

Reaction Energy and Reaction Kinetics



Many chemical reactions give off or take in energy as heat.

Thermochemistry

SECTION 17-1

OBJECTIVES

- Define *temperature* and state the units in which it is measured.
- Define *heat* and state its units.
- Perform specific-heat calculations.
- Explain heat of reaction, heat of formation, heat of combustion, and enthalpy change.
- Solve problems involving heats of reaction, heats of formation, and heats of combustion.

Virtually every chemical reaction is accompanied by a change in energy. Chemical reactions usually absorb or release energy as heat. You learned in Chapter 12 that heat is also absorbed or released in physical changes, such as melting a solid or condensing a vapor. **Thermochemistry** is the study of the transfers of energy as heat that accompany chemical reactions and physical changes.

Heat and Temperature

The energy absorbed or released as heat in a chemical or physical change is measured in a **calorimeter**. In one kind of calorimeter, known quantities of reactants are sealed in a reaction chamber, which is immersed in a known quantity of water in an insulated vessel. Therefore, the energy given off (or absorbed) during the reaction is equal to the energy absorbed (or given off) by the known quantity of water. The amount of energy is determined from the temperature change of the known mass of surrounding water. The data collected from calorimetry experiments are temperature changes because heat cannot be measured directly; but temperature, which is affected by the transfer of energy as heat, is directly measurable. To see why this is so, let us look at the definitions of heat and temperature and at how temperature is measured.

Temperature is a measure of the average kinetic energy of the particles in a sample of matter. The greater the kinetic energy of the particles in a sample, the higher the temperature and the hotter it feels. To assign a numerical value to temperature, it is necessary to define a temperature scale. For calculations in thermochemistry, we use the Celsius and Kelvin scales. A Celsius temperature can be converted to Kelvin temperature by adding 273.15, although in most calculations in this book, it is acceptable to add 273.

The ability to measure temperature is thus based on heat transfer. The amount of energy transferred as heat is usually measured in joules. A **joule** is the SI unit of heat as well as all other forms of energy. The joule, abbreviated J, is derived from the units for force and length.

$$\text{N} \times \text{m} = \frac{\text{kg} \times \text{m}^2}{\text{s}^2}$$

Because the joule is a rather small unit compared with other units for heat, the kilojoule, kJ, is also commonly used as a unit for heat.

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FIGURE 17-1 The direction of energy transfer is determined by the temperature differences between the objects within a system. The energy is transferred as heat from the hotter brass bar to the cooler water. This energy transfer will continue until the bar and the water reach the same temperature.

Heat can be thought of as the energy transferred between samples of matter because of a difference in their temperatures. Energy transferred as heat always moves spontaneously from matter at a higher temperature to matter at a lower temperature, as shown in Figure 17-1. The temperature of the cool water in the beaker increases as energy flows into it. Likewise, the temperature of the hot brass bar decreases as energy flows away from it. When the temperature of the water equals the temperature of the brass bar, energy is no longer transferred as heat within the system.

Heat Capacity and Specific Heat

The quantity of energy transferred as heat during a temperature change depends on the nature of the material changing temperature, the mass of the material changing temperature, and the size of the temperature change. One gram of iron heated to 100.0°C and cooled to 50.0°C in a calorimeter transfers 22.5 J of energy to the surrounding water. But one gram of silver transfers 11.8 J of energy under the same conditions. The difference results from the metals' differing capacities for absorbing this energy. A quantity called specific heat can be used to compare heat absorption capacities for different materials. **Specific heat** is the amount of energy required to raise the temperature of one gram of substance by one Celsius degree (1°C) or one kelvin (1 K) (because the sizes of the degree divisions on both scales are equal). Values of specific heat can be given in units of joules per gram per Celsius degree, $\text{J}/(\text{g}\cdot^{\circ}\text{C})$, joules per gram per kelvin, $\text{J}/(\text{g}\cdot\text{K})$, or calories per gram per Celsius degree, $\text{cal}/(\text{g}\cdot^{\circ}\text{C})$. Table 17-1 gives the specific heats of some common substances. Notice the extremely high specific heat of water, one of the highest of most common substances.

Specific heat is usually measured under constant pressure conditions, so its symbol, c_p , contains a subscripted p as a reminder to the reader.

TABLE 17-1 Specific Heats of Some Common Substances at 298.15 K

| Substance | Specific heat J/(g·K) |
|-------------------------------|-----------------------|
| Water (<i>l</i>) | 4.18 |
| Water (<i>s</i>) | 2.06 |
| Water (<i>g</i>) | 1.87 |
| Ammonia (<i>g</i>) | 2.09 |
| Benzene (<i>l</i>) | 1.74 |
| Ethanol (<i>l</i>) | 2.44 |
| Ethanol (<i>g</i>) | 1.42 |
| Aluminum (<i>s</i>) | 0.897 |
| Calcium (<i>s</i>) | 0.647 |
| Carbon, graphite (<i>s</i>) | 0.709 |
| Copper (<i>s</i>) | 0.385 |
| Gold (<i>s</i>) | 0.129 |
| Iron (<i>s</i>) | 0.449 |
| Mercury (<i>l</i>) | 0.140 |
| Lead (<i>s</i>) | 0.129 |

In the following mathematical equation, c_p is the specific heat at a given pressure, q is the energy lost or gained, m is the mass of the sample, and ΔT represents the difference between the initial and final temperatures.

$$c_p = \frac{q}{m \times \Delta T}$$

This equation can be rearranged to give an equation that can be used to find the quantity of energy gained or lost with a change in temperature.

$$q = c_p \times m \times \Delta T$$

SAMPLE PROBLEM 17-1

A 4.0 g sample of glass was heated from 274 K to 314 K, a temperature increase of 40 K, and was found to have absorbed 32 J of energy as heat.

- What is the specific heat of this type of glass?
- How much energy will the same glass sample gain when it is heated from 314 K to 344 K?

SOLUTION**1 ANALYZE**

Given: $m = 4.0$ g

$\Delta T = 40$ K

$q = 32$ J

Unknown: c_p in J/(g·K)

2 PLAN

- a. The specific heat, c_p , of the glass is calculated using the equation given for specific heat.

$$c_p = \frac{q}{m \times \Delta T}$$

- b. The rearranged specific heat equation is used to find the energy gained when the glass was heated.

$$q = c_p \times m \times \Delta T$$

3 COMPUTE

a. $\frac{32 \text{ J}}{(4.0 \text{ g})(40 \text{ K})} = 0.20 \text{ J}/(\text{g}\cdot\text{K})$

b. $\frac{0.20 \text{ J}}{(\text{g}\cdot\text{K})} (4.0 \text{ g})(71 \text{ K} - 41 \text{ K})$

$\frac{0.20 \text{ J}}{(\text{g}\cdot\text{K})} (4.0 \text{ g})(30 \text{ K}) = 24 \text{ J}$

4 EVALUATE

The units combine or cancel correctly to give the specific heat in $\text{J}/(\text{g}\cdot\text{K})$ and the energy in J. Both answers are correct given to two significant figures.

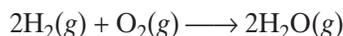
PRACTICE

- | | |
|---|--------------------------------|
| 1. Determine the specific heat of a material if a 35 g sample absorbed 48 J as it was heated from 293 K to 313 K. | <i>Answer</i> 0.069 J/(g·K) |
| 2. If 980 kJ of energy are added to 6.2 L of water at 291 K, what will the final temperature of the water be? | <i>Answer</i> 329 K |

Heat of Reaction

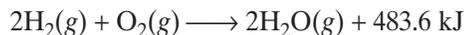
The **heat of reaction** is the quantity of energy released or absorbed as heat during a chemical reaction. You can think of heat of reaction as the difference between the stored energy of the reactants and the products.

