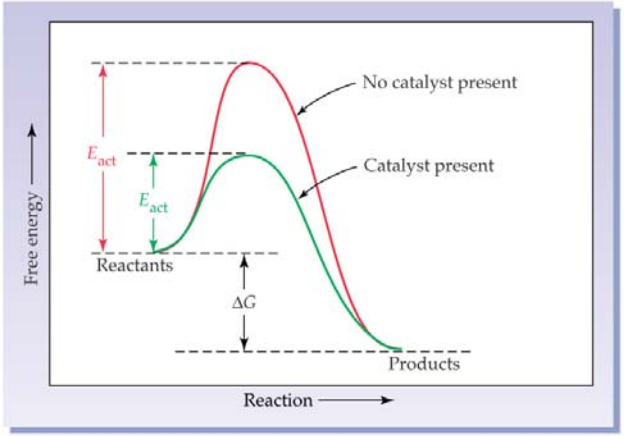


Chapter Seven

Chemical Reactions: Energy, Rates, and Equilibrium

Endothermic vs. Exothermic

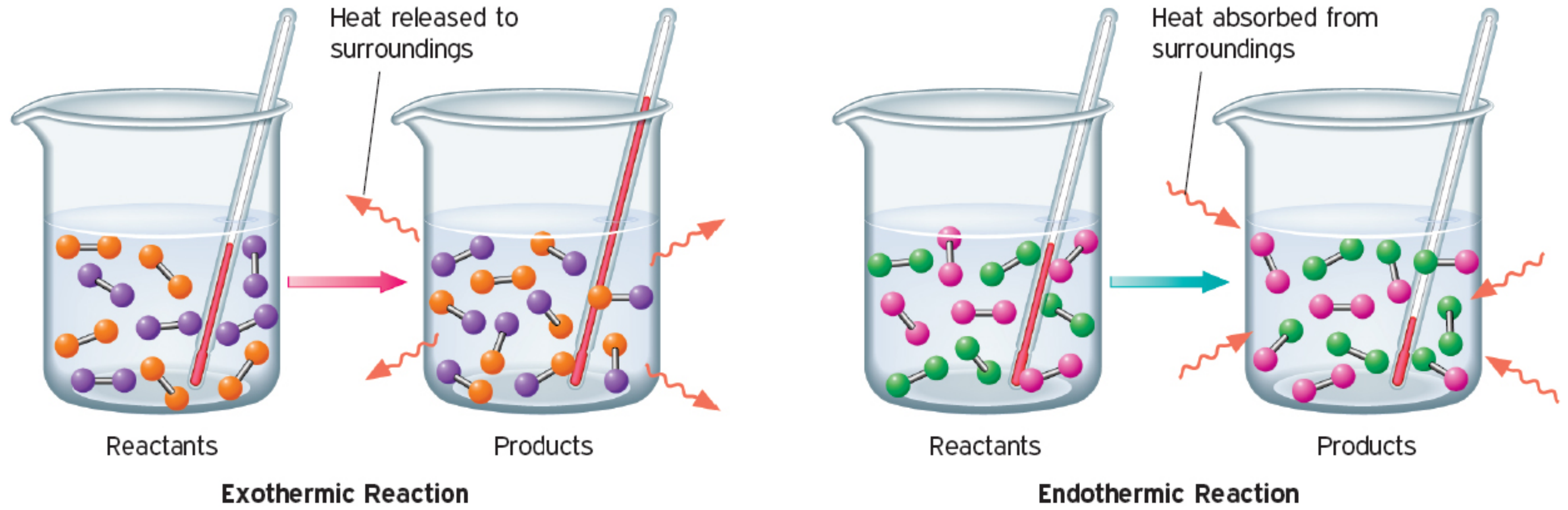


FIGURE 5.8 Reactions can be **exothermic,** releasing heat to the surroundings, or **endothermic,** absorbing heat from the surroundings. Note that this schematic is not to scale.

- ***Endothermic***: A process or reaction that absorbs heat and has a positive ΔH.
- ***Exothermic***: A process or reaction that releases heat and has a negative ΔH.
- ***Law of conservation of energy***: Energy can be neither created nor destroyed in any physical or chemical change.
- ***Heat of reaction***: Represented by ΔH, is the difference between the energy absorbed in breaking bonds and that released in forming bonds. ΔH is also known as enthalpy change.

7.2 Exothermic and Endothermic Reactions

- When the total strength of the bonds formed in the products is greater than the total strength of the bonds broken in the reactants, energy is released and a reaction is *exothermic*. All combustion reactions are exothermic.

An exothermic reaction—negative ΔH

Heat is a product.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) + 213\text{ kcal}$$

or

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -213\text{ kcal/mol}$$

■ When the total energy of the bonds formed in the products is less than the total energy of the bonds broken in the reactants, energy is absorbed and the reaction is endothermic.

An endothermic reaction—positive ΔH

Heat is a reactant.

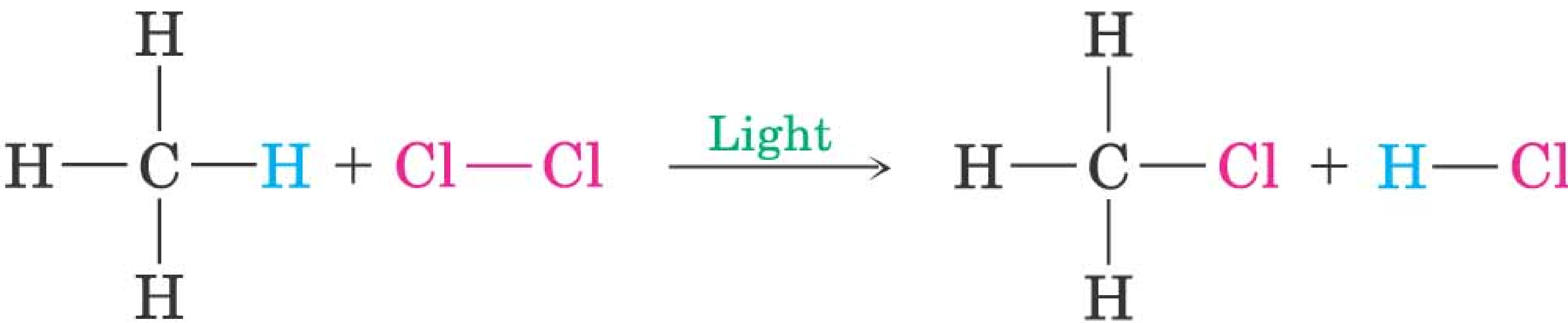
$$N_2(g) + O_2(g) + 43\text{ kcal} \longrightarrow 2\,NO(g)$$

or

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H = +43\text{ kcal/mol}$$

7.1 Heat Changes During Chemical Reactions

- ***Bond dissociation energy***: The amount of energy that must be supplied to break a bond and separate the atoms in an isolated gaseous molecule.
- The triple bond in N_2 has a bond dissociation energy 226 kcal/mole, while the single bond in Cl_2 has a bond dissociation energy 58 kcal/mole

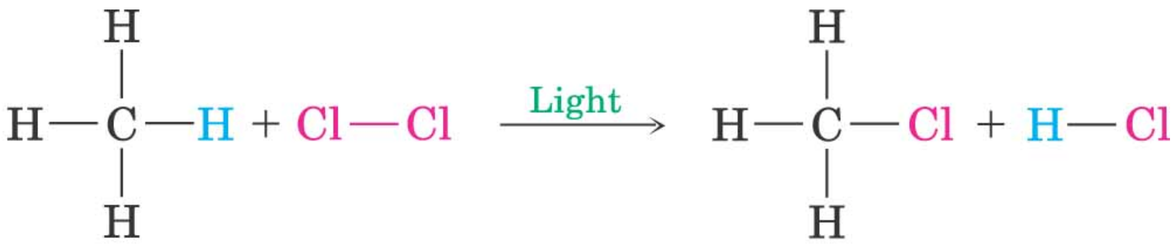


Methane **Chlorine** **Chloromethane**

Describing a Reaction: Bond Dissociation Energies

- Bond dissociation energy (***D***): Heat change that occurs when a bond is broken
- The energy is mostly determined by the type of bond, independent of the molecule
  - The C-H bond in methane requires a net heat input of 105 kcal/mol to be broken at 25 ^{o}C.
- Changes in bonds can be used to calculate net changes in heat

