time.
 - the **orientation factor**, p — the fraction of collisions with the correct orientation.

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The Frequency Factor

- The **exponential factor**, f , is the fraction of collisions with enough energy to react:

$$f = e^{-E_a/RT}$$
 where R is the *gas constant* ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).
- At higher temperatures, the distribution of collision energies broadens and shifts to higher energies, enlarging the fraction of collisions with energy greater than E_a . This makes f a larger number.

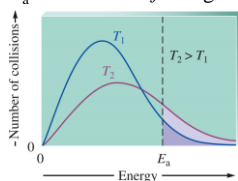


Figure 12.11

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Reaction Rate and Temperature

- The **collision frequency**, Z , is the number of collisions which occur in a given unit of time.
- For a gas at room temperature and a pressure of 1 atmosphere, each molecule undergoes about 10^9 collisions per second, or 1 collision every 10^{-9} s.
 - If every collision resulted in a reaction, every gas-phase reaction would be over in 10^{-9} s. Most reactions are obviously much slower than this.
 - For a reaction where E_a is 75 kJ/mol, at 298 K $f = 7 \times 10^{-14}$ — only 7 collisions in 100 trillion are energetic enough to cause a reaction to occur!
- The collision frequency is directly proportional to the concentration of the reactants.

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Molecular Orientation

- Not all collisions with energy greater than E_a lead to a reaction: the molecules have to be facing each other the right way when they hit each other.
- The fraction of collisions having the right orientation is called the **orientation factor, p** .

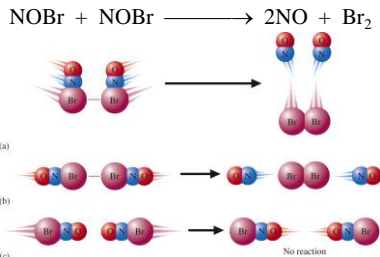
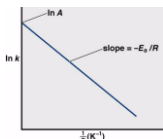


Figure 12.11

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Using the Arrhenius Equation

- Making a graph of $\ln k$ (y-axis) vs. $1/T$ (x-axis) gives a straight line with a slope of $-E_a/R$.



- Another method of calculating E_a is to use an alternate form of the Arrhenius equation, in which the rate constants, k_1 and k_2 , at two different temperatures, T_1 and T_2 , are known:

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

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Catalysis

The Arrhenius Equation

- All of these factors can be combined into a single equation:

$$k = pZf = pZe^{-E_a/RT}$$

- p and Z are often combined into a **frequency factor, A** ($A = pZ$); in this form, this equation is known as the **Arrhenius equation** (Svante Arrhenius, 1889):

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

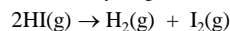
- Rearranging the Arrhenius equation, we can obtain the form of an equation of a line:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

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Examples: The Arrhenius Equation

- The decomposition of hydrogen iodide,



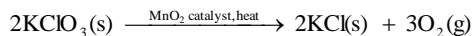
has rate constants of $9.51 \times 10^{-9} \text{ L mol}^{-1} \text{ s}^{-1}$ at 500. K and $1.10 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ at 600. K. Find E_a in units of kJ/mol.

Answer: 176 kJ/mol

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Catalysts

- A **catalyst** increases the rate of a chemical reaction without itself being consumed.
 - All of the catalyst added at the start of a reaction is present chemically unchanged at the end.
 - Because the catalyst is not consumed, very small, non-stoichiometric amounts are usually used.
- Decomposition of Potassium Chlorate:



- Even under strong heating, KClO_3 decomposes very slowly, but if a catalyst of MnO_2 is added, the reaction's speed increases dramatically.

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Catalyzed Reaction Pathways

- A catalyst *lowers* E_a for the reaction, making the rate constant larger and the rate faster.
 - For equilibria, catalysts speed up both the forward and reverse reactions; the reaction will not form *more* product, but it will produce it *faster*.
- A catalyst usually alters the mechanism of the reaction, providing a lower-energy rxn pathway.

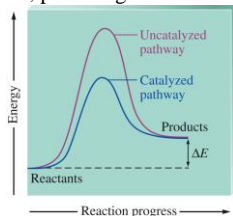


Figure 12.13

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Catalyzed Reaction Pathways

- Because the activation energy is lowered, there are a greater number of effective collisions in the catalyzed pathway, allowing the reactants to become products at a higher rate.