If a mixture of hydrogen and oxygen is ignited, water will form and energy will be released explosively. The energy that is released comes from the reactants as they form products. Because energy is released, the reaction is exothermic, and the energy of the product, water, must be less than the energy of the reactants before ignition. The following chemical equation for this reaction indicates that when 2 mol of hydrogen gas at room temperature are burned, 1 mol of oxygen gas is consumed and 2 mol of water vapor are formed.

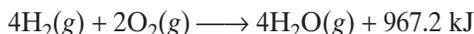


The equation does not tell you that energy is evolved as heat during the reaction. Experiments have shown that 483.6 kJ of energy are evolved when 2 mol of gaseous water are formed at 298.15 K from its elements.

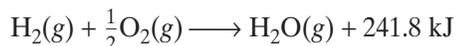
Modifying the chemical equation to show the amount of energy produced during the reaction gives the following expression.



This expression is an example of a **thermochemical equation**, an equation that includes the quantity of energy released or absorbed as heat during the reaction as written. In any thermochemical equation, we must always interpret the coefficients as *numbers of moles* and never as *numbers of molecules*. The quantity of energy released as heat in this or any reaction depends on the amounts of reactants and products. The quantity of energy released during the formation of water from H_2 and O_2 is proportional to the quantity of water formed. Producing twice as much water vapor would require twice as many moles of reactants and would release 2×483.6 kJ of energy as heat, as shown in the following thermochemical equation.

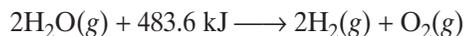


Producing one-half as much water would require one-half as many moles of reactants and would release only one-half as much energy, or $1/2 \times 483.6$ kJ. The thermochemical equation for this reaction follows.



Fractional coefficients are sometimes used in thermochemical equations.

The situation is reversed in an endothermic reaction because products have a higher energy than reactants. The decomposition of water vapor is endothermic; it is the reverse of the reaction that forms water vapor. The amount of energy absorbed by water molecules to form hydrogen and oxygen equals the amount of energy released when the elements combine to form the water. This is to be expected because the difference between the energy of reactants and products is unchanged. Energy now appears on the reactant side of the thermochemical equation that follows, indicating that it was absorbed during the reaction.

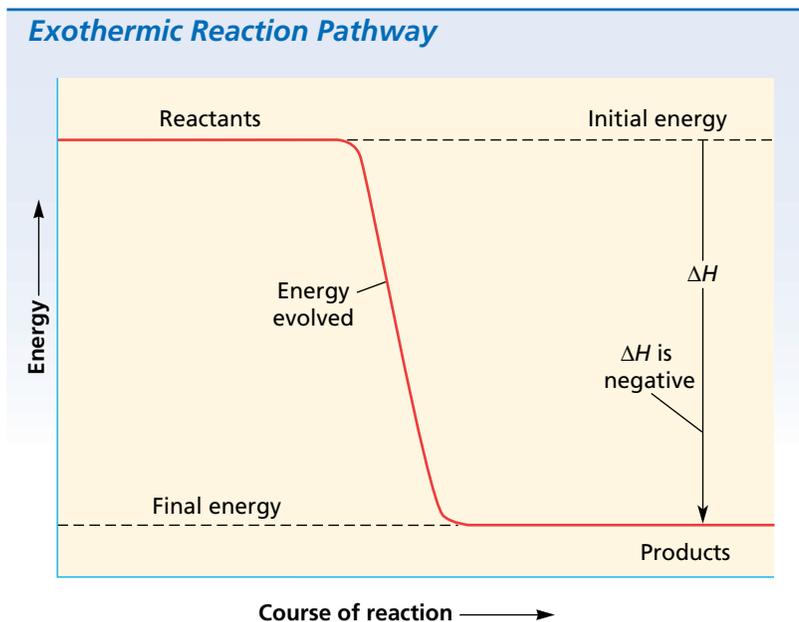


The physical states of reactants and products must always be included in thermochemical equations because they influence the overall amount of energy exchanged. For example, the energy needed for the decomposition of water would be greater than 483.6 kJ if we started with ice because extra energy would be needed to melt the ice and to change the liquid into a vapor.

The energy absorbed or released as heat during a chemical reaction at constant pressure is represented by ΔH . The H is the symbol for a quantity called *enthalpy*. Enthalpy has traditionally been defined as the heat content of a system at constant pressure. However, the term “heat content” is misleading. Also, it is not practical to talk just about enthalpy as a quantity, because we have no way to directly measure the enthalpy of a system. Only *changes* in enthalpy can be measured. The Greek



FIGURE 17-2 In an exothermic chemical reaction, the enthalpy change is negative, meaning energy is released from the system as heat.



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letter Δ (a capital “delta”) stands for “change in.” Therefore, ΔH is read as “change in enthalpy.” An **enthalpy change** is the amount of energy absorbed or lost by a system as heat during a process at constant pressure. The enthalpy change is always the difference between the enthalpies of the products and the reactants. The following equation expresses an enthalpy change mathematically.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Thermochemical equations are usually written by designating the value of ΔH rather than writing the energy as a reactant or product. By convention, for an exothermic reaction, ΔH is always given a minus sign because the system loses energy. So the thermochemical equation for the exothermic formation of 2 mol of gaseous water from its elements now has the following form.



Figure 17-2 graphically shows the course of an exothermic reaction. The initial energy of the reactants is greater than the final energy of the products. This means energy is evolved, or given off, during the reaction; this is described as a negative enthalpy change.

For an endothermic reaction, ΔH is always given a positive value because the system gains energy. Thus, the endothermic decomposition of 2 mol of gaseous water has the following thermochemical equation.



The course of an endothermic reaction is illustrated in Figure 17-3.

Endothermic Reaction Pathway

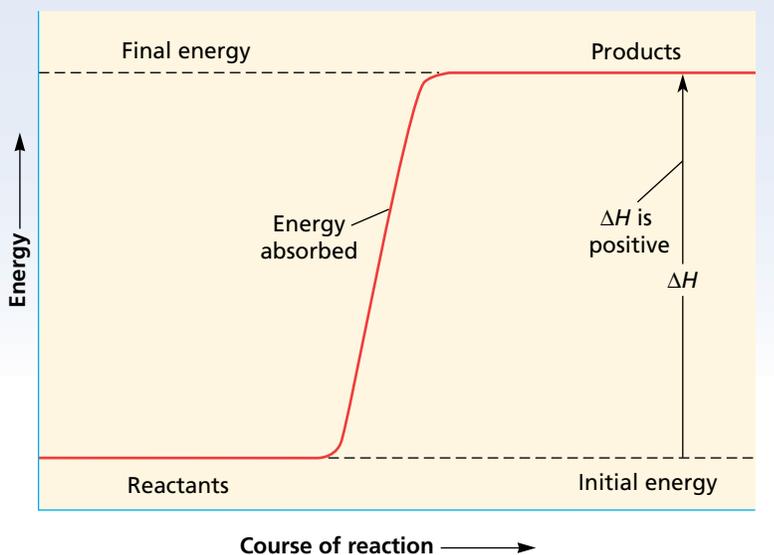


FIGURE 17-3 In an endothermic chemical reaction, the enthalpy change is positive because energy is absorbed into the system as heat.

Energy is absorbed in this reaction, meaning that the initial energy of the reactants is lower than the final energy of the products. In this case, ΔH is designated as positive.

Keep in mind the following concepts when using thermochemical equations.

1. The coefficients in a balanced thermochemical equation represent the numbers of *moles* of reactants and products and never the numbers of *molecules*. This allows us to write these coefficients as fractions rather than whole numbers when necessary.
2. The physical state of the product or reactant involved in a reaction is an important factor and therefore must be included in the thermochemical equation.
3. The change in energy represented by a thermochemical equation is directly proportional to the number of moles of substances undergoing a change. For example, if 2 mol of water are decomposed, twice as much energy, 483.6 kJ, is needed than for the decomposition of 1 mol of water.
4. The value of the energy change, ΔH , is usually not significantly influenced by changing temperature.

