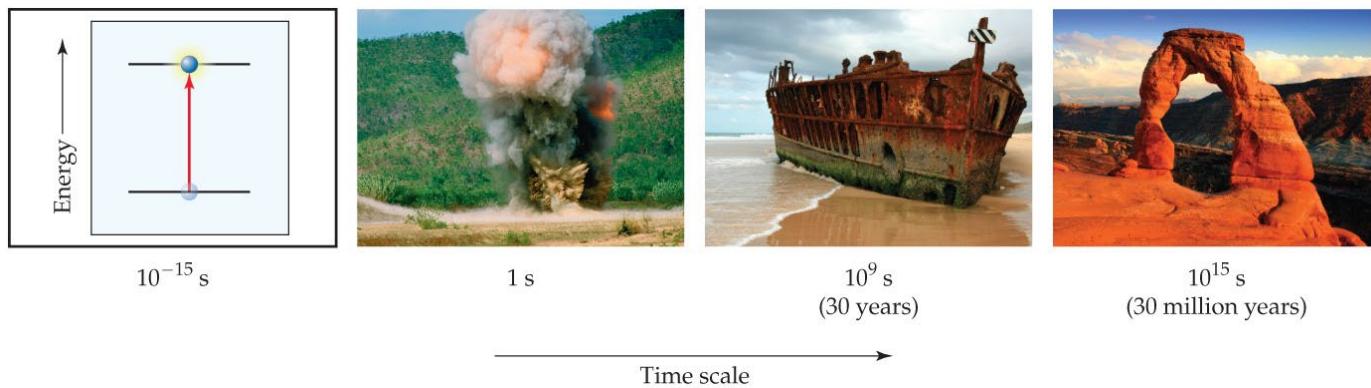


# Lecture Presentation Chapter 14

## Chemical Kinetics

# Chemical Kinetics

- In chemical kinetics we study the rate (or speed) at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism**, a molecular-level view of the path from reactants to products.



Chemical  
Kinetics

# Factors that Affect Reaction Rates

- 1) Physical state of the reactants
- 2) Reactant concentrations
- 3) Reaction temperature
- 4) Presence of a catalyst

# Physical State of the Reactants

- The more readily the reactants collide, the more rapidly they react.
- Homogeneous reactions are often faster.
- Heterogeneous reactions that involve solids are faster if the surface area is increased; i.e., a fine powder reacts faster than a pellet or tablet.

# Reactant Concentrations

- Increasing reactant concentration generally increases reaction rate.
- Since there are more molecules, more collisions occur.



Steel wool heated in air (about 20% O<sub>2</sub>) glows red-hot but oxidizes to Fe<sub>2</sub>O<sub>3</sub> slowly



Red-hot steel wool in 100% O<sub>2</sub> burns vigorously, forming Fe<sub>2</sub>O<sub>3</sub> quickly

# Temperature

- Reaction rate generally increases with increased temperature.
- Kinetic energy of molecules is related to temperature.
- At higher temperatures, molecules move more quickly, increasing numbers of collisions and the energy the molecules possess during the collisions.

# Presence of a Catalyst

- Catalysts affect rate without being in the overall balanced equation.
- Catalysts affect the kinds of collisions, changing the mechanism (individual reactions that are part of the pathway from reactants to products).
- Catalysts are critical in many biological reactions.

# Reaction Rate

- **Rate** is a change in concentration over a time period:  $\Delta[\ ]/\Delta t$ .
- $\Delta$  means “change in.”
- $[ ]$  means molar concentration.
- $t$  represents time.
- Types of rate measured:
  - average rate
  - instantaneous rate
  - initial rate

# Following Reaction Rates



Table 14.1 Rate Data for Reaction of  $\text{C}_4\text{H}_9\text{Cl}$  with Water

| Time, t (s) | [ $\text{C}_4\text{H}_9\text{Cl}$ ] (M) | Average Rate (M/s)     |
|-------------|---|------------------------|
| 0.0         | 0.1000                                  | $1.9 \times 10^{-4}$   |
| 50.0        | 0.0905                                  | $1.7 \times 10^{-4}$   |
| 100.0       | 0.0820                                  | $1.6 \times 10^{-4}$   |
| 150.0       | 0.0741                                  | $1.4 \times 10^{-4}$   |
| 200.0       | 0.0671                                  | $1.22 \times 10^{-4}$  |
| 300.0       | 0.0549                                  | $1.01 \times 10^{-4}$  |
| 400.0       | 0.0448                                  | $0.80 \times 10^{-4}$  |
| 500.0       | 0.0368                                  | $0.560 \times 10^{-4}$ |
| 800.0       | 0.0200                                  |                        |
| 10,000      | 0                                       |                        |

- Rate of a reaction is measured using the concentration of a reactant or a product over time.
- In this example,  $[\text{C}_4\text{H}_9\text{Cl}]$  is followed.

# Following Reaction Rates



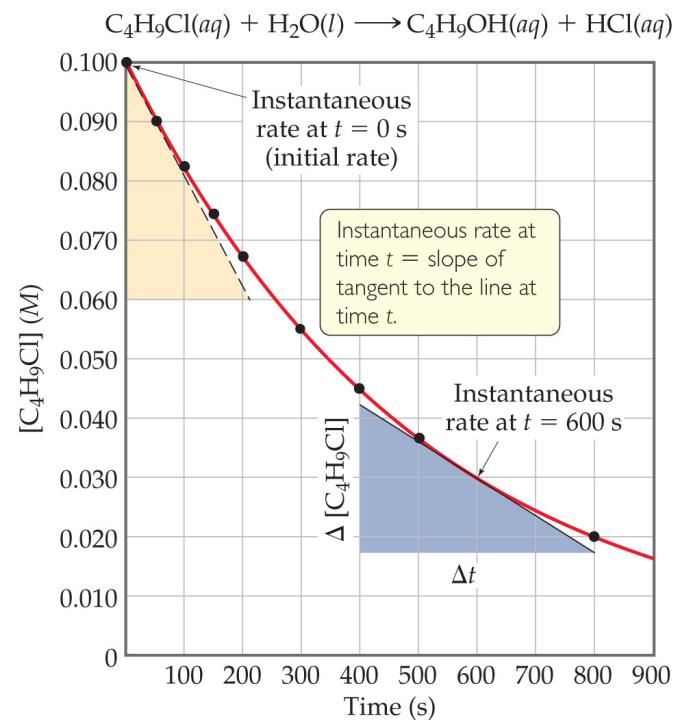
Table 14.1 Rate Data for Reaction of  $\text{C}_4\text{H}_9\text{Cl}$  with Water