Calculation of an Energy Change from Bond Dissociation Energies



- Addition of Cl-Cl to CH_4
- Breaking: C-H D = 438 kJ/mol
  Cl-Cl D = 243 kJ/mol
- Forming: C-Cl D = 351 kJ/mol
  H-Cl D = 432 kJ/mol

Energy of bonds broken = 438 + 243 = 681 kJ/mol

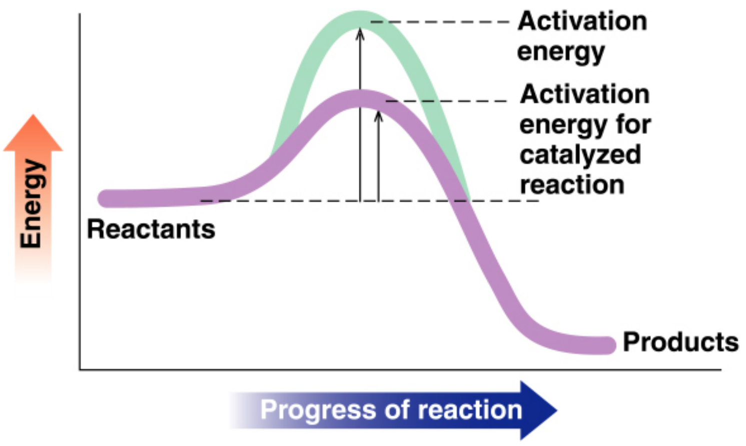
Energy of bonds formed = 351 + 432 = 783 kJ/mol

$\Delta H^o = 681 - 783$ kJ/mol = -102 kJ/mol

Chapter 7 Chemical Reactions

Energy in Chemical Reactions

Rate of Reaction

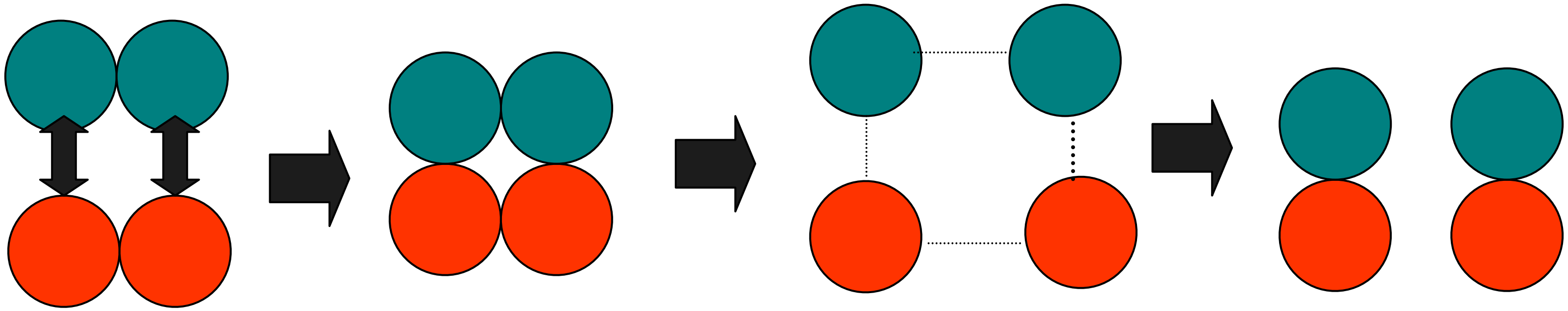


Reaction Conditions

- A chemical reaction occurs when the reacting molecules collide.
- Collisions between molecules must have sufficient energy to break the bonds in the reactants.
- Once the bonds between atoms of the reactants are broken, new bonds can form to give the product.

Chemical Reactions

- In the reaction $H_2 + I_2 \longrightarrow 2\,HI$, the bonds of H_2 and I_2 must break, and bonds for HI must form.



$H_2 + I_2$ collision bonds break 2HI

Exothermic Reaction

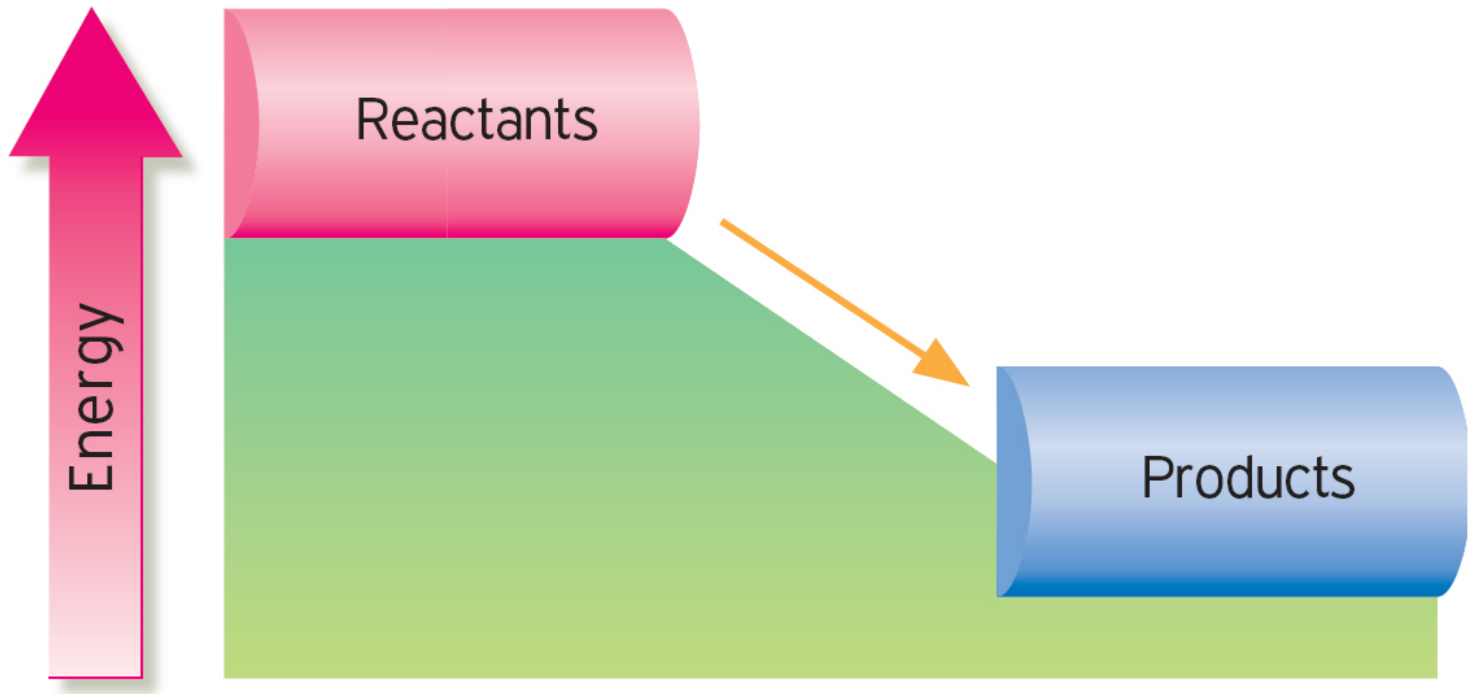


FIGURE 5.4 Chemical reactions tend to occur when substances go downhill in terms of energy.