Heat of Formation

The formation of water from hydrogen and oxygen is a composition reaction—the formation of a compound from its elements. Thermochemical data are often recorded as the heats of such composition reactions. *The molar heat of formation is the energy released or absorbed as heat when one mole of a compound is formed by combination of its elements.*

To make comparisons meaningful, heats of formation are given for the standard states of reactants and products—these are the states found at atmospheric pressure and, usually, room temperature (298.15 K). Thus, the standard state of water is liquid, not gas or solid. The standard state of iron is solid, not a molten liquid. To signify that a value represents measurements on substances in their standard states, a ⁰ sign is added to the enthalpy symbol, giving ΔH^0 for the standard heat of a reaction. Adding a subscript *f*, as in ΔH_f^0 , further indicates a standard heat of formation.

Some standard heats of formation are given in Appendix Table A-14 (page 902). Each entry in the table is the heat of formation for the synthesis of *one mole* of the compound listed from its elements in their standard states. The thermochemical equation to accompany each heat of formation shows the formation of one mole of the compound from its elements in their standard states.

Stability and Heat of Formation

If a large amount of energy is released when a compound is formed, the compound has a high negative heat of formation. Such compounds are very stable. Once they start, the reactions forming them usually proceed vigorously and without outside assistance.

Elements in their standard states are *defined* as having $\Delta H_f^0 = 0$. The ΔH_f^0 of carbon dioxide is -393.5 kJ/mol of gas produced. Therefore, carbon dioxide is more stable than the elements from which it was formed. You can see in Appendix Table A-14 (page 902) that the majority of the heats of formation are negative.

Compounds with relatively positive values of heats of formation, or only slightly negative values, are relatively unstable and will spontaneously decompose into their elements if the conditions are appropriate. Hydrogen iodide, HI, is a colorless gas that decomposes somewhat when stored at room temperature. It has a relatively high positive heat of formation of $+26.5$ kJ/mol. As it decomposes, violet iodine vapor becomes visible throughout the container of the gas.

Compounds with a high positive heat of formation are sometimes very unstable and may react or decompose violently. For example, ethyne (acetylene), C_2H_2 , ($\Delta H_f^0 = +226.7$ kJ/mol) reacts violently with oxygen and must be stored in cylinders as a solution in acetone. Mercury fulminate, $HgC_2N_2O_2$, has a very high heat of formation of $+270$ kJ/mol. Its instability makes it useful as a detonator for explosives.

Heat of Combustion

Combustion reactions produce a considerable amount of energy in the form of light and heat when a substance is combined with oxygen. *The energy released as heat by the complete combustion of one mole of a*

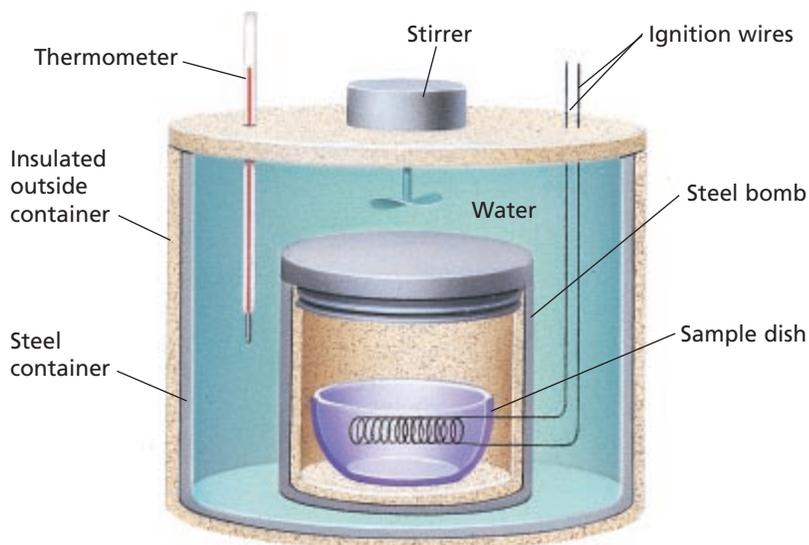


FIGURE 17-4 This is a diagram of a simple combustion calorimeter. A weighed sample is ignited by an electric spark and burned in the sample dish in an atmosphere of pure oxygen. The energy generated by the combustion reaction warms the steel bomb and the water surrounding it. The thermometer measures the initial and final temperatures of the water, and this temperature change is then used to calculate the energy evolved by the reaction as heat.

substance is called the **heat of combustion** of the substance. Heat of combustion is defined in terms of *one mole of reactant*, whereas the heat of formation is defined in terms of *one mole of product*. All substances are in their standard state. The general enthalpy notation, ΔH , applies to heats of reaction, but the addition of a subscripted *c*, ΔH_c , refers specifically to heat of combustion. A list of heats of combustion can be found in Appendix Table A-5 (page 896).

Carbon dioxide and water are the products of the complete combustion of organic compounds containing only carbon and hydrogen or carbon, hydrogen, and oxygen. Knowing this, we can write the thermochemical equation for the combustion of any organic compound listed by balancing the equation for the reaction of one mole of the compound. For example, propane is a major component of the fuel used for outdoor gas grills. Its reaction with oxygen in the air, forming carbon dioxide and water as products and releasing energy in the form of heat and light, is a common example of combustion. The complete combustion of one mole of propane, C_3H_8 , is described by the following thermochemical equation.

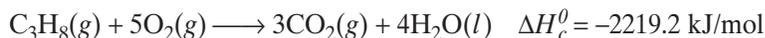


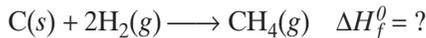
Figure 17-4 shows a combustion calorimeter, one of the instruments used to determine heats of combustion.

Calculating Heats of Reaction

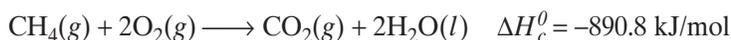
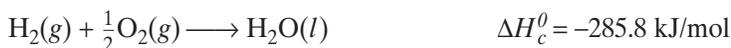
Thermochemical equations can be rearranged and added to give enthalpy changes for reactions not included in the data tables. The basis for calculating heats of reaction is known as **Hess's law**: *The overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps in the process.* The energy difference between reactants and

products is independent of the route taken to get from one to the other. In fact, measured heats of reaction can be combined to calculate heats of reaction that are difficult or impossible to actually measure.

To demonstrate how to apply Hess's law, we will work through the calculation of the heat of formation for the formation of methane gas, CH_4 , from its elements, hydrogen gas and solid carbon (graphite), at 298.15 K (25°C).



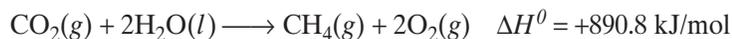
In order to calculate the change in enthalpy for this reaction, we can use the combustion reactions of the elements, carbon and hydrogen, and of methane.



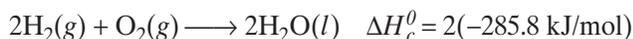
The general principles for combining thermochemical equations follow.

1. If a reaction is reversed, the sign of ΔH is also reversed.
2. Multiply the coefficients of the known equations so that when added together they give the desired thermochemical equation.

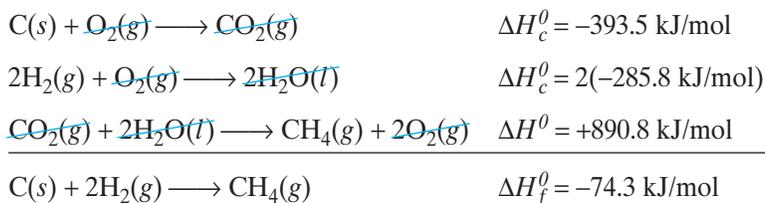
In this case, reverse the combustion equation for methane, and remember to change the sign of ΔH from negative to positive. This will change the exothermic reaction to an endothermic one.