| Time, t (s) | [ $\text{C}_4\text{H}_9\text{Cl}$ ] (M) | Average Rate (M/s)     |
|-------------|---|------------------------|
| 0.0         | 0.1000                                  | $1.9 \times 10^{-4}$   |
| 50.0        | 0.0905                                  | $1.7 \times 10^{-4}$   |
| 100.0       | 0.0820                                  | $1.6 \times 10^{-4}$   |
| 150.0       | 0.0741                                  | $1.4 \times 10^{-4}$   |
| 200.0       | 0.0671                                  | $1.22 \times 10^{-4}$  |
| 300.0       | 0.0549                                  | $1.01 \times 10^{-4}$  |
| 400.0       | 0.0448                                  | $0.80 \times 10^{-4}$  |
| 500.0       | 0.0368                                  | $0.560 \times 10^{-4}$ |
| 800.0       | 0.0200                                  |                        |
| 10,000      | 0                                       |                        |

- The average rate is calculated by the  $-(\text{change in } [\text{C}_4\text{H}_9\text{Cl}]) \div (\text{change in time})$ .
- The table shows the average rate for a variety of time intervals.

# Plotting Rate Data

- A plot of the data gives more information about rate.
- The slope of the curve at one point in time gives the **instantaneous rate**.
- The instantaneous rate at time zero is called the **initial rate**; this is often the rate of interest to chemists.
- This figure shows instantaneous and initial rate of the earlier example.



Note: Reactions typically slow down over time!

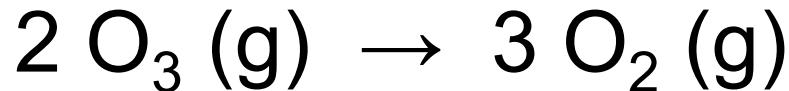
# Relative Rates

- As was said, rates are followed using a reactant or a product. Does this give the same rate for each reactant and product?
- Rate is dependent on stoichiometry.
- If we followed *use* of  $\text{C}_4\text{H}_9\text{Cl}$  and compared it to *production* of  $\text{C}_4\text{H}_9\text{OH}$ , the values would be the same. Note that the *change* would have opposite signs—one goes down in value, the other goes up.

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

# Relative Rates and Stoichiometry

- What if the equation is *not* 1:1?
- What will the relative rates be for:



$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

# Determining Concentration Effect on Rate

- How do we determine what effect the concentration of each reactant has on the rate of the reaction?
- We keep every concentration constant *except* for one reactant and see what happens to the rate. *Then*, we change a different reactant. We do this until we have seen how *each* reactant has affected the rate.

# An Example of How Concentration Affects Rate

- Experiments 1–3 show how  $[\text{NH}_4^+]$  affects rate.
- Experiments 4–6 show how  $[\text{NO}_2^-]$  affects rate.
- Result: The **rate law**, which shows the relationship between rate and concentration for all reactants:

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

Table 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

| Experiment Number | Initial $\text{NH}_4^+$ Concentration (M) | Initial $\text{NO}_2^-$ Concentration (M) | Observed Initial Rate (M/s) |
|-------------------|---|---|-----------------------------|
| 1                 | 0.0100                                    | 0.200                                     | $5.4 \times 10^{-7}$        |
| 2                 | 0.0200                                    | 0.200                                     | $10.8 \times 10^{-7}$       |
| 3                 | 0.0400                                    | 0.200                                     | $21.5 \times 10^{-7}$       |
| 4                 | 0.200                                     | 0.0202                                    | $10.8 \times 10^{-7}$       |
| 5                 | 0.200                                     | 0.0404                                    | $21.6 \times 10^{-7}$       |
| 6                 | 0.200                                     | 0.0808                                    | $43.3 \times 10^{-7}$       |

The data in the table below were obtained for the reaction:



| Experiment Number | [A] (M) | [B] (M) | Initial Rate (M/s) |
|-------------------|---------|---------|--------------------|
| 1                 | 0.273   | 0.763   | 2.83               |
| 2                 | 0.273   | 1.526   | 2.83               |
| 3                 | 0.819   | 0.763   | 25.47              |

5) The rate law for this reaction is rate = \_\_\_\_\_.

- A)  $k[\text{A}][\text{B}]$
- B)  $k[\text{P}]$
- C)  $k[\text{A}]^2[\text{B}]$
- D)  $k[\text{A}]^2[\text{B}]^2$
- E)  $k[\text{A}]^2$

# More about Rate Law

- The exponents tell the **order** of the reaction with respect to each reactant.
- In our example from the last slide:

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

- The order with respect to each reactant is 1. (It is *first order* in  $\text{NH}_4^+$  and  $\text{NO}_2^-$ .)
- The *reaction is second order* ( $1 + 1 = 2$ ; we just add up all of the reactants' orders to get the reaction's order).
- What is  $k$ ? It is the **rate constant**. It is a temperature-dependent quantity.

# First Order Reactions

- Some rates depend *only* on one reactant to the first power.
- These are *first order* reactions.
- The rate law becomes:

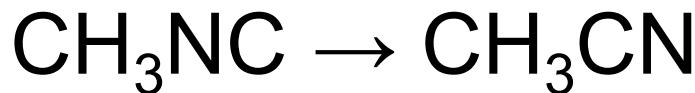
$$\text{Rate} = k [A]$$

# Relating k to [A] in a First Order Reaction

- $\text{rate} = k [A]$
- $\text{rate} = -\Delta [A] / \Delta t$
- So:  $k [A] = -\Delta [A] / \Delta t$
- Rearrange to:  $\Delta [A] / [A] = -k \Delta t$
- Integrate:  $\ln ([A] / [A]_o) = -k t$
- Rearrange:  $\ln [A] = -k t + \ln [A]_o$
- Note: this follows the equation of a line:  
 $y = m x + b$
- So, a plot of  $\ln [A]$  vs.  $t$  is linear.