Low Energy Barrier = Fast Reaction

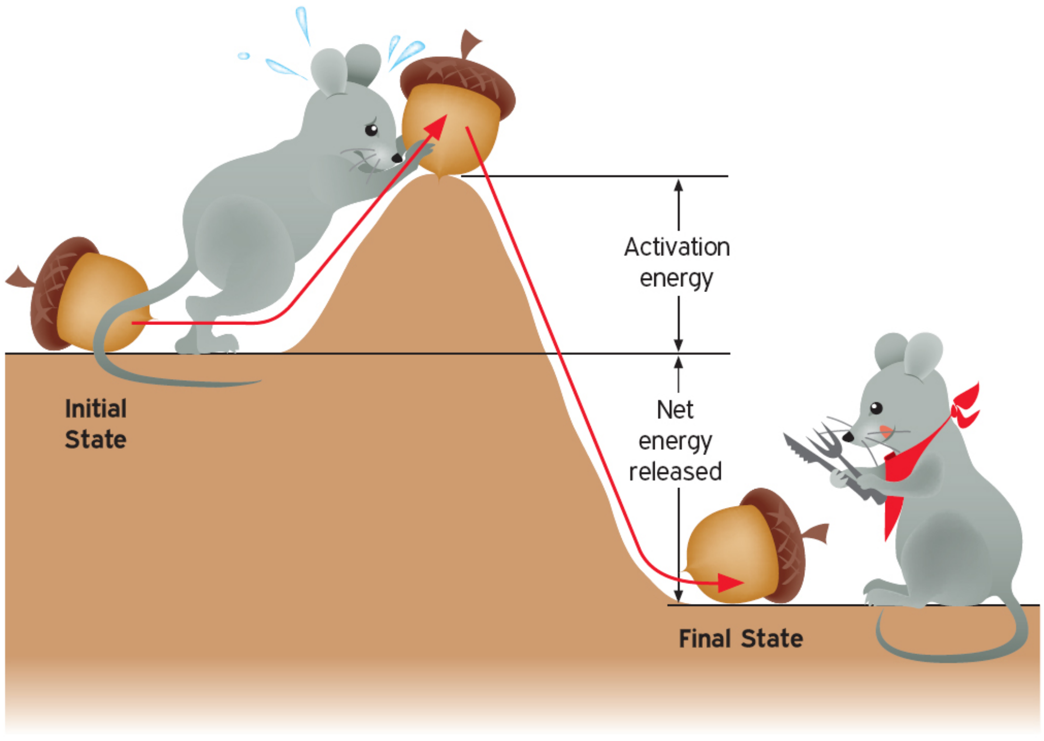
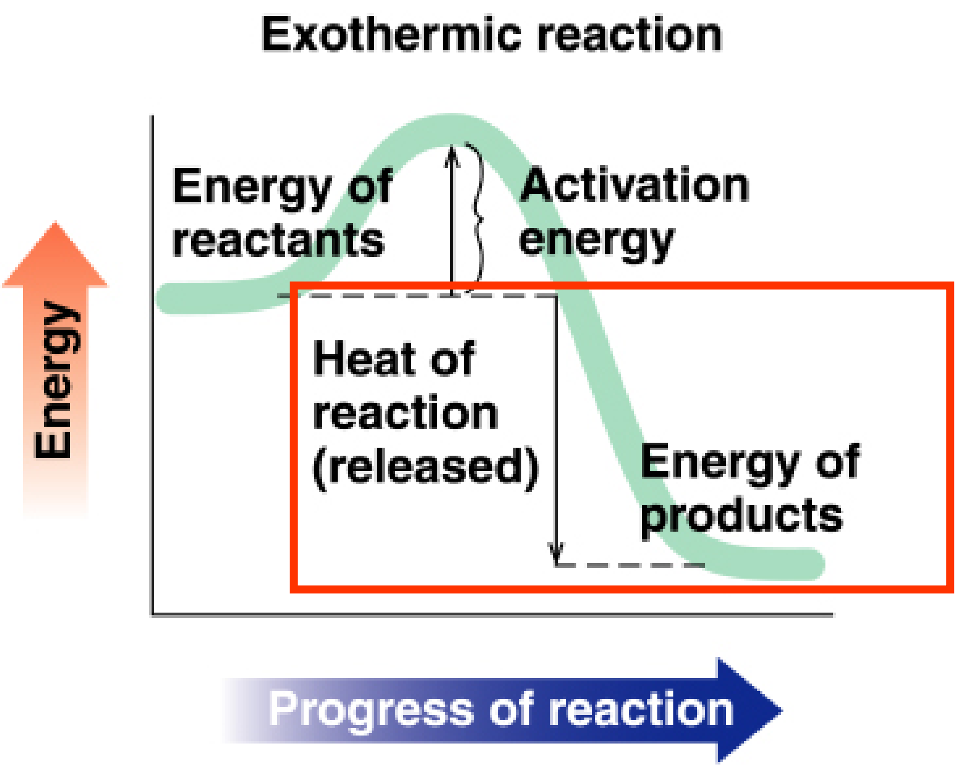


FIGURE 5.16 The activation energy of a chemical reaction is like the hill that this acorn must be hoisted over before it rolls down the mountain. Energy must be supplied to the acorn to get it into position to roll down. Similarly, energy must be supplied to reactants in order for them to "roll downhill" to products.

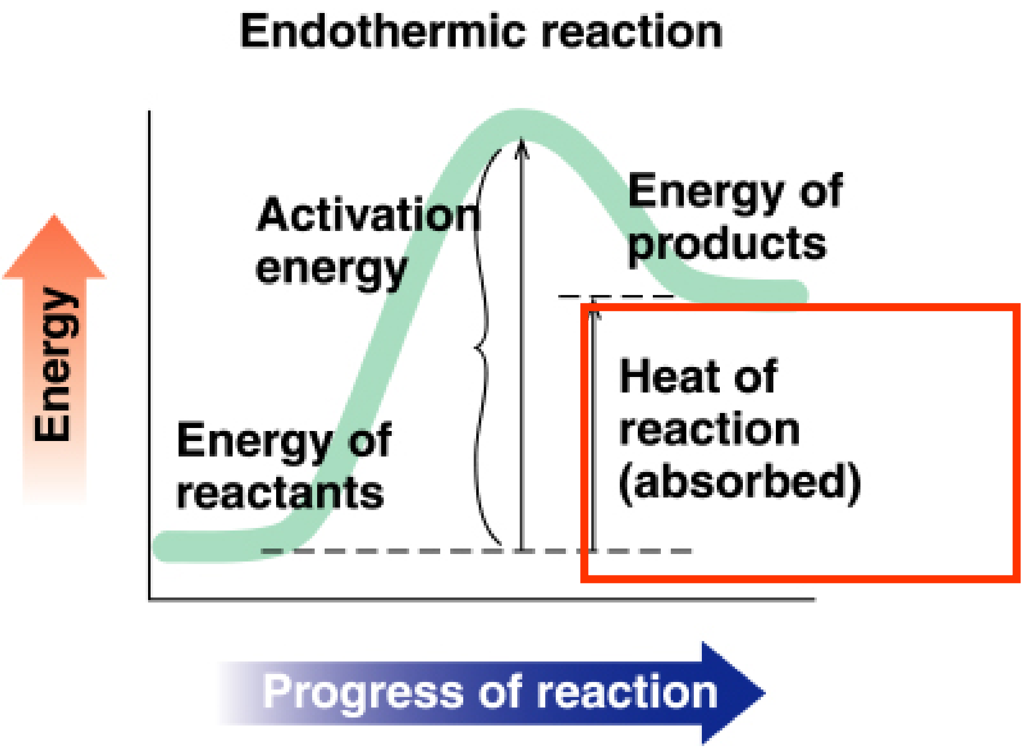
Exothermic Reactions

- The heat of reaction is the difference in the energy of the reactants and the products.
- An exothermic reaction releases heat because the energy of the products is less that the reactants.



Endothermic Reactions

- In an endothermic reaction, heat is absorbed because the energy of the products is greater that that of the reactants.