Now we notice that 2 formula units of water are used as a reactant; therefore, 2 formula units of water will be needed as a product. In the combustion reaction for hydrogen as it is written, it only produces one formula unit of water. We must multiply the coefficients of this combustion reaction and the value of ΔH by 2 in order to obtain the desired quantity of water.

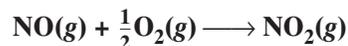


We are now ready to add the three equations together using Hess's law to give the heat of formation for methane and the balanced equation.

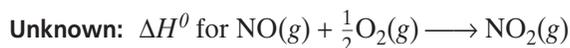


SAMPLE PROBLEM 17-2

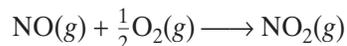
Calculate the heat of reaction for the combustion of nitrogen monoxide gas, NO, to form nitrogen dioxide gas, NO₂, as given in the following thermochemical equation.



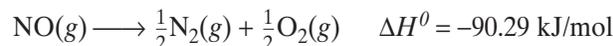
Use the heat-of-formation data in Appendix Table A-14 (page 902). Solve by combining the known thermochemical equations. Verify the result by using the general equation for finding heats of reaction from heats of formation.

SOLUTION
1 ANALYZE

2 PLAN

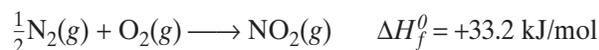
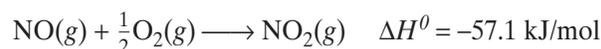
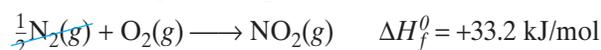
The ΔH requested can be found by adding the ΔH s of the component reactions as specified in Hess's law. The desired equation has NO(g) and $\frac{1}{2}\text{O}_2(g)$ as reactants and NO₂(g) as the product.



We need an equation with NO as a reactant. Reversing the first reaction for the formation of NO from its elements and the sign of ΔH yields the following thermochemical equation.



The other equation should have NO₂ as a product, so we can retain the second equation for the formation of NO₂ from its elements as it stands.


3 COMPUTE


Note the cancellation of the $\frac{1}{2}\text{N}_2(g)$ and the partial cancellation of the $\text{O}_2(g)$.

4 EVALUATE

The unnecessary reactants and products cancel to give the desired equation. The general relationship between the heat of a reaction and the heats of formation of the reactants and products is described in the following word equation.

$$\Delta H^\circ = \text{sum of } \Delta H_f^\circ \text{ of products} - \text{sum of } \Delta H_f^\circ \text{ of reactants}$$

To find the necessary sums, the ΔH_f^0 value for each reactant and each product must be multiplied by its respective coefficient in the desired equation. For the reaction of NO with O₂, applying this equation gives the following value for ΔH^0 .

$$\begin{aligned}\Delta H^0 &= \Delta H_f^0(\text{NO}_2) - [\Delta H_f^0(\text{NO}) + 0] \\ &= +33.2 \text{ kJ/mol} - 90.29 \text{ kJ/mol} = -57.1 \text{ kJ/mol}\end{aligned}$$

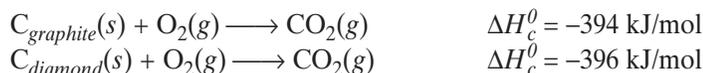
Note that zero is the assigned value for the heats of formation of elements in their standard states.

PRACTICE

1. Calculate the heat of reaction for the combustion of methane gas, CH₄, to form CO₂(g) + H₂O(l). *Answer*
-890.2 kJ/mol
2. Carbon occurs in two distinct forms. It can be the soft, black material found in pencils and lock lubricants, called graphite, or it can be the hard, brilliant gem we know as diamond. Calculate ΔH^0 for the conversion of graphite to diamond for the following reaction. *Answer*
2 kJ/mol

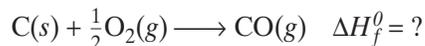


The combustion reactions you will need follow.

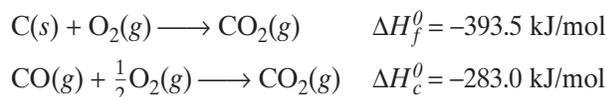


Determining Heat of Formation

When carbon is burned in a limited supply of oxygen, carbon monoxide is produced. In this reaction, carbon is probably first oxidized to carbon dioxide. Then part of the carbon dioxide is reduced with carbon to give some carbon monoxide. Because these two reactions occur simultaneously and we get a mixture of CO and CO₂, it is not possible to directly measure the heat of formation of CO(g) from C(s) and O₂(g).



However, we do know the heat of formation of carbon dioxide and the heat of combustion of carbon monoxide.



We reverse the second equation because we need CO as a product. Adding gives the desired heat of formation of carbon monoxide.

Heats of Reaction

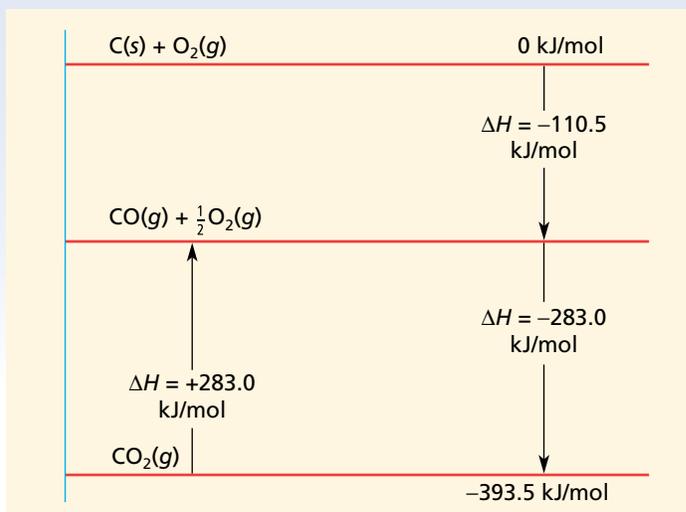


FIGURE 17-5 This diagram shows the heat of reaction for carbon dioxide, CO_2 , and carbon monoxide, CO .

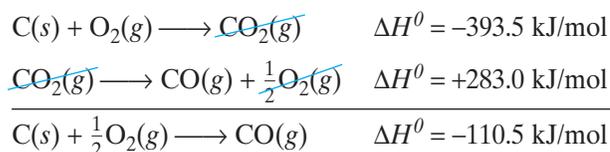


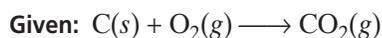
Figure 17-5 is a model for the process described in this section. If we plot the reactions based on their relative energy, you can see the relationship among the values obtained for the heat of formation of carbon monoxide. The formation of CO_2 is plotted at a level corresponding to -393.5 kJ/mol . The diagram shows the reverse of the combustion reaction ($+283.0 \text{ kJ/mol}$) is added to that level. From the diagram, you see the difference, which represents the formation of CO . This value is -110.5 kJ/mol .

SAMPLE PROBLEM 17-3

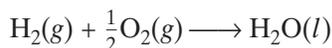
Calculate the heat of formation of pentane, C_5H_{12} , using the information on heats of formation in Appendix Table A-14 (page 902) and the information on heats of combustion in Appendix Table A-5 (page 896). Solve by combining the known thermochemical equations.