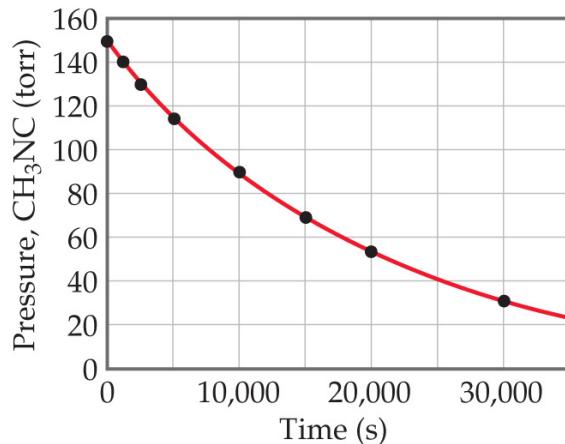
# An Example: Conversion of Methyl Isonitrile to Acetonitrile

- The equation for the reaction:

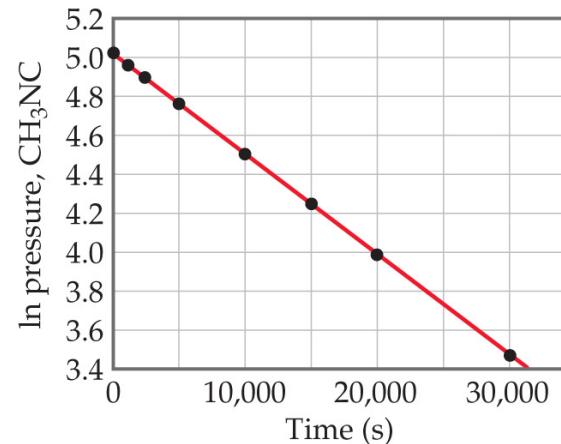


- It is first order.

$$\text{Rate} = k [\text{CH}_3\text{NC}]$$



(a)



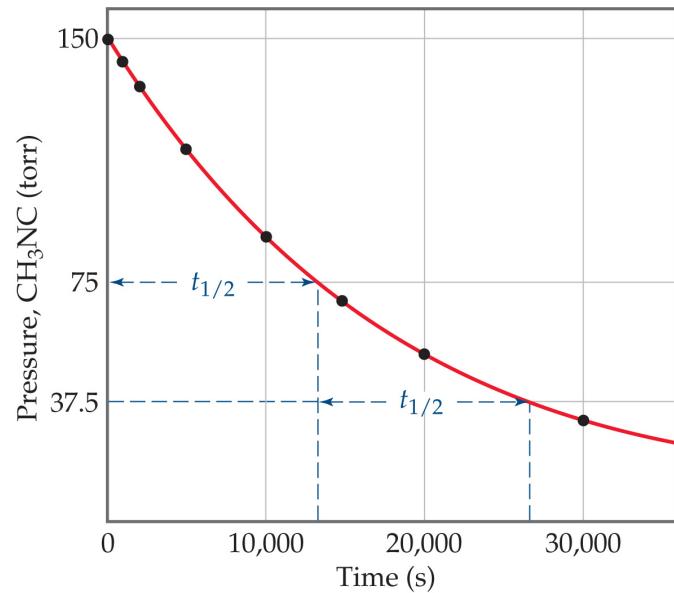
(b)

# Finding the Rate Constant, $k$

- Besides using the rate law, we can find the rate constant from the plot of  $\ln [A]$  vs.  $t$ .
- Remember the integrated rate law:
$$\ln [A] = -k t + \ln [A]_0$$
- The plot will give a line. Its slope will equal  $-k$ .

# Half-life

- Definition: The amount of time it takes for one-half of a reactant to be used up in a chemical reaction.
- First Order Reaction:
  - $\ln [A] = -k t + \ln [A]_0$
  - $\ln ([A]_0/2) = -k t_{1/2} + \ln [A]_0$
  - $-\ln ([A]_0/2) + \ln [A]_0 = k t_{1/2}$
  - $\ln ([A]_0 / [A]_0/2) = k t_{1/2}$
  - $\ln 2 = k t_{1/2}$  or  $t_{1/2} = 0.693/k$



# Second Order Reactions

- Some rates depend *only* on a reactant to the second power.
- These are *second order* reactions.
- The rate law becomes:

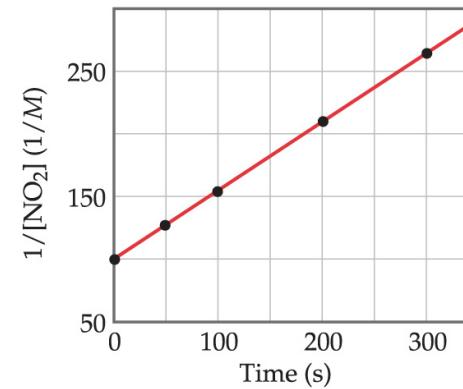
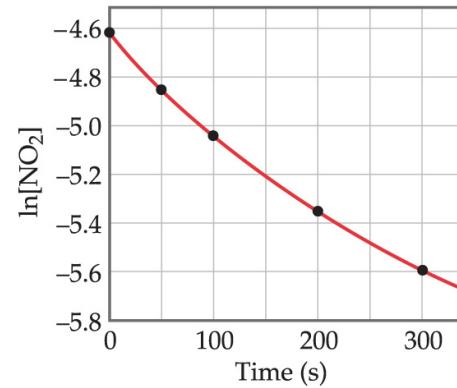
$$\text{Rate} = k [A]^2$$

# Solving the Second Order Reaction for $A \rightarrow$ Products

- rate =  $k [A]^2$
- rate =  $-\Delta [A] / \Delta t$
- So,  $k [A]^2 = -\Delta [A] / \Delta t$
- Rearranging:  $\Delta [A] / [A]^2 = -k \Delta t$
- Using calculus:  $1/[A] = 1/[A]_0 + k t$
- Notice: The linear relationships for first order and second order reactions differ!