Learning Check

Identify each reaction as

1) exothermic or 2) endothermic

A. $N_2 + 3H_2 \longrightarrow 2NH_3 + 22\ \text{kcal}$

B. $CaCO_3 + 133\ \text{kcal} \longrightarrow CaO + CO_2$

C. $2SO_2 + O_2 \longrightarrow 2SO_3 + \text{heat}$

Solution

Identify each reaction as

1) exothermic or 2) endothermic

1 A. $N_2 + 3H_2 \longrightarrow 2NH_3 + 22\text{ kcal}$

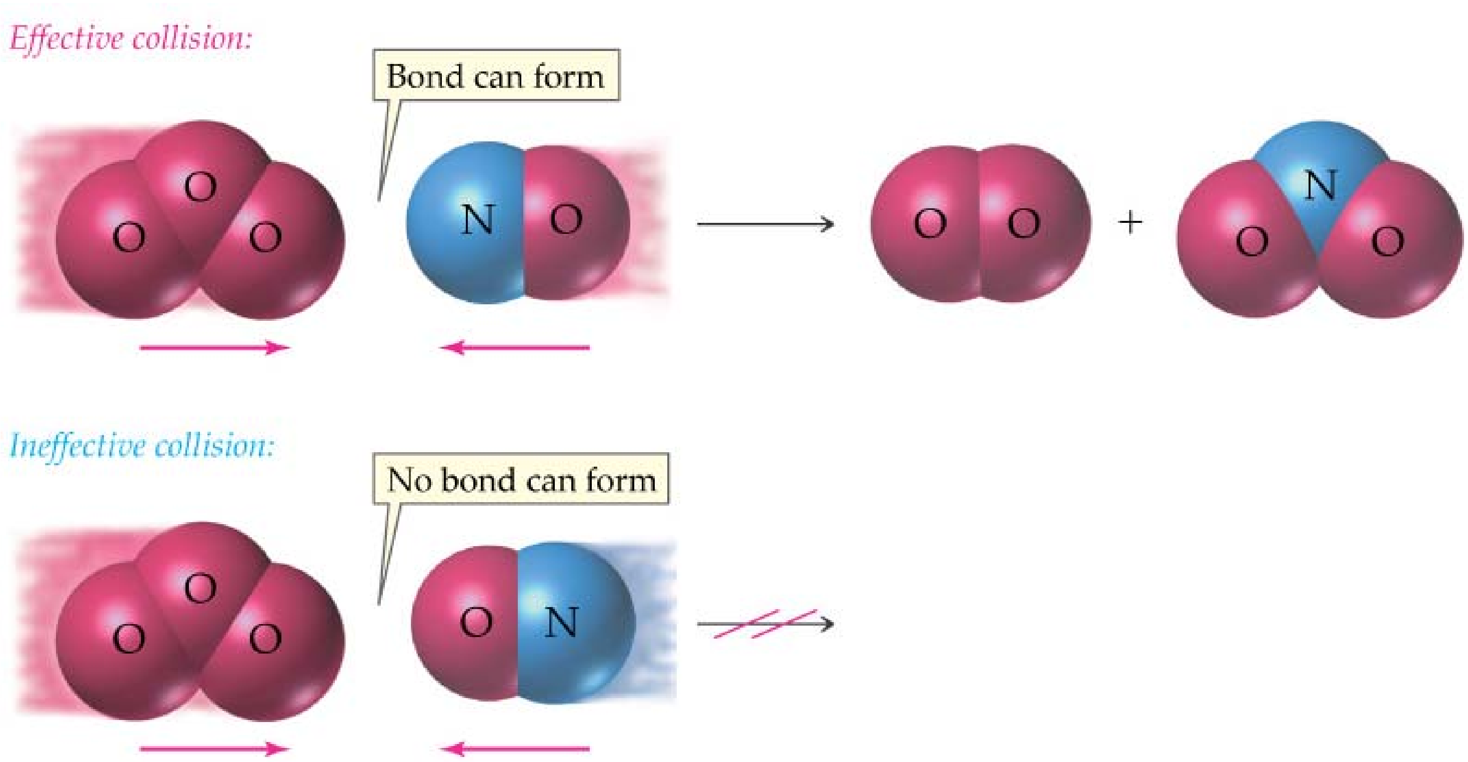
2 B. $CaCO_3 + 133\text{ kcal} \longrightarrow CaO + CO_2$

1 C. $2SO_2 + O_2 \longrightarrow 2SO_3 + \text{heat}$

7.4 How Do Chemical Reactions Occur? Reaction Rates:

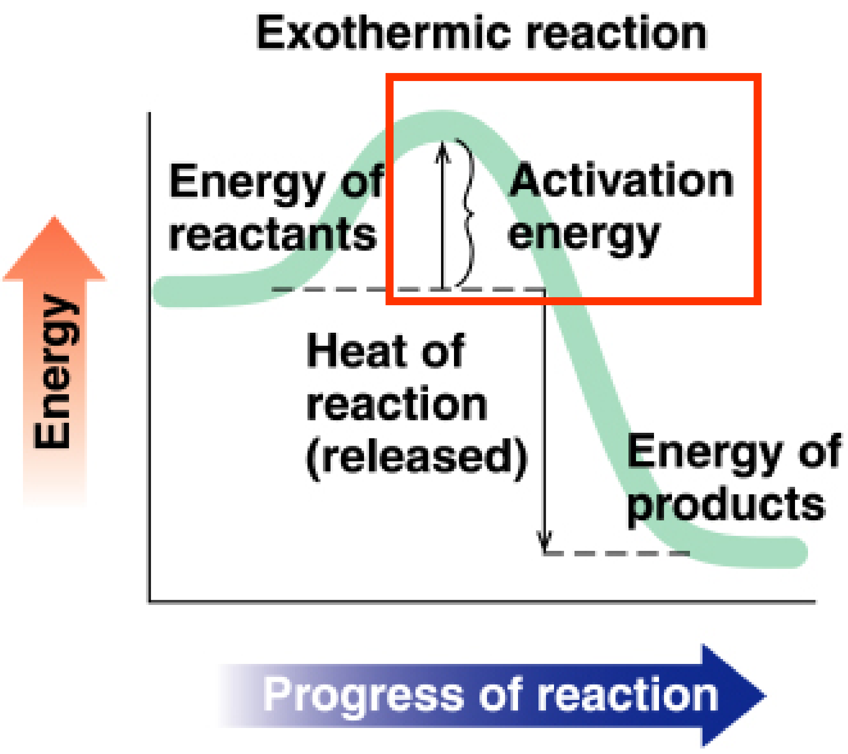
- For a chemical reaction to occur:
- Reactant particle must collide.
- Some chemical bonds have to break.

- Some chemical bonds have to form.
- Not all collision leads to product; only the colliding molecules approaching with right orientation will form bond.



Activation Energy

- The activation energy is the minimum energy needed for a reaction to take place.
- When a collision has the energy that is equal to or greater than the activation energy, reaction can occur.



Rate of Reaction

- **The rate of a reaction is the speed at which product forms.**
- **Adding more of the reactants speeds up a reaction by increasing the number of collisions that occur.**
- **Raising the temperature speeds up a reaction by providing the energy of activation to more colliding molecules.**

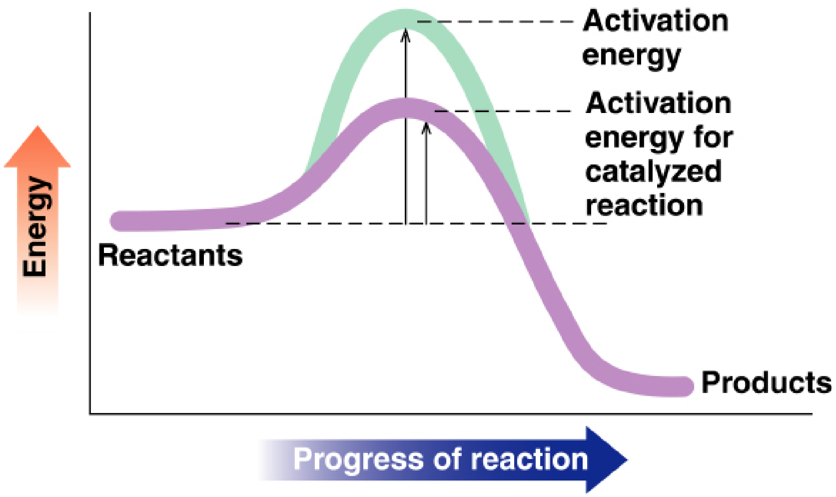
Factors that Increase Rate

Table 6.6 Factors That Increase Reaction Rate

Factor	Reason
More reactants	More collisions
Higher temperature	More collisions, more collisions with energy of activation
Adding a catalyst	Lowers energy of activation

Effect of Catalysts

- A catalyst speeds up the rate of a reaction by lowering the energy of activation.
- Then more collisions can result in reaction and the formation of products.
- A catalyst is not used up during the reaction.



Learning Check

State the effect of each on the rate of reaction.

1) increases rate   2) decreases rate

3) does not change the rate

A. Increasing the temperature.

B. Removing some of the reactants.

C. Adding a catalyst.

D. Placing the reaction flask in ice.

Solution

State the effect of each on the rate of reaction.