SOLUTION

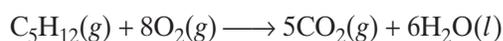
1 ANALYZE



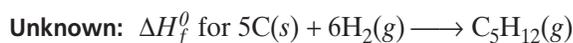
$$\Delta H_f^0 = -393.5 \text{ kJ/mol}$$



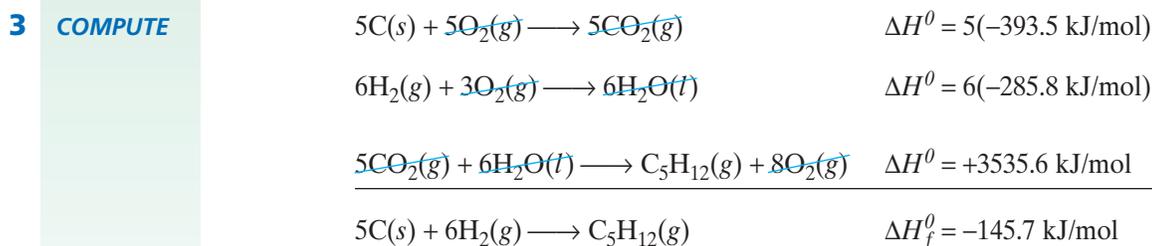
$$\Delta H_f^0 = -285.8 \text{ kJ/mol}$$



$$\Delta H_c^0 = -3535.6 \text{ kJ/mol}$$



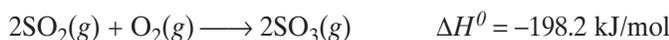
- 2 PLAN** Combine the given equations according to Hess's law. We need C_5H_{12} as a product, so we reverse the equation for combustion of C_5H_{12} and the sign for ΔH_c^0 . Multiply the equation for formation of CO_2 by 5 to give 5C as a reactant. Multiply the equation for formation of H_2O by 6 to give $6H_2$ as a reactant.



- 4 EVALUATE** The unnecessary reactants and products cancel to give the correct equation.

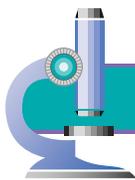
PRACTICE

- Calculate the heat of formation of butane, C_4H_{10} , using the balanced chemical equation and information in Appendix Table A-5 (page 896) and Table A-14 (page 902). Write out the solution according to Hess's law. *Answer*
-125.4 kJ/mol
- Calculate the heat of combustion of 1 mol of nitrogen, N_2 , to form NO_2 using the balanced chemical equation and Appendix Table A-14 (page 902). (Hint: The heat of combustion of N_2 will be equal to the sum of the heats of formation of the combustion products of N_2 minus the heat of formation of N_2 .) *Answer*
+ 66.4 kJ/mol
- Calculate the heat of formation for sulfur dioxide, SO_2 , from its elements, sulfur and oxygen. Use the balanced chemical equation and the following information. *Answer*
-296.1 kJ/mol



SECTION REVIEW

- What is meant by enthalpy change?
- What is meant by heat of reaction?
- Describe the relationship between a compound's stability and its heat of formation.
- What is the importance of Hess's law to thermodynamic calculations?
- How much energy would be absorbed as heat by 75 g of iron when heated from 295 K to 301 K?
- When 1 mol of methane is burned at constant pressure, 890 kJ of energy is released as heat. If a 3.2 g sample of methane is burned at constant pressure, what will be the value of ΔH ? (Hint: Convert the grams of methane to moles. Also make sure your answer has the correct sign for an exothermic process.)



Self-Heating Meals

Who would have thought that corrosion could be useful? The HeaterMeals Company did. This company uses the properties of salt-water corrosion to heat TV-type dinners, and now it is taking packaged foods to a new level of convenience.

HeaterMeals' products, as their name implies, come with a self-contained heat source. Each meal contains a package of food, a tray that holds a porous pouch containing Mg and Fe alloy, and a 2 oz pouch filled with salt water. When the salt water is poured into the tray with the porous pouch, it begins to vigorously corrode the metals. The sealed, precooked food package is then placed on top of the tray and returned to its box, where the temperature of the food package is raised by 100°F, heating the meal in 14 min.

Corrosion, the process by which a metal reacts with air or water, is usually an undesirable event, such as when iron corrodes to form rust. With HeaterMeals, however, the corrosion process is speeded up to produce an exothermic reaction—with the excess heat as the desired result.

According to Drew McLandrich, of The HeaterMeals Company, the idea for using self-heating metallic



This product uses supercorrosion to give you a hot meal.

alloy powders has been around since the 1930s. “But,” says McLandrich, “there really have been no significant uses of the product until the Desert Storm conflict, which led to the military’s

taking this technology and adopting it for field use so that soldiers could heat a meal-ready-to-eat.”

“We’ve made about 80 million heaters for the military in the last 10 years. Lately we’ve been successfully marketing them to long-distance truck drivers. The product is in about 800 truck stops in 48 states.

The company has plans to develop other products using the controlled use of “supercorrosion.” “A beverage could be heated,” says McLandrich, “and we do have prototypes for a baby-bottle warmer. We’re also working on making a portable hot cup of coffee or a hot cup of tea or cocoa.”

So the next time you need a hot meal and there are no kitchens or restaurants around, consider the possibilities of supercorrosion and exothermic reactions.

How did the development of self-heating metallic alloy powders benefit the military?

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SCILINKSSM
NSTA

TOPIC: Supercorrosion
GO TO: www.scilinks.org
sciLINKS CODE: HC2173

SECTION 17-2

OBJECTIVES

- Explain the relationship between enthalpy change and the tendency of a reaction to occur.
- Explain the relationship between entropy change and the tendency of a reaction to occur.
- Discuss the concept of free energy, and explain how the value of this quantity is calculated and interpreted.
- Describe the use of free energy change to determine the tendency of a reaction to occur.

Driving Force of Reactions

The change in energy of a reaction system is one of two factors that allow chemists to predict whether a reaction will occur spontaneously and to explain how it occurs. The randomness of the particles in a system is the second factor affecting whether a reaction will occur spontaneously.

Enthalpy and Reaction Tendency

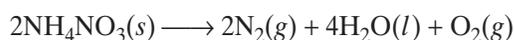
The great majority of chemical reactions in nature are exothermic. As these reactions proceed, energy is liberated and the products have less energy than the original reactants. The products are also more resistant to change, more stable, than the original reactants. The tendency throughout nature is for a reaction to proceed in a direction that leads to a lower energy state.

We might think that endothermic reactions, in which energy is absorbed, cannot occur spontaneously because the products are at higher potential energy and are less stable than the original reactants. They would be expected to proceed only with the assistance of an outside influence, such as continued heating. However, some endothermic reactions *do* occur spontaneously. We conclude that something other than enthalpy change must help determine whether a reaction will occur.

Entropy and Reaction Tendency

A naturally occurring endothermic process is melting. An ice cube melts spontaneously at room temperature as energy is transferred from the warm air to the ice. The well-ordered arrangement of water molecules in the ice crystal is lost, and the less-orderly liquid phase of higher energy content is formed. A system that can go from one state to another without an enthalpy change does so by becoming more disordered.

Look at the physical states of the reactants in the chemical equation for the decomposition of ammonium nitrate.



CHEMISTRY



Module 9: Thermochemistry

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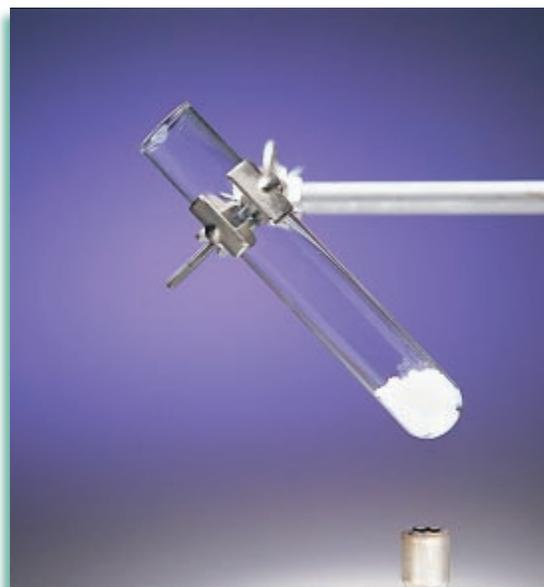
TOPIC: Entropy
GO TO: www.scilinks.org
sciLINKS CODE: HC2174

On the left side are 2 mol of solid ammonium nitrate. The right-hand side of the equation shows 3 mol of gaseous molecules plus 4 mol of a liquid. The arrangement of particles on the right-hand side of the equation is more random than the arrangement on the left side of the equation and hence is less ordered. Figures 17-6(a) and (b) show the reactant and products of this decomposition reaction.