# An Example of a Second Order Reaction: Decomposition of $\text{NO}_2$

- A plot following  $\text{NO}_2$  decomposition shows that it must be second order because it is linear for  $1/[\text{NO}_2]$ , *not* linear for  $\ln [\text{NO}_2]$ .
- Equation:

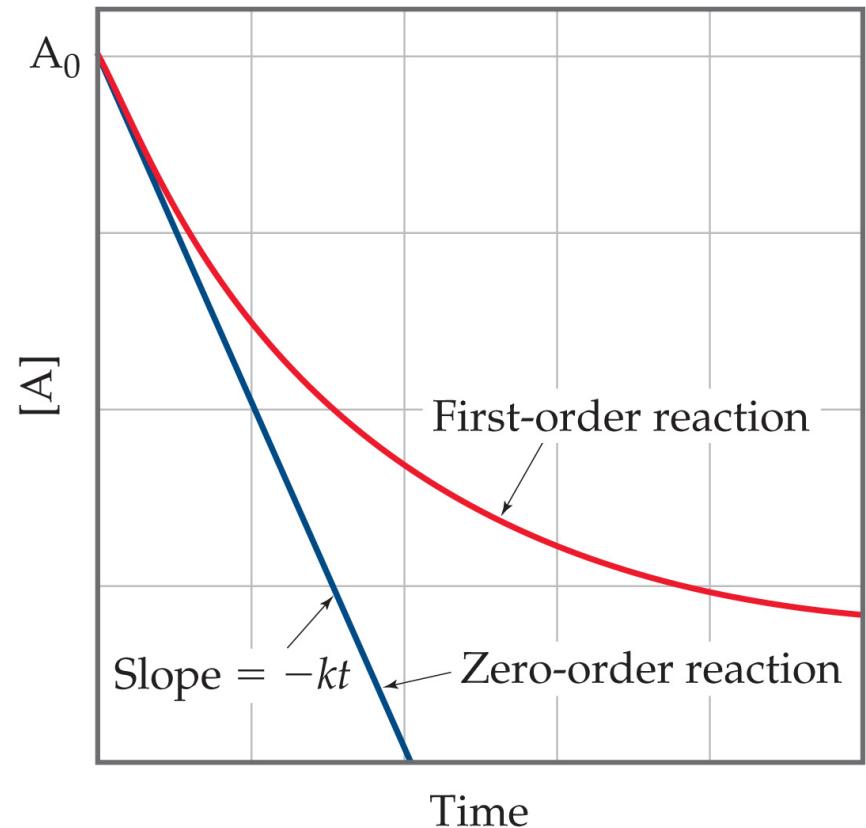


# Half-Life and Second Order Reactions

- Using the integrated rate law, we can see how half-life is derived:
  - $1/[A] = 1/[A]_0 + k t$
  - $1/([A]_0/2) = 1/[A]_0 + k t_{1/2}$
  - $2/[A]_0 - 1/[A]_0 = k t_{1/2}$
  - $t_{1/2} = 1 / (k [A]_0)$
- So, half-life is a concentration dependent quantity for second order reactions!

# Zero Order Reactions

- Occasionally, rate is *independent* of the concentration of the reactant:
- Rate =  $k$
- These are *zero order* reactions.
- These reactions are linear in concentration.

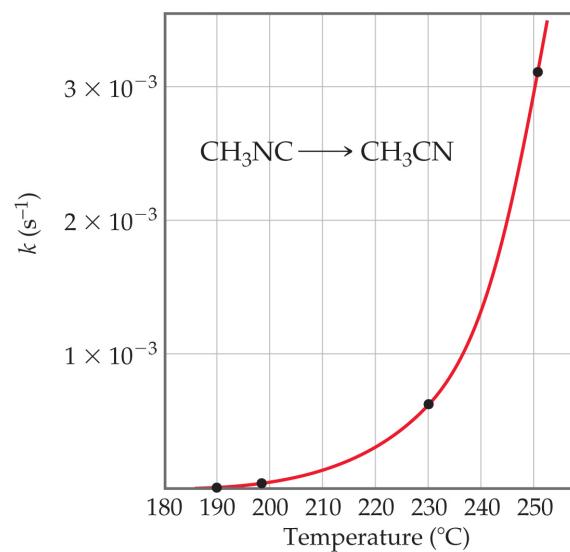
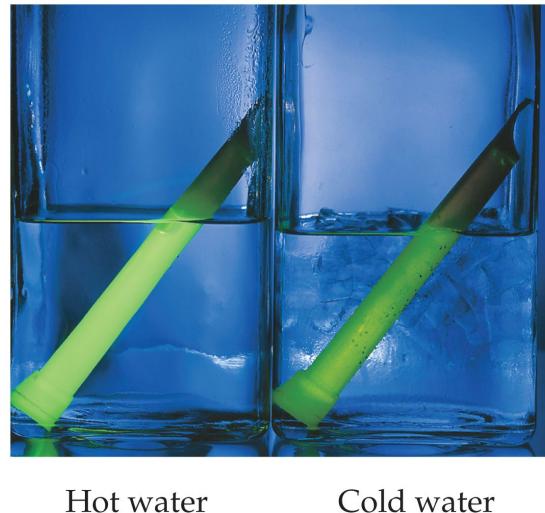


# Factors That Affect Reaction Rate

1. Temperature
2. Frequency of collisions
3. Orientation of molecules
4. Energy needed for the reaction to take place (activation energy)

# Temperature and Rate

- Generally, as temperature increases, rate increases.
- The rate constant is temperature dependent: it increases as temperature increases.
- Rate constant doubles (approximately) with every 10 °C rise.