1) increases rate 2) decreases rate

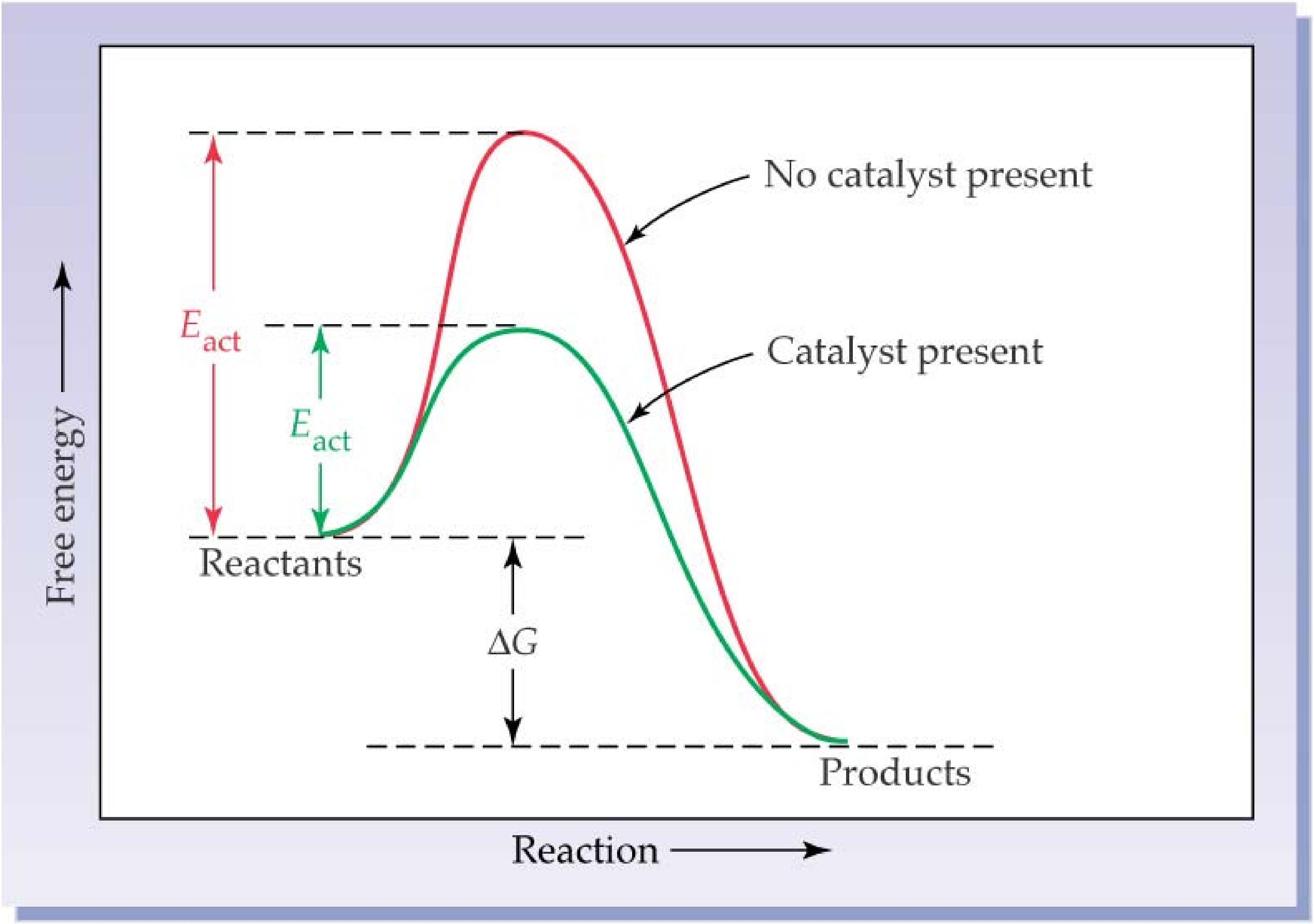
3) does not change the rate

<u> 1 </u>A. Increasing the temperature

<u> 2 </u>B. Removing some of the reactants

<u> 1 </u>C. Adding a catalyst

<u> 2 </u>D. Placing the reaction flask in ice


No catalyst present
Catalyst present
E_{act}
E_{act}
Reactants
ΔG
Products
Free energy
Reaction

1Equilibrium.rm McG 1/4

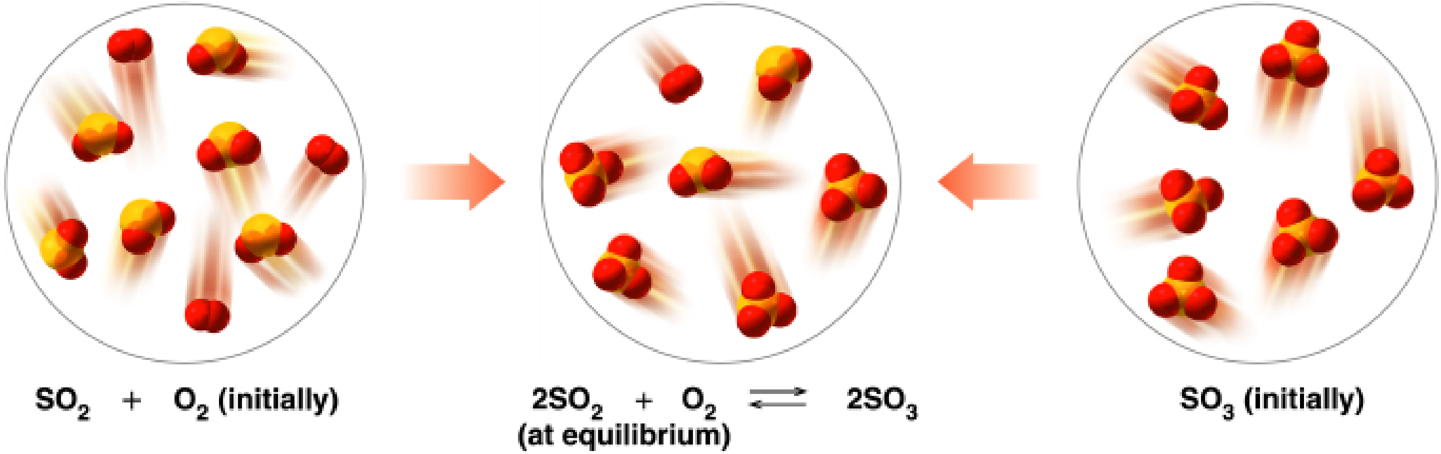
Chemical Equilibrium

In chemical equilibrium

- **The rate of the forward reaction becomes equal to the rate of the reverse reaction.**
- **There is no further change in the amounts of reactant and product.**
- **Reactions continue at equal rates in both directions.**

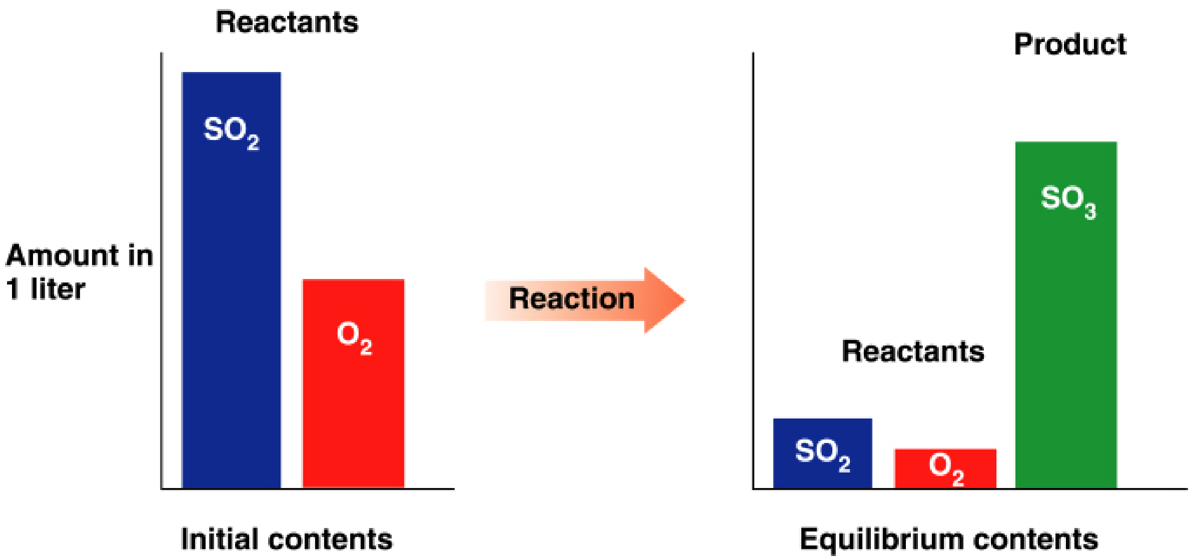
Reaching Chemical Equilibrium

- **A container filled with SO_2 and O_2 or only SO_3 eventually contains mostly SO_3 and small amounts of O_2 and SO_2.**
- **Equilibrium is reached in both situations.**