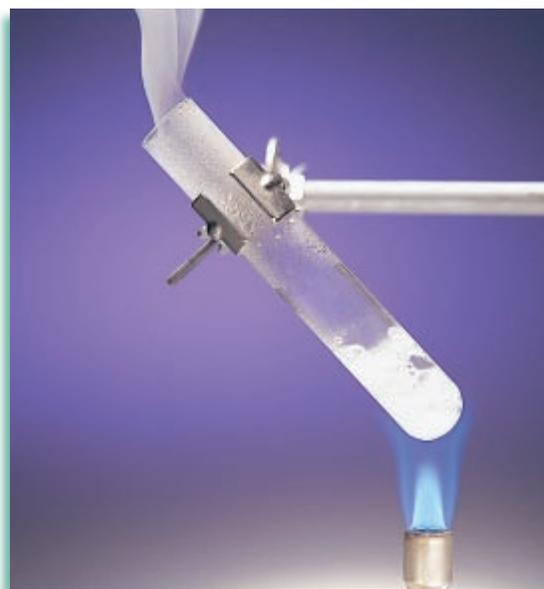
These examples illustrate that there is a tendency in nature to proceed in a direction that increases the disorder of a system. A disordered system is one that lacks a regular arrangement of its parts. This tendency toward disorder is called entropy. **Entropy, S** , can be defined in a simple qualitative way as *a measure of the degree of randomness of the particles, such as molecules, in a system*. In order to understand the concept of entropy, consider solids, liquids, and gases. In a solid, the particles are fixed in position in their small regions of space, but they are vibrating back and forth. Even so, we can determine with fair precision the location of the particles. The degree of randomness is low, so the entropy is low. When the solid melts, the particles are still very close together but they can move about somewhat. The system is more random, and it is more difficult to describe the location of the particles. The entropy is higher. When the liquid evaporates, the particles are moving rapidly and are also much farther apart. Locating an individual particle is much more difficult and the system is much more random. The entropy of the gas is still higher than that of the liquid. A general but not absolute rule is that the entropy of liquids is higher than that of solids, and the entropy of gases is higher than that of liquids. But this rule must be used with caution. For example, the entropy of liquid mercury is much lower than that of some solids.

At absolute zero, random motion ceases, so the entropy of a pure crystalline solid is by definition zero at absolute zero. As energy is added, the randomness of the molecular motion increases. Measurements of energy absorbed and calculations are used to determine the absolute entropy or standard molar entropy, and values are then recorded in tables. These molar values are reported as $\text{kJ}/(\text{mol}\cdot\text{K})$. Entropy change, which can also be measured, is defined as the difference between the entropy of the products and the reactants. Therefore, an increase in entropy is represented by a positive value for ΔS , and a decrease in entropy is represented by a negative value for ΔS .

The process of forming a solution almost always involves an increase in entropy because there is an increase in randomness. This is true for mixing gases, dissolving a liquid in another liquid, and dissolving a solid in a liquid.



(a)



(b)

FIGURE 17-6 When ammonium nitrate, NH_4NO_3 , decomposes, the entropy of the reaction system increases as (a) one solid reactant becomes (b) two gaseous products and one liquid product.

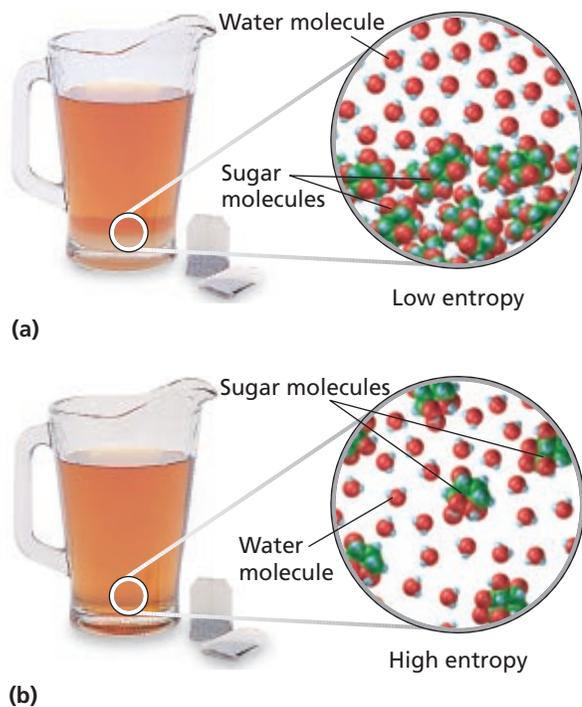


FIGURE 17-7 When a solid dissolves in a liquid, the entropy of the system increases.

CHEMISTRY INTERACTIVE TUTOR
 Module 9: Thermochemistry

Figure 17-7 illustrates the entropy change that takes place when solid sugar is dissolved in liquid tea. In the sugar-water system shown in Figure 17-7(a), the solid sugar has just been added to the tea, but most of it has not yet dissolved. The entropy is low because the majority of the sugar molecules are in one region at the bottom of the pitcher and the majority of the water molecules can be found everywhere else in the pitcher. After the sugar dissolves in the tea, shown in Figure 17-7(b), the sugar molecules are thoroughly mixed throughout the tea solution. Sugar molecules and water molecules might be found anywhere in the solution, so the entropy, the randomness, of the system increases. This would give ΔS a positive value for this solid-liquid system. You can imagine the same series of events happening for a system of gases mixing with each other or a system of liquids mixing. In each case, ΔS would have a positive value once the solution was formed.

Free Energy

Processes in nature are driven in two directions: toward lowest enthalpy and toward highest entropy. When these two oppose each other, the dominant factor determines the direction of change. To predict which factor will dominate for a given system, a function has been defined to relate the enthalpy and entropy factors at a given temperature. *This combined enthalpy-entropy function is called the free energy, G , of the system.* This function simultaneously assesses both the enthalpy-change and entropy-change tendencies. Natural processes proceed in the direction that lowers the free energy of a system.

Only the *change* in free energy can be measured. The change in free energy can be defined in terms of the changes in enthalpy and entropy. *At a constant pressure and temperature, the free-energy change, ΔG , of a system is defined as the difference between the change in enthalpy, ΔH , and the product of the Kelvin temperature and the entropy change, which is defined as $T\Delta S$.*

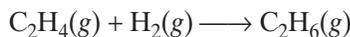
$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Note that this expression is for substances in their standard states. The product $T\Delta S$ and the quantities ΔG and ΔH have the same units, usually kJ/mol. The units of ΔS for use in this equation are usually kJ/(mol·K).

Each of the variables in the free-energy equation can have positive or negative values. This leads to four possible combinations of terms.

Table 17-2 (page 529) shows us that if ΔH is negative and ΔS is positive, then both terms on the right in the free energy equation are negative. Both factors contribute to the process being spontaneous.

Therefore, ΔG will always be negative, and the reaction is definitely spontaneous. On the other hand, if ΔH is positive (endothermic process) and ΔS is negative (decrease in randomness), then the reaction as written will definitely not occur. When the enthalpy and entropy changes are operating in different directions, sometimes one will predominate and sometimes the other will predominate. There are cases in which the enthalpy change is negative and the entropy change is negative. The enthalpy factor leads to a spontaneous process, but the negative entropy change opposes this. This is true in the following reaction. (The entropy decreases because there is a decrease in moles of gas.)