# Frequency of Collisions

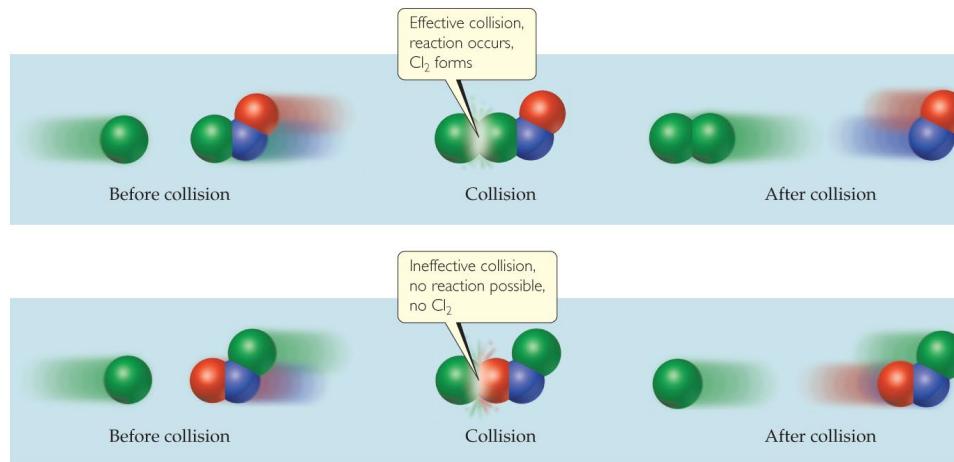
- The **collision model** is based on the kinetic molecular theory.
- Molecules must collide to react.
- If there are more collisions, more reactions can occur.
- So, if there are more molecules, the reaction rate is faster.
- Also, if the temperature is higher, molecules move faster, causing more collisions and a higher rate of reaction.

# The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.

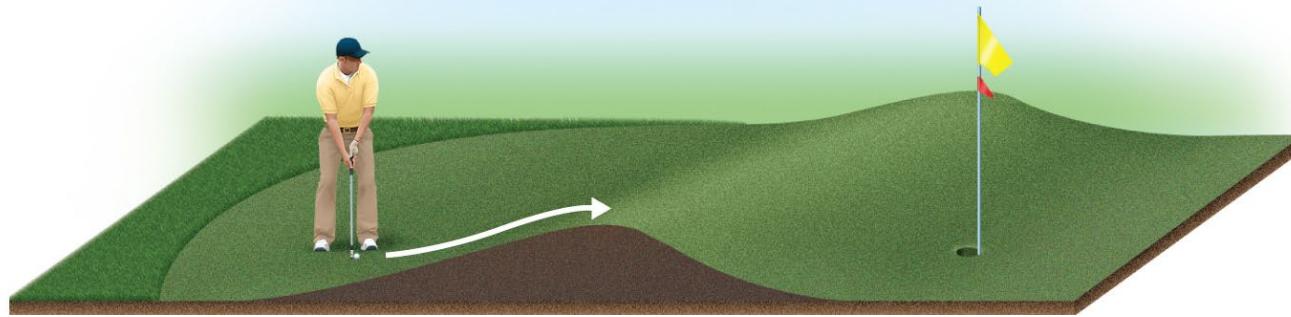
# Orientation of Molecules

- Molecules can often collide without forming products.
- Aligning molecules properly can lead to chemical reactions.
- Bonds must be broken and made and atoms need to be in proper positions.



# Energy Needed for a Reaction to Take Place (Activation Energy)

- The minimum energy needed for a reaction to take place is called **activation energy**.
- An energy barrier must be overcome for a reaction to take place, much like the ball must be hit to overcome the barrier in the figure below.



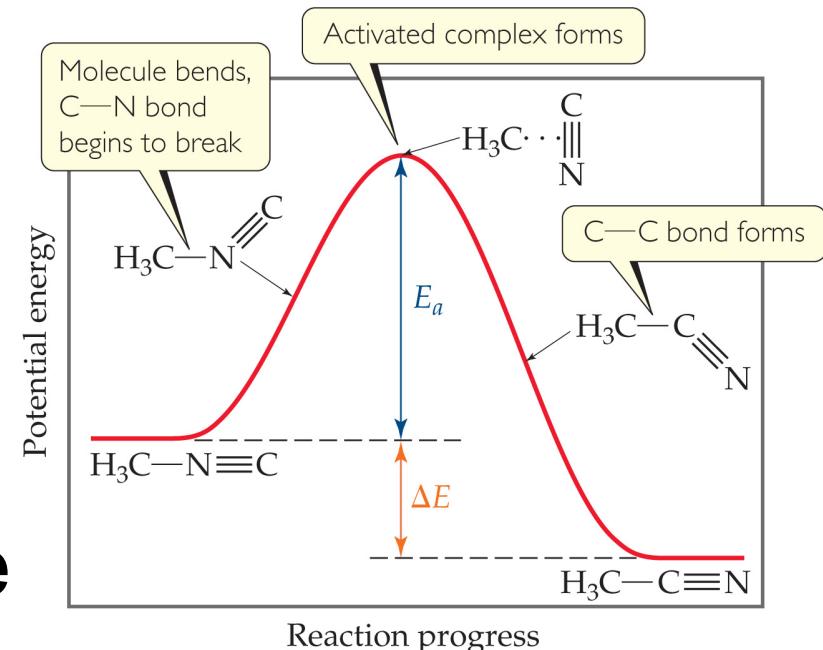
Chemical  
Kinetics

# Transition State (Activated Complex)

- Reactants gain energy as the reaction proceeds until the particles reach the maximum energy state.
- The organization of the atoms at this highest energy state is called the **transition state** (or activated complex).
- The energy needed to form this state is called the *activation energy*.