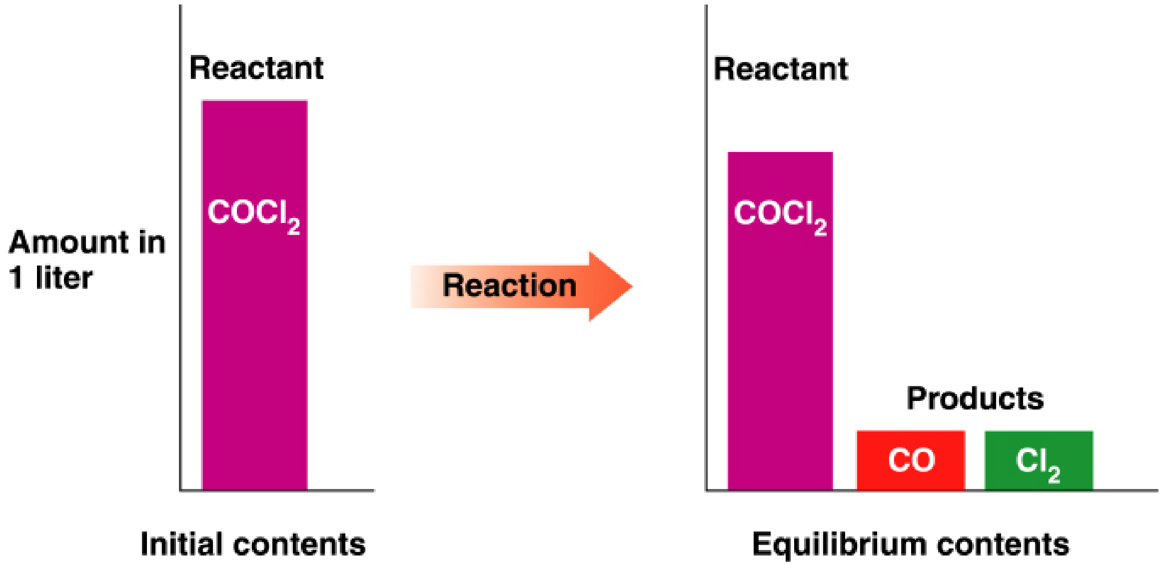
Equilibrium can Favor Product

- **If equilibrium is reached after most of the forward reaction has occurred, the system favors the product.**



Equilibrium Can Favor Reactant

- **If equilibrium is reached when very little of the forward reaction has occurred, the system favors the reactants.**



LeChâtelier's Principle

- For a system at equilibrium, a change in the amounts of reactants or products or the temperature causes stress.
- LeChâtelier's principle states that the equilibrium will shift to relieve the stress.
- That means that the rate of the forward and reverse reaction will change until they are equal again.

Effect of Adding Reactant

- Consider the equilibrium system for the reaction $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$
- If one of the reactants (H_2 or F_2) is added, there is an increase in the number of collisions.
- To remove this stress, the rate of the forward reaction increases and forms more HF product.
- Because more HF is produced, the effect of adding a reactant shifts the equilibrium towards the products.

Effect of Adding Product

- If more of the product HF is added, there is an increase in collisions of HF molecules.
- To remove this stress, the rate of the reverse reaction increases and forms more H_2 and F_2 reactants.
- The effect of adding a product shifts the equilibrium towards the reactants.

Adding H_2

$$H_2(g) \quad + \quad F_2(g) \rightleftharpoons 2HF(g)$$

Adding HF

Effect of Removing Reactant

- If some reactant, H_2 or F_2, is removed, there are fewer collisions between reacting molecules.
- The rate of the forward reaction decreases.
- Removing a reactant shifts the equilibrium towards the reactants.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

Removing H_2 or F_2

Effect of Removing Product

- **If some product HF is removed, the rate of the reverse reaction decreases.**
- **Removing some product shifts the equilibrium towards the products.**

Removing HF

$$H_2(g) \quad + \quad F_2(g) \rightleftharpoons 2HF(g)$$

Effect of Temperature

- When the temperature for an exothermic reaction is lowered (heat removed), the equilibrium shifts towards the products.
- When the temperature of an exothermic reaction is raised (heat added), the equilibrium shifts towards the reactants.

Removing heat $\Rightarrow$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22\ \text{kcal}$$

$\Leftarrow$ Adding heat

Effect of Temperature

- **When the temperature is lowered (heat removed) for an endothermic reaction, the equilibrium shifts towards the reactants.**
- **When the temperature is raised (heat added) for an endothermic reaction, the equilibrium shifts towards the products.**

Adding heat

$$CaCO_3 + 133\ \text{kcal} \rightleftharpoons CaO + CO_2$$

Removing heat

Summary of Changes on Equilibrium

Table 6.7 Effects of Changes on Equilibrium

Factor	Change (stress)	Reaction Favored to Remove Stress
Concentration	Add more reactant	Forward
	Remove reactant	Reverse
	Add product	Reverse
	Remove product	Forward
Temperature	Raise *T* of endothermic reaction	Forward
	Lower *T* of endothermic reaction	Reverse
	Raise *T* of exothermic reaction	Reverse
	Lower *T* of exothermic reaction	Forward