There is a fairly large decrease in entropy, $\Delta S^\circ = -0.1207 \text{ kJ}/(\text{mol}\cdot\text{K})$. However, the reaction is strongly exothermic, with a $\Delta H^\circ = -136.9 \text{ kJ}/\text{mol}$. The reaction proceeds because the enthalpy term predominates.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -136.9 \text{ kJ}/\text{mol} - 298 \text{ K}[-0.1207 \text{ kJ}/(\text{mol}\cdot\text{K})] \\ &= -101.1 \text{ kJ}/\text{mol}\end{aligned}$$

We can contrast this with the common commercial process for the manufacture of syngas, a mixture of CO and H_2 . (This gas mixture is the starting point for the synthesis of a number of large-volume commercial chemicals, such as methanol, CH_3OH .)



This reaction is endothermic, with $\Delta H^\circ = +206.1 \text{ kJ}/\text{mol}$ and $\Delta S^\circ = +0.215 \text{ kJ}/(\text{mol}\cdot\text{K})$, at standard conditions. The resulting ΔG is positive at room temperature. This tells us that the reaction will not occur at room temperature even though the entropy change is favorable.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = +206.1 \text{ kJ}/\text{mol} - 298 \text{ K}[+0.215 \text{ kJ}/(\text{mol}\cdot\text{K})] \\ &= +142.0 \text{ kJ}/\text{mol}\end{aligned}$$

TABLE 17-2 Relating Enthalpy, Entropy, and Free Energy Changes to Reaction Occurrence

| ΔH | ΔS | ΔG |
|--------------------------|--------------------------|---|
| - value (exothermic) | + value (disordering) | always negative |
| - value (exothermic) | - value (ordering) | negative at <i>lower</i> temperatures |
| + value (endothermic) | + value (disordering) | negative at <i>higher</i> temperatures |
| + value (endothermic) | - value (ordering) | never negative |

SAMPLE PROBLEM 17-4

For the reaction $\text{NH}_4\text{Cl}(s) \longrightarrow \text{NH}_3(g) + \text{HCl}(g)$, at 298.15 K, $\Delta H^\circ = 176 \text{ kJ/mol}$ and $\Delta S^\circ = 0.285 \text{ kJ}/(\text{mol}\cdot\text{K})$. Calculate ΔG° , and tell whether this reaction can proceed in the forward direction at 298.15 K.

SOLUTION

1 ANALYZE

Given: $\Delta H^\circ = 176 \text{ kJ/mol}$ at 298.15 K
 $\Delta S^\circ = 0.285 \text{ kJ}/(\text{mol}\cdot\text{K})$ at 298.15 K
Unknown: ΔG° at 298.15 K

2 PLAN

$$\Delta S, \Delta H, T \rightarrow \Delta G$$

The value of ΔG can be calculated according to the following equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

3 COMPUTE

$$\begin{aligned}\Delta G^\circ &= 176 \text{ kJ/mol} - 298 \text{ K} [0.285 \text{ kJ}/(\text{mol}\cdot\text{K})] \\ &= 176 \text{ kJ/mol} - 84.9 \text{ kJ/mol} \\ &= 91 \text{ kJ/mol}\end{aligned}$$

4 EVALUATE

The answer is reasonably close to an estimated value of 110, calculated as $200 - (300 \times 0.3)$. The positive value of ΔG shows that this reaction does not occur naturally at 298.15 K.

PRACTICE

1. For the vaporization reaction $\text{Br}_2(l) \longrightarrow \text{Br}_2(g)$, $\Delta H^\circ = 31.0 \text{ kJ/mol}$ and $\Delta S^\circ = 93.0 \text{ J}/(\text{mol}\cdot\text{K})$. At what temperature will this process be spontaneous? *Answer*
above 333 K

SECTION REVIEW

1. What kind of enthalpy change favors a spontaneous reaction?
2. What is entropy, and how does it relate to spontaneity of reactions?
3. List several changes that result in an entropy increase.
4. Define *free energy*, and explain how its change is calculated.
5. Explain the relationship between free-energy change and spontaneity of reactions.
6. In the reaction in Sample Problem 17-4, why does the entropy increase?
7. How should increasing temperature affect the value of ΔG for the reaction in Sample Problem 17-4?
8. Predict the sign of ΔS° for each of the following reactions:
 - a. the thermal decomposition of solid calcium carbonate
$$\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$$
 - b. the oxidation of SO_2 in air
$$2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g)$$

The Reaction Process

SECTION 17-3

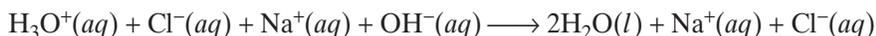
OBJECTIVES

- Explain the concept of reaction mechanism.
- Use the collision theory to interpret chemical reactions.
- Define *activated complex*.
- Relate activation energy to heat of reaction.

The enthalpy change, entropy change, and free energy of a chemical reaction are independent of the actual route by which a reaction occurs. What happens between the initial and final states of a reaction system is described by the energy pathway that a reaction follows and the changes that take place on the molecular level when substances interact.

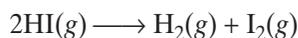
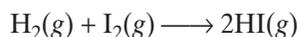
Reaction Mechanisms

If you mix aqueous solutions of HCl and NaOH, an extremely rapid neutralization reaction occurs.



The reaction is practically instantaneous; the rate is limited only by the speed with which the H_3O^+ and OH^- ions can diffuse through the water to meet each other. On the other hand, reactions between ions of the same charge and between molecular substances are not instantaneous. Negative ions repel each other, and the electron clouds of molecules repel each other strongly at very short distances. Therefore, only ions or molecules with very high kinetic energy can overcome repulsive forces and get close enough to react. In this section we will limit our discussion to reactions between molecules.

Colorless hydrogen gas consists of pairs of hydrogen atoms bonded together as diatomic molecules, H_2 . Violet-colored iodine vapor is also diatomic, consisting of pairs of iodine atoms bonded together as I_2 molecules. A chemical reaction between these two gases at elevated temperatures produces hydrogen iodide, HI, a colorless gas. Hydrogen iodide molecules, in turn, tend to decompose and re-form hydrogen and iodine molecules, producing the violet gas shown in Figure 17-8. The following chemical equations describe these two reactions.



Such equations indicate only which molecular species disappear as a result of the reactions and which species are produced. They do not show the **reaction mechanism**, *the step-by-step sequence of reactions by which the overall chemical change occurs*.

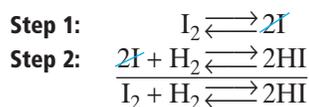


FIGURE 17-8 Clear hydrogen iodide gas, HI, decomposes into clear hydrogen gas and violet iodine gas.

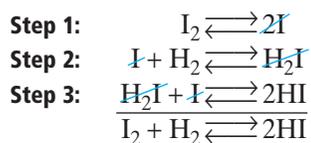
Although only the net chemical change is directly observable for most chemical reactions, experiments can often be designed that suggest the probable sequence of steps in a reaction mechanism. Each reaction step is usually a simple process. The equation for each step represents the *actual* atoms, ions, or molecules that participate in that step. Even a reaction that appears from its balanced equation to be a simple process may actually be the result of several simple steps.

For many years, the formation of hydrogen iodide was considered a simple one-step process. It was thought to involve the interaction of two molecules, H_2 and I_2 , in the forward reaction and two HI molecules in the reverse reaction. Experiments eventually showed, however, that a direct reaction between H_2 and I_2 does not take place.