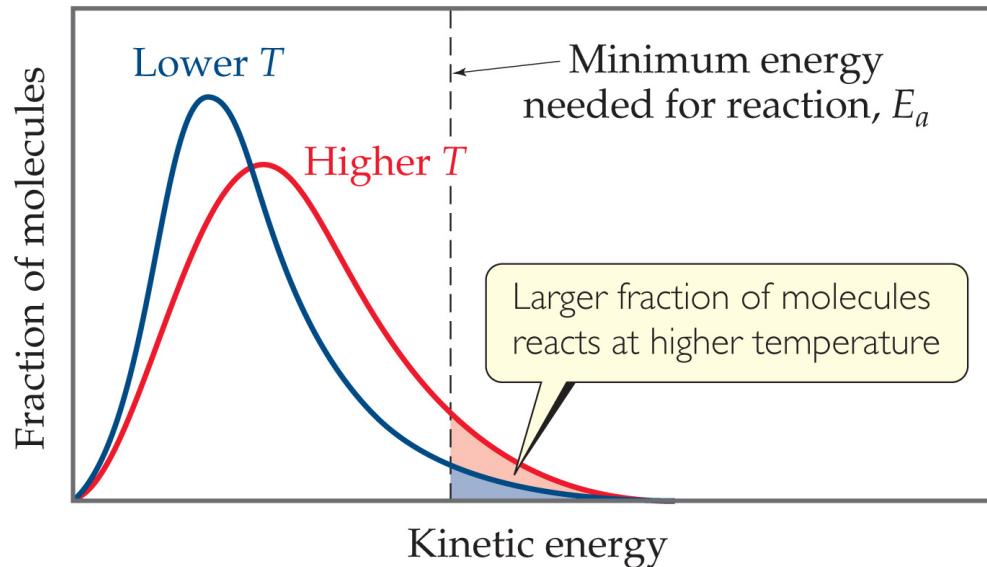
# Reaction Progress

- Plots are made to show the energy possessed by the particles as the reaction proceeds.
- At the highest energy state, the transition state is formed.
- Reactions can be endothermic or exothermic after this.



# Distribution of the Energy of Molecules

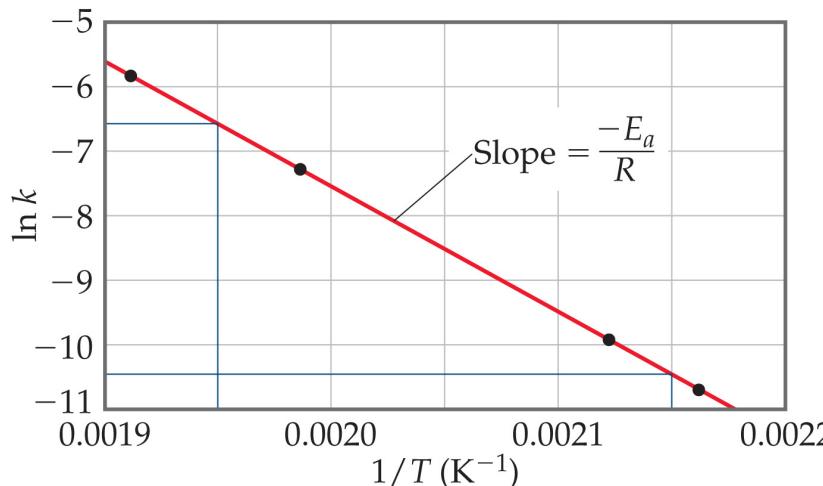
- Gases have an average temperature, but each individual molecule has its own energy.
- At higher energies, more molecules possess the energy needed for the reaction to occur.



# The Relationship Between Activation Energy & Temperature

- Arrhenius noted relationship between activation energy and temperature:  $k = Ae^{-E_a/RT}$
- Activation energy can be determined graphically by reorganizing the equation:  $\ln k = -E_a/RT + \ln A$

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



# Law vs. Theory

- Kinetics gives *what* happens. We call the description the *rate law*.
- *Why* do we observe that rate law? We explain with a *theory* called a **mechanism**.
- A mechanism is a series of stepwise reactions that show how reactants become products.

# Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an **elementary reaction** or **elementary process**.

# Molecularity

Table 14.3 Elementary Reactions and Their Rate Laws

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

The **molecularity** of an elementary reaction tells how many molecules are involved in that step of the mechanism.

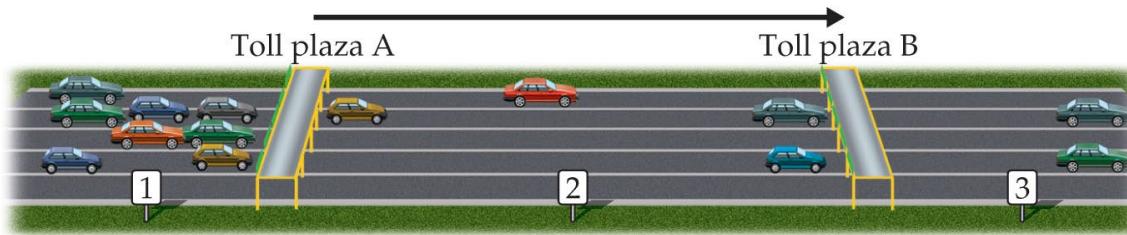
# Termolecular?

- Termolecular steps require three molecules to simultaneously collide with the proper orientation *and* the proper energy.
- These are rare, if they indeed do occur.
- These *must* be slower than unimolecular or bimolecular steps.
- **Nearly all mechanisms use *only* unimolecular or bimolecular reactions.**

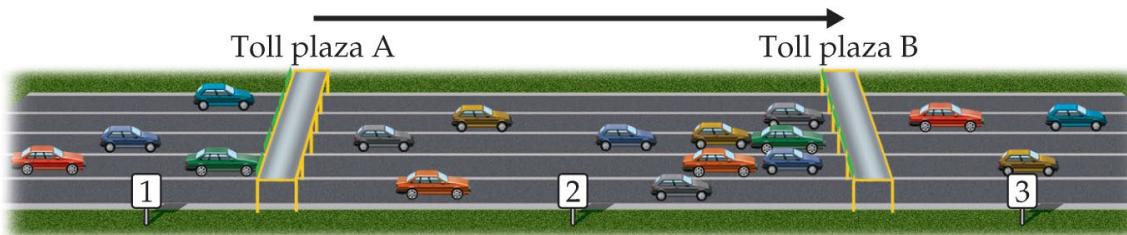


# What Limits the Rate?

- The overall reaction cannot occur faster than the slowest reaction in the mechanism.
- We call that the **rate-determining step**.



(a) Cars slowed at toll plaza A, rate-determining step is passage through A



(b) Cars slowed at toll plaza B, rate-determining step is passage through B

# What is Required of a Plausible Mechanism?

- The *rate law* must be able to be devised from the rate-determining step.
- The *stoichiometry* must be obtained when all steps are added up.
- Each step must balance, like any equation.
- All intermediates are made and used up.
- Any catalyst is used and regenerated.