Learning Check

Indicate the effects of the changes on equilibrium for

$$N_2(g) + O_2(g) + \text{heat} \rightleftharpoons 2\,NO(g)$$

1) Shifts towards the products

2) Shifts towards the reactants

A. Adding NO

B. Adding N_2

C. Raising the temperature

D. Removing O_2

Solution

Indicate the effects of the changes on equilibrium for

$N_2(g) + O_2(g) + heat \rightleftharpoons 2\ NO(g)$

1) Shifts towards the products

2) Shifts towards the reactants

2 **A. Adding NO**

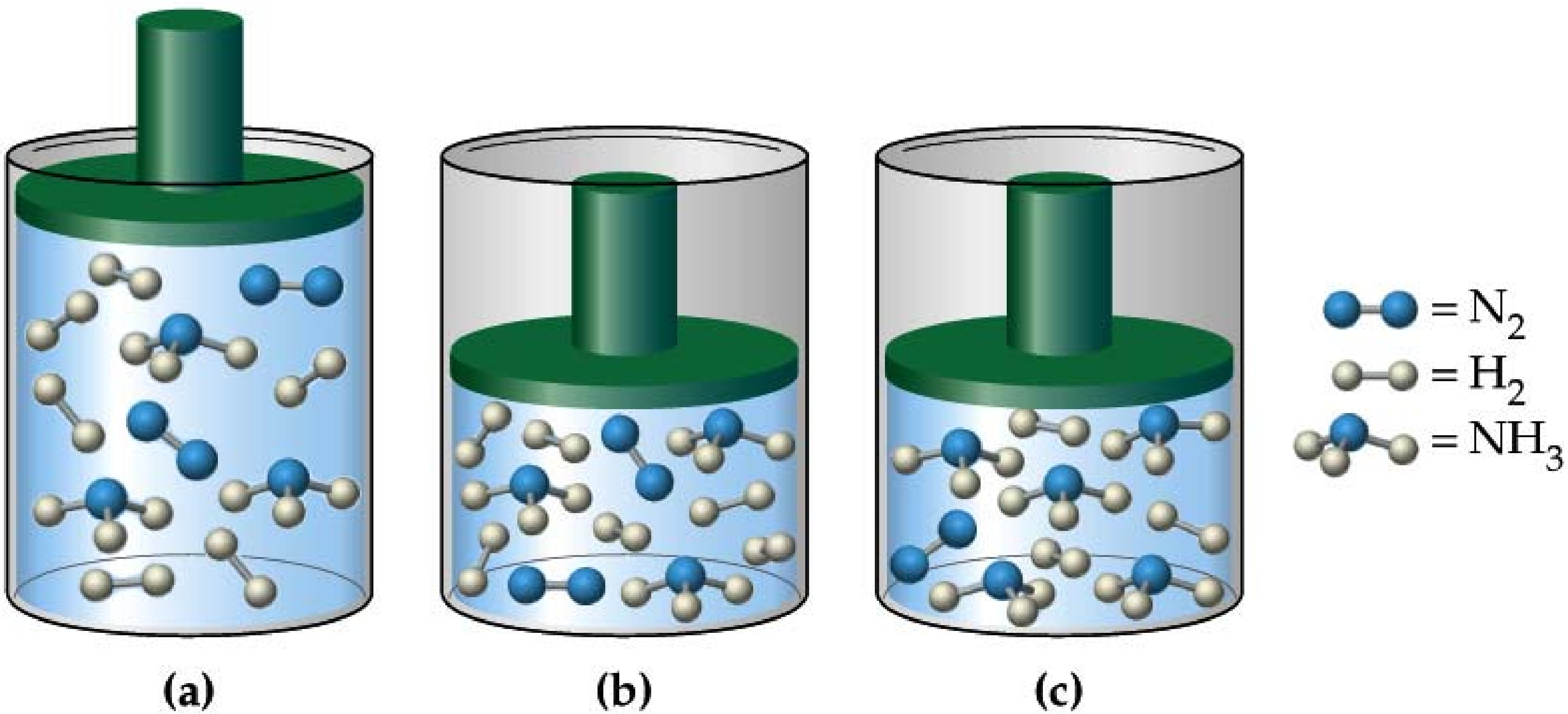
1 **B. Adding N_2**

1 **C. Raising the temperature**

2 **D. Removing O_2**

Increasing the pressure

- $N_2(g)$ + 3 $H_2(g)$ æ 2 $NH_3(g)$ K_c =



- In a reaction where one of the reactants or products is a gas, increase in pressure shifts the equilibrium in the direction that decreases the number of molecules in the gas phase and thus decrease the pressure.

7.8 Equilibrium Equations and Equilibrium Constants

- Consider the following general equilibrium reaction:

$$aA + bB + \ldots \rightarrow mM + nN + \ldots$$

- Where A, B, … are the reactants; M, N, …. Are the products; a, b, ….m, n, …. are coefficients in the balanced equation. At equilibrium, the composition of the reaction mixture obeys an equilibrium equation.

- The equilibrium constant K is the number obtained by multiplying the equilibrium concentrations of the products and dividing by the equilibrium concentrations of the reactants, with the concentration each substance raised to a power equal to its coefficient in the balanced equation.
- The value of K varies with temperature.

Product concentrations

Equilibrium equation $$K = \frac{[M]^m[N]^n \cdots}{[A]^a[B]^b \cdots}$$

Reactant concentrations

Equilibrium constant

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (g) at 74^0C are [CO] = 0.012 M, [Cl_2] = 0.054 M, and [$COCl_2$] = 0.14 M. Calculate the equilibrium constants.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

Chapter Summary

- The strength of a covalent bond is measured by its *bond dissociation energy*.
- For any reaction, the heat released or absorbed by changes in bonding is called the *heat of reaction*, or *enthalpy change*, ΔH.
- *Exothermic reaction*: If there is a net amount of heat released as a result of bond breaking and bond formation. These reactions have positive ΔH.
- *Endothermic reaction*: If there is a net amount of heat absorbed as a result of bond breaking and bond formation. These reactions have negative ΔH.

Chapter Summary Contd.

- Spontaneous reactions have negative *Free energy*.
- Non-spontaneous reactions have positive *Free energy*.
- The exact amount of collision energy for a reaction to take place is called *activation energy*.
- A high activation energy results in a slow reaction.
- A low activation energy results in a fast reaction.
- A reaction that can occur in either the forward or reverse direction is a *reversible reaction.*

Chapter Summary Contd.

- At *equilibrium* the forward and reverse reactions occur at the same rate.
- Rate constant of a reversible reaction allows to predict the extent of equilibrium.
- *Le Chatelier's principle* states that when a stress is applied to a system in equilibrium, the equilibrium shifts to relieve the stress.
- *Le Chatelier's principle* allows prediction of the effects of change in temperature, pressure, and concentration on equilibrium state.

- **End of Chapter 7**

Personal Response System Questions for use with Fundamentals of General, Organic, and Biological Chemistry, 5th ed. Media Update Edition McMurry and Castellion

Chapter 7

When potassium is added to water contained in a beaker, the reaction shown below occurs, and the beaker feels hot to the touch.

$$K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

This reaction is

1. endothermic and $\Delta H = –$
2. endothermic and $\Delta H = +$
3. exothermic and $\Delta H = –$
4. exothermic and $\Delta H = +$

When potassium is added to water contained in a beaker, the reaction shown below occurs, and the beaker feels hot to the touch.

$$K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

This reaction is

1. endothermic and $\Delta H = -$
2. endothermic and $\Delta H = +$
3. exothermic and $\Delta H = -$
4. exothermic and $\Delta H = +$

When potassium is added to water contained in a beaker, the reaction shown below occurs, and the beaker feels hot to the touch.

$$K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

During this reaction

1. entropy decreases and $\Delta S = -$
2. entropy decreases and $\Delta S = +$
3. entropy increases and $\Delta S = -$
4. entropy increases and $\Delta S = +$

When potassium is added to water contained in a beaker, the reaction shown below occurs, and the beaker feels hot to the touch.

$$K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

During this reaction

1. entropy decreases and $\Delta S = –$
2. entropy decreases and $\Delta S = +$
3. entropy increases and $\Delta S = –$
4. entropy increases and $\Delta S = +$

When potassium is added to water contained in a beaker, the reaction shown below occurs, and the beaker feels hot to the touch.

$$K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

This reaction is

1. nonspontaneous and $\Delta G = –$
2. nonspontaneous and $\Delta G = +$
3. spontaneous and $\Delta G = –$
4. spontaneous and $\Delta G = +$

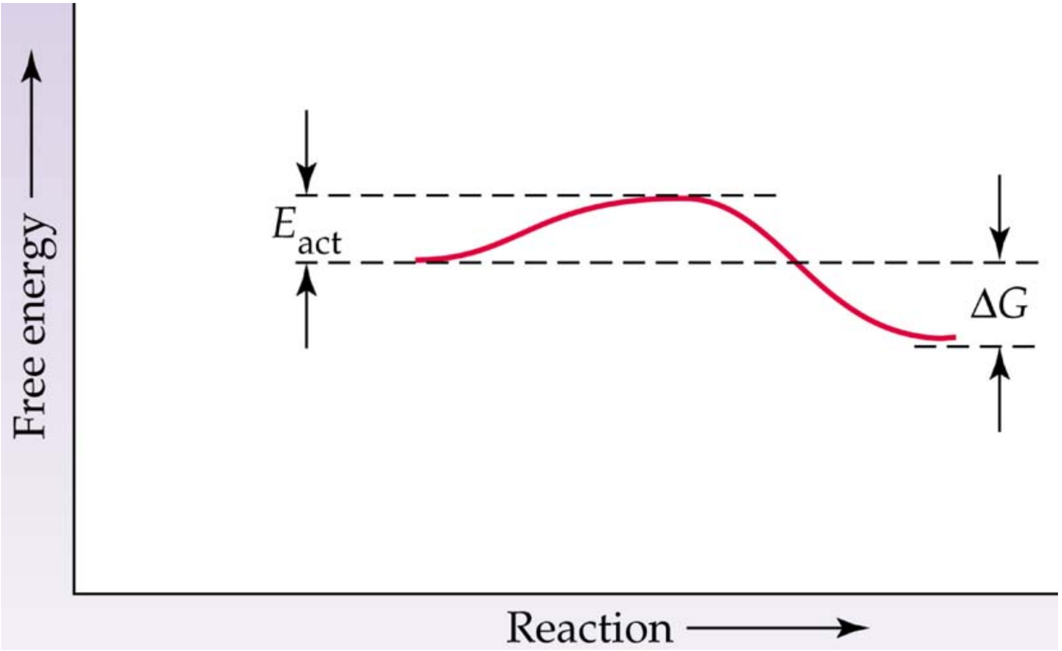
When potassium is added to water contained in a beaker, the reaction shown below occurs, and the beaker feels hot to the touch.