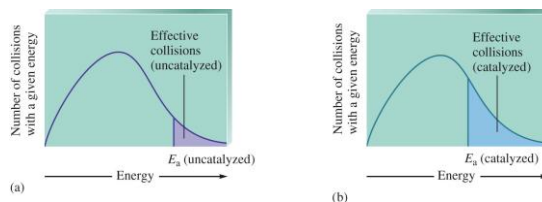
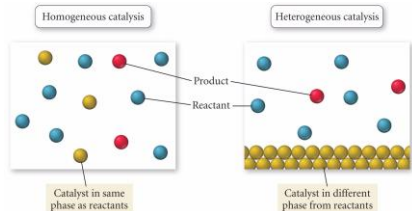


Figure 12.14

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Homogeneous and Heterogeneous Catalysts

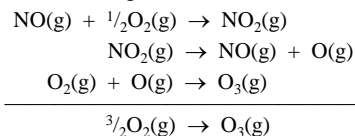
- A **homogeneous catalyst** is in the *same phase* as the reactants (e.g., catalytic destruction of ozone).
- A **heterogeneous catalyst** is in a *separate phase* from the reactants. The catalyst is usually a solid interacting with gaseous or liquid reagents. Usually, catalysts with large surface areas are used (powders or finely divided metals). (e.g., catalytic converters)



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Examples of Homogeneous Catalysts

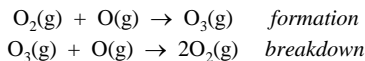
- In the lower atmosphere, nitric oxide, NO, is produced in internal combustion engines at high temperatures:
- $$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$$
- Some NO is converted back into N_2 in the catalytic converter, but a significant amount escapes into the atmosphere, where it acts as a catalyst in the formation of ozone, O_3 , a powerful oxidizing agent, which is toxic in high concentrations.



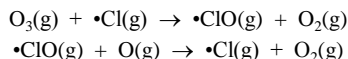
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Examples of Homogeneous Catalysts

- In the stratosphere, ozone, O_3 , is continually formed and broken down, preventing much of the sun's high-energy UV light from reaching the Earth's surface.



- Chlorine atoms, broken off from chlorofluorocarbons (CFCs) in the upper atmosphere, catalyze the breakdown of ozone:

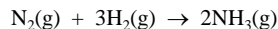


- A chlorine atom can destroy up to 100,000 ozone molecules before returning to the lower atmosphere.

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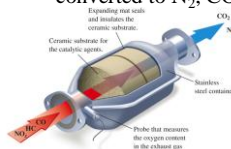
Examples of Heterogeneous Catalysts

- The *Haber process* for the synthesis of ammonia is catalyzed by iron with traces of aluminum and potassium oxides:



- Catalytic cracking* of long-chain hydrocarbons in crude oil produces smaller fragments that can be used for gasoline and diesel fuels.

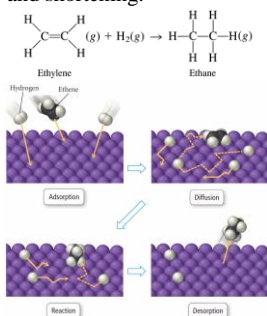
- In cars, nitrogen oxides, fuel fragments, and CO are converted to N_2 , CO_2 and H_2O by passing engine exhaust through a *catalytic converter* (contains platinum, rhodium, or palladium dispersed on an underlying high surface area ceramic structure).



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Examples of Heterogeneous Catalysts

- Catalytic hydrogenation of carbon-carbon double bonds is used in the conversion of vegetable oils to margarine and shortening:



MOQ: Surface Reaction-Hydrogenation

Figure 12.15

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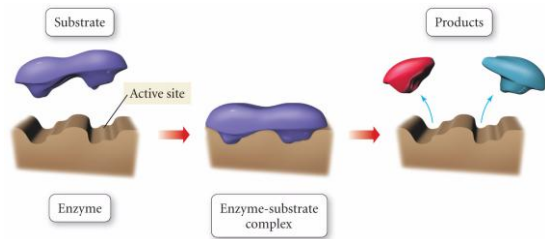
Biological Catalysts — Enzymes

- The rates of many biological reactions are sped up by biological catalysts called **enzymes**.
 - Enzymes are usually large protein molecules with complex three-dimensional shapes whose function has been perfected through evolution.
 - The **active site** of an enzyme has the right shape and properties to bind a receptor molecule (the **substrate**) in the same way that a lock fits a particular key.
 - When the substrate binds to the active site, the activation energy of the reaction is lowered, allowing the reaction to take place more easily and much faster than it would outside of the presence of the enzyme.