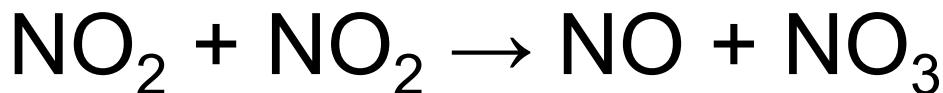
# A Mechanism With a Slow Initial Step

- Overall equation:  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$
- Rate law:  $\text{Rate} = k [\text{NO}_2]^2$
- If the first step is the rate-determining step, the coefficients on the reactants side are the same as the order in the rate law!
- So, the first step of the mechanism begins:

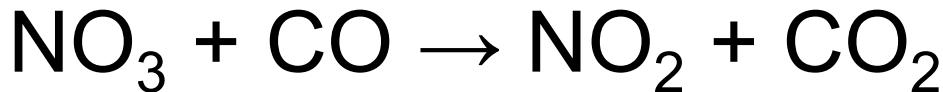


# A Mechanism With a Slow Initial Step (continued)

- The easiest way to complete the first step is to make a product:



- We do not see  $\text{NO}_3$  in the stoichiometry, so it is an **intermediate**, which needs to be used in a faster next step.

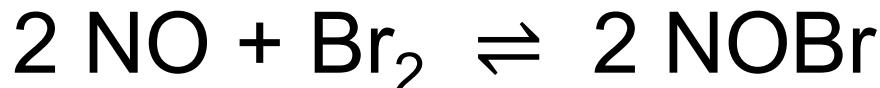


# A Mechanism With a Slow Initial Step (completed)

- Since the first step is the slowest step, it gives the rate law.
- If you add up all of the individual steps (2 of them), you get the stoichiometry.
- Each step balances.
- This is a plausible mechanism.

# A Mechanism With a Fast Initial Step

- Equation for the reaction:



- The rate law for this reaction is found to be

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

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

# A Mechanism With a Fast Initial Step (continued)

- The rate law indicates that a quickly established equilibrium is followed by a slow step.
- Step 1:  $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$
- Step 2:  $\text{NOBr}_2 + \text{NO} \rightarrow 2 \text{NOBr}$

# What is the Rate Law?

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

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

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

# [NOBr<sub>2</sub>] (An Intermediate)?

- NOBr<sub>2</sub> can react two ways:
  - With NO to form NOBr.
  - By decomposition to reform NO and Br<sub>2</sub>.
- The reactants and products of the first step are in equilibrium with each other.
- For an equilibrium (as we will see in the next chapter):

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

# The Rate Law (Finally!)

- Substituting for the forward and reverse rates:

$$k_1 [NO] [Br_2] = k_{-1} [NOBr_2]$$

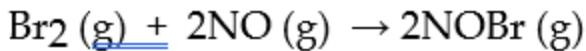
- Solve for  $[NOBr_2]$ , then substitute into the rate law:

$$\text{Rate} = k_2 (k_1/k_{-1}) [NO] [Br_2] [NO]$$

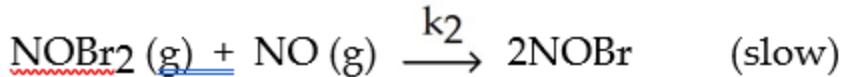
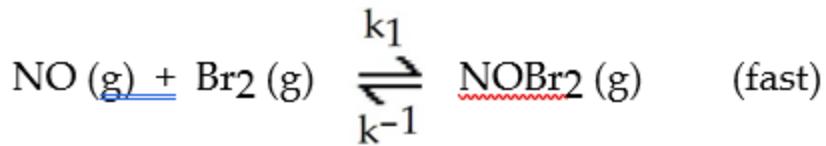
- This gives the observed rate law!

$$\text{Rate} = k [NO]^2 [Br_2]$$

A possible mechanism for the overall reaction



is

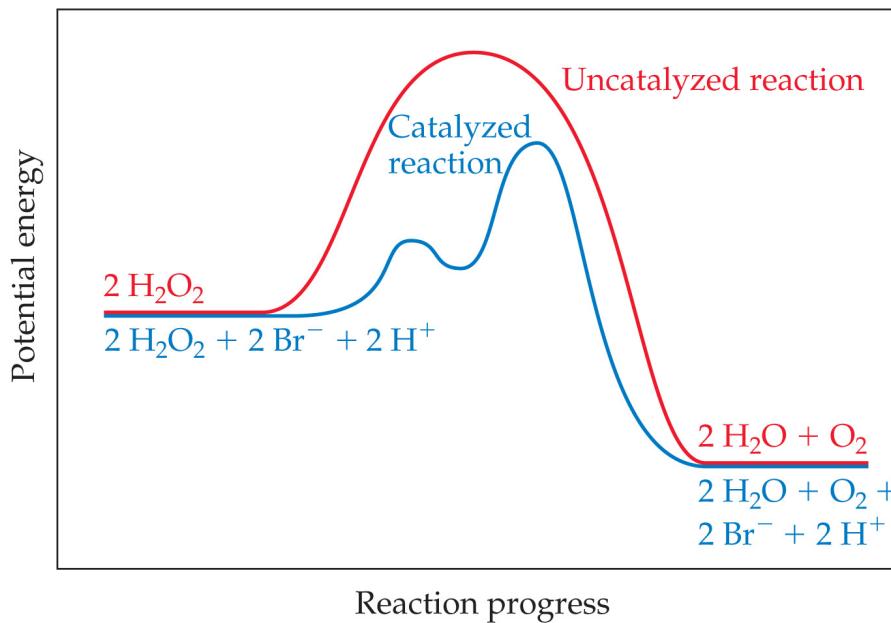


The rate law for formation of NOBr based on this mechanism is rate = \_\_\_\_\_.