$$K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$$

This reaction is

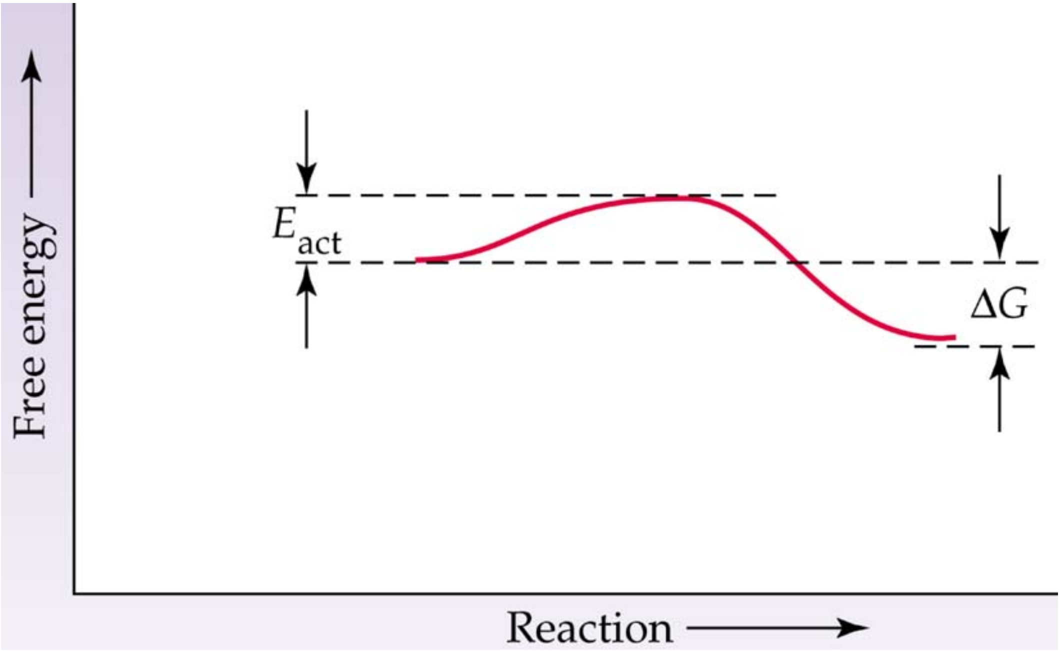
1. nonspontaneous and ΔG = –
2. nonspontaneous and ΔG = +
3. spontaneous and ΔG = –
4. spontaneous and ΔG = +

Shown is an energy diagram for a reaction with a small activation energy and products having less energy than reactants. This reaction is



1. nonspontaneous and fast.
2. nonspontaneous and slow.
3. spontaneous and fast.
4. spontaneous and slow.

Shown is an energy diagram for a reaction with a small activation energy and products having less energy than reactants. This reaction is



1. nonspontaneous and fast.
2. nonspontaneous and slow.
3. spontaneous and fast.
4. spontaneous and slow.

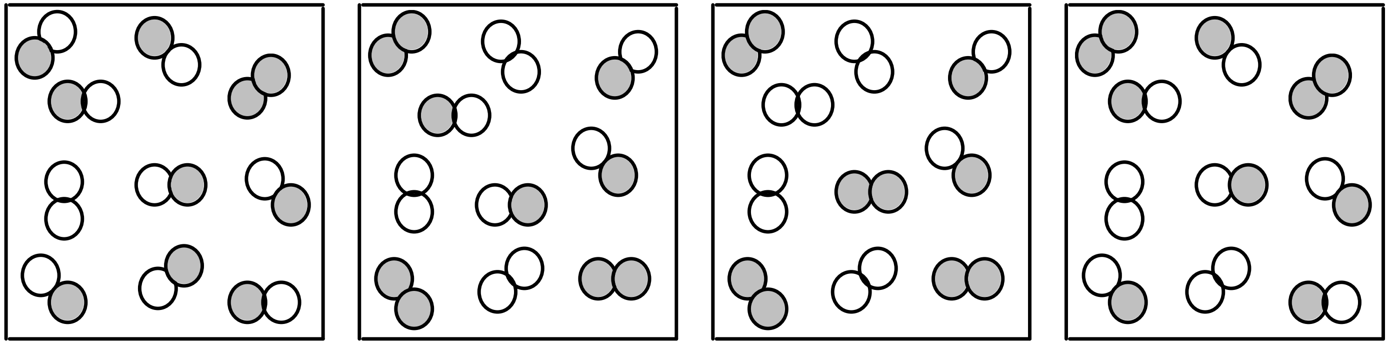
When a catalyst is added to a reaction to increase its rate of reaction the

1. activation energy is lowered and ΔG becomes more negative.
2. activation energy is lowered and ΔG remains unchanged.
3. activation energy is raised and ΔG becomes more positive.
4. activation energy is raised and ΔG remains unchanged.

When a catalyst is added to a reaction to increase its rate of reaction the

1. activation energy is lowered and ΔG becomes more negative.
2. activation energy is lowered and ΔG remains unchanged.
3. activation energy is raised and ΔG becomes more positive.
4. activation energy is raised and ΔG remains unchanged.

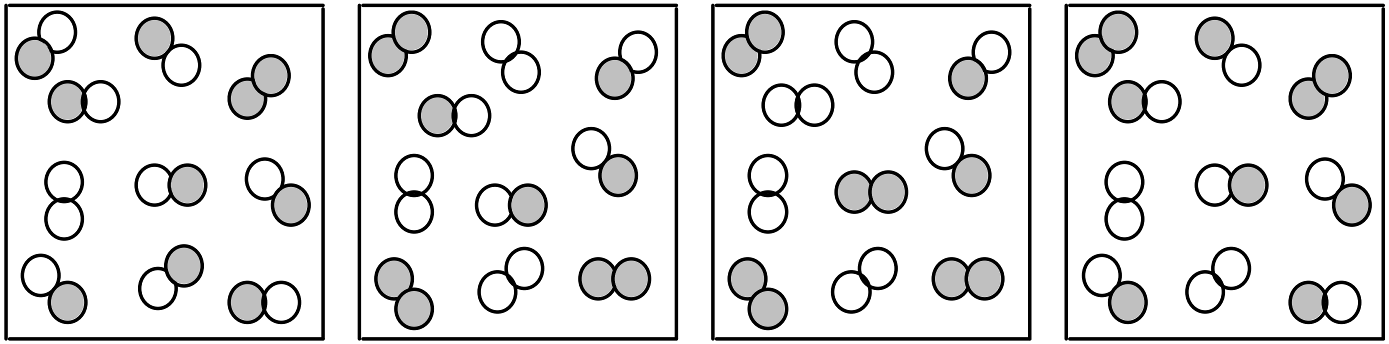
The pictures below represent four similar reactions that have achieved equilibrium. A atoms are unshaded. B, C, D, and E atoms are unshaded. Which reaction has the largest equilibrium constant?



$A_2 + B_2 \rightleftarrows 2\ AB$ $A_2 + C_2 \rightleftarrows 2\ AC$ $A_2 + D_2 \rightleftarrows 2\ AD$ $A_2 + E_2 \rightleftarrows 2\ AE$

1. $A_2 + B_2 \rightarrow 2\ AB$
2. $A_2 + C_2 \rightarrow 2\ AC$
3. $A_2 + D_2 \rightarrow 2\ AD$
4. $A_2 + E_2 \rightarrow 2\ AE$

The pictures below represent four similar reactions that have achieved equilibrium. A atoms are unshaded. B, C, D, and E atoms are unshaded. Which reaction has the largest equilibrium constant?



$A_2 + B_2 \rightleftarrows 2\ AB$ $A_2 + C_2 \rightleftarrows 2\ AC$ $A_2 + D_2 \rightleftarrows 2\ AD$ $A_2 + E_2 \rightleftarrows 2\ AE$

1. $A_2 + B_2 \rightarrow 2\ AB$
2. $A_2 + C_2 \rightarrow 2\ AC$
3. $A_2 + D_2 \rightarrow 2\ AD$
4. $A_2 + E_2 \rightarrow 2\ AE$

For the reaction of hydrogen and oxygen to produce gaseous water shown below, what effect will
a) increasing the temperature and b) increasing the pressure (by decreasing the volume of the reaction vessel) have on the concentration of $H_2O(g)$ formed in this equilibrium?

$$2\ H_2(g) + O_2(g) \rightleftarrows 2\ H_2O(g) \quad \Delta H = -58\ \text{kcal/mol}$$

1. a) decrease; b) decrease
2. a) decrease; b) increase
3. a) increase; b) decrease
4. a) increase; b) increase

For the reaction of hydrogen and oxygen to produce gaseous water shown below, what effect will
a) increasing the temperature and b) increasing the pressure (by decreasing the volume of the reaction vessel) have on the concentration of $H_2O(g)$ formed in this equilibrium?

$$2\ H_2(g) + O_2(g) \rightleftarrows 2\ H_2O(g) \quad \Delta H = –58\ \text{kcal/mol}$$

1. a) decrease; b) decrease
2. a) decrease; b) increase
3. a) increase; b) decrease
4. a) increase; b) increase