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Biological Catalysts — Enzymes

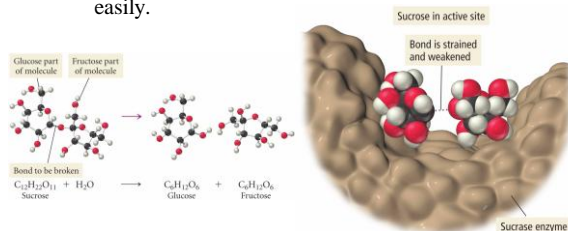
- Once the reaction is completed, the enzyme releases the product molecule(s), and is ready to accept a new substrate molecule.



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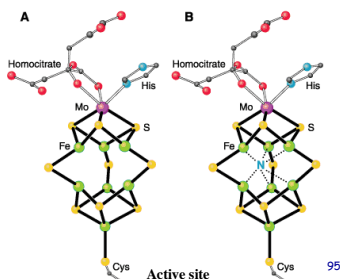
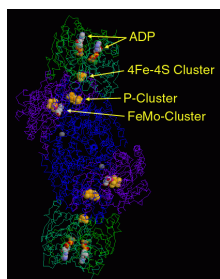
Examples of Enzymes

- The enzyme **sucrase** catalyzes the breakdown of the disaccharide sucrose (table sugar) into the simpler sugars glucose and fructose.
 - When a sucrose molecule binds to the active site of sucrase, the bond between the two halves of the molecule is strained, allowing it to break more easily.



Examples of Enzymes

- Nitrogenase** catalyzes the conversion of atmospheric nitrogen (N_2) to ammonia in bacteria associated with leguminous plants. It involves a series of iron-sulfur proteins associated with molybdenum ions.



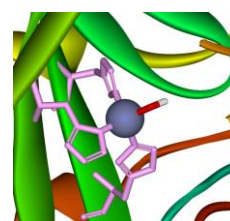
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Examples of Enzymes

- Carbonic anhydrase** catalyzes the reaction of CO_2 with water to form bicarbonate (HCO_3^-), allowing air-breathing organisms to soak up CO_2 from the tissues and release it in the lungs. This also assists in regulating the acidity levels of blood. The active sites of most carbonic anhydrases contain a zinc ion.



Human carbonic anhydrase II

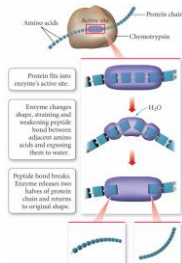
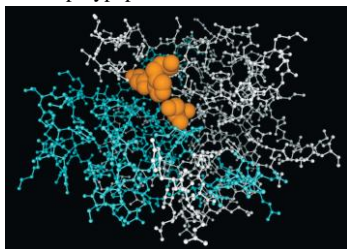


Active site

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Examples of Enzymes

- *Chymotrypsin* is a digestive enzyme secreted by the pancreas into the small intestine that catalyzes the breakdown of proteins (specifically in areas of the protein containing the amino acids tyrosine, tryptophan, or phenylalanine) to form smaller polypeptides and amino acids.

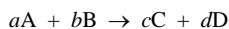


The End



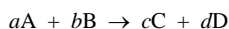
Formula Summary

- For a reaction of the form



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

- For a reaction of the form



the **Rate Law** is: $\text{Rate} = k [A]^m [B]^n$

Formula Summary

- **Integrated Rate Laws:**

– First order:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad t_{1/2} = \frac{\ln 2}{k}$$

– Second order:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad t_{1/2} = \frac{1}{k[A]_0}$$

- **Arrhenius equation:**

$$k = Ae^{-E_a/RT} \quad \ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$