- A)  $k_1[\text{NO}]^{1/2}$
- B)  $k_1[\text{Br}_2]^{1/2}$
- C)  $(k_2 k_1 / k^{-1})[\text{NO}]^2 [\text{Br}_2]$
- D)  $(k_1 / k^{-1})^2 [\text{NO}]^2$
- E)  $(k_2 k_1 / k^{-1})[\text{NO}][\text{Br}_2]^2$

# Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.

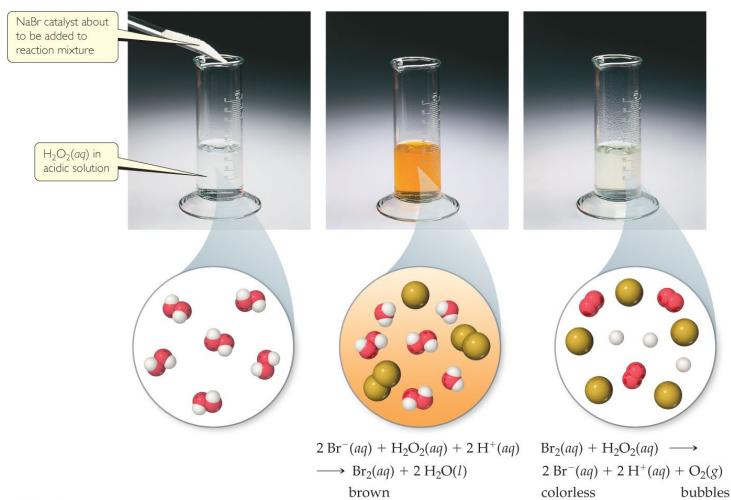


# Types of Catalysts

- 1) Homogeneous catalysts
- 2) Heterogeneous catalysts
- 3) Enzymes

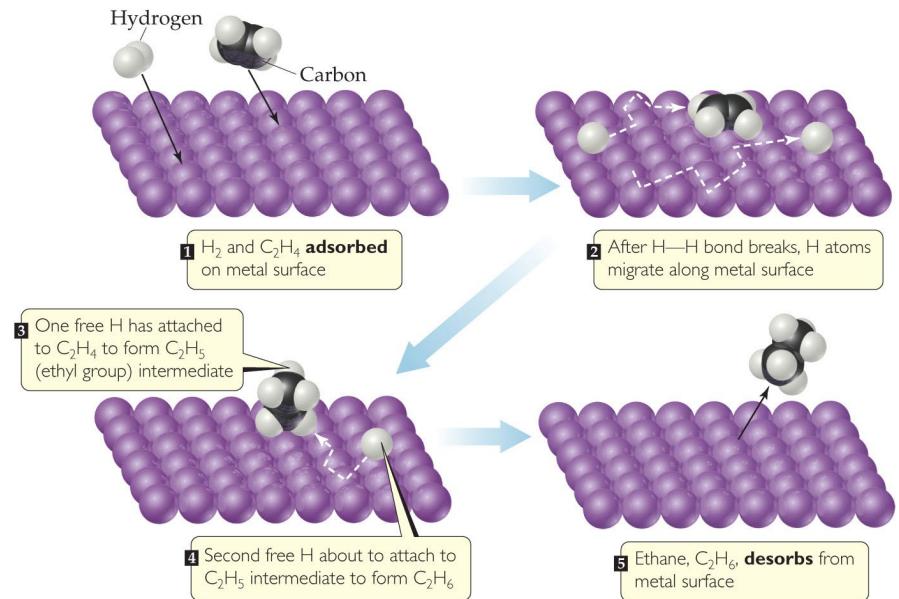
# Homogeneous Catalysts

- The reactants and catalyst are in the same phase.
- Many times, reactants and catalyst are dissolved in the same solvent, as seen below.



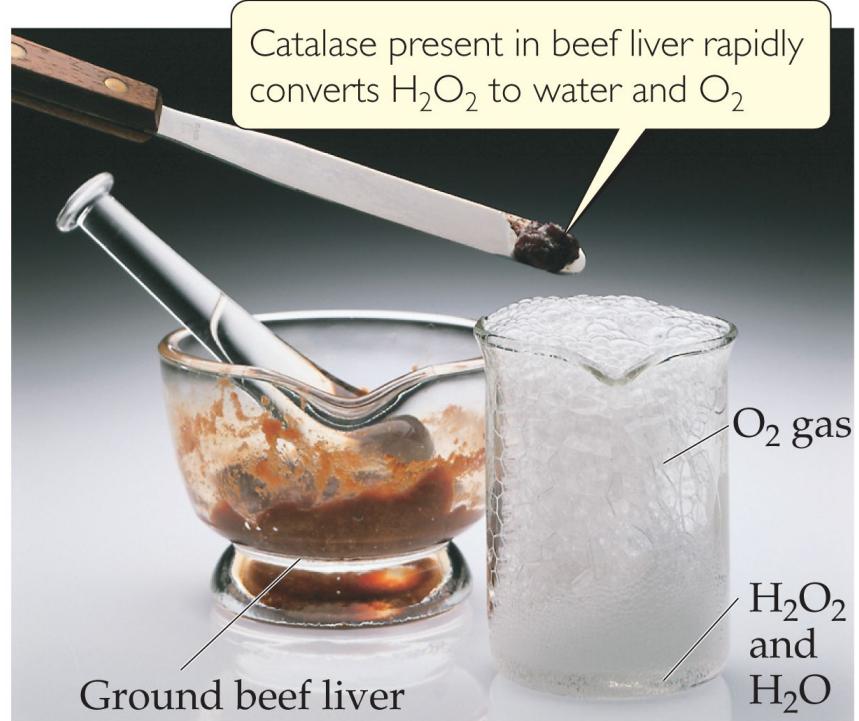
# Heterogeneous Catalysts

- The catalyst is in a different phase than the reactants.
- Often, gases are passed over a solid catalyst.
- The adsorption of the reactants is often the rate-determining step.



# Enzymes

- **Enzymes** are biological catalysts.
- They have a region where the reactants attach. That region is called the **active site**. The reactants are referred to as **substrates**.



# Lock-and-Key Model

- In the enzyme–substrate model, the substrate fits into the active site of an enzyme, much like a key fits into a lock.
- They are specific.