Alternative mechanisms for the reaction were proposed based on the experimental results. The steps in each reaction mechanism had to add together to give the overall equation. Note that two of the species in the mechanism steps— I and H_2I —do not appear in the net equation. *Species that appear in some steps but not in the net equation are known as intermediates.* (Notice that they cancel each other out in the following mechanisms.) The first possible mechanism has the following two-step pathway.



The second possible mechanism has a three-step pathway.



The reaction between hydrogen gas and iodine vapor to produce hydrogen iodide gas is an example of a **homogeneous reaction**, a *reaction whose reactants and products exist in a single phase*—in this case, the gas phase. This reaction system is also an example of a homogeneous chemical system because all reactants and products in all intermediate steps are in the same phase.

Collision Theory

In order for reactions to occur between substances, their particles (molecules, atoms, or ions) must collide. Furthermore, these collisions must result in interactions. *The set of assumptions regarding collisions and reactions is known as collision theory.* Chemists use this theory to interpret many of their observations about chemical reactions.

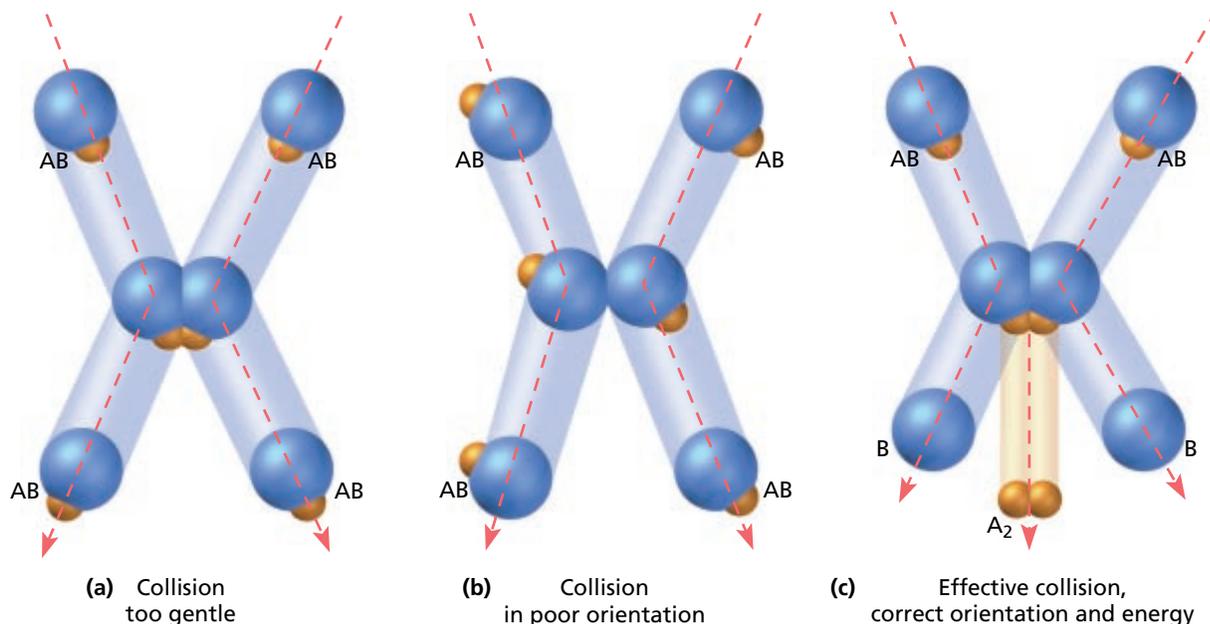
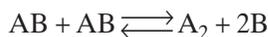


FIGURE 17-9 Three possible collision patterns for AB molecules are shown. Not every collision produces a chemical reaction.

Consider what might happen on a molecular scale in one step of a homogeneous reaction system. We will analyze a proposed first step in a hypothetical decomposition reaction.



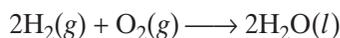
According to the collision theory, the two AB molecules must collide in order to react. Furthermore, they must collide while favorably oriented and with enough energy to merge the valence electrons and disrupt the bonds of the molecules. If they do so, a reshuffling of bonds leads to the formation of the products, one A_2 molecule and two B atoms. An effective collision is modeled in Figure 17-9(c).

If a collision is too gentle, the two molecules simply rebound from each other unchanged. This effect is illustrated in Figure 17-9(a). Similarly, a collision in which the reactant molecules are poorly oriented has little effect. The colliding molecules rebound without reacting. A poorly oriented collision is shown in Figure 17-9(b).

Thus, collision theory provides two reasons why a collision between reactant molecules may fail to produce a new chemical species: the collision is not energetic enough to supply the required energy, or the colliding molecules are not oriented in a way that enables them to react with each other.

Activation Energy

Consider the reaction for the formation of water from the diatomic gases oxygen and hydrogen according to the following equation.



Reaction Pathways for Forward and Reverse Reactions

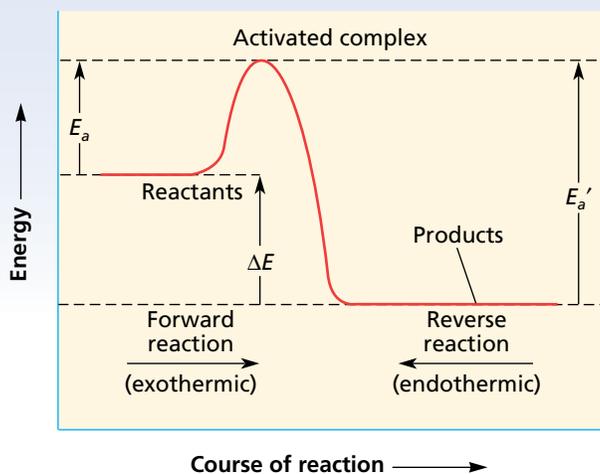


FIGURE 17-10 The difference between the activation energies for the reverse and forward reactions of a reversible reaction equals the energy change in the reaction, ΔE . The quantity for ΔE is the same for both directions, but is negative for the exothermic direction and positive for the endothermic direction.

mic, an initial input of energy is needed to overcome the repulsion forces that occur between reactant molecules when they are brought very close together. This initial energy input activates the reaction.

Once an exothermic reaction is started, the energy released is enough to sustain the reaction by activating other molecules. Thus, the reaction rate keeps increasing. It is limited only by the time required for reactant particles to acquire the energy and make contact. Energy from a flame or a spark, or the energy associated with high temperatures or radiations, may start exothermic reactants along the pathway of reaction. A generalized reaction pathway for an exothermic reaction is shown as the forward reaction in Figure 17-10. The minimum amount of energy needed to activate this reaction is the activation energy represented by E_a . **Activation energy** is the minimum energy required to transform the reactants into an activated complex.

The reverse reaction, decomposition of water molecules, is endothermic because the water molecules lie at an energy level that is lower than that of the hydrogen and oxygen molecules. The water molecules require a larger activation energy before they can decompose to reform oxygen and hydrogen. The energy needed to activate an endothermic reaction is greater than that required for the original exothermic change and is represented by E_a' in Figure 17-10. The difference between E_a' and E_a is equal to the energy change in the reaction, ΔE . This energy change has the same numerical value for the forward reaction as it has for the reverse reaction but with the opposite sign.

The heat of formation is quite high: $\Delta H_f^\circ = -285.8$ kJ/mol at 298.15 K. The free-energy change is also large: $\Delta G^\circ = -237.1$ kJ/mol. Why, then, don't oxygen and hydrogen combine spontaneously and immediately to form water when they are mixed at room temperature?

Hydrogen and oxygen gases exist as diatomic molecules. When the molecules approach each other, the electron clouds repel each other and the molecules bounce off and never actually meet. In order for a reaction to occur, the colliding molecules must have enough kinetic energy to actually intermingle the valence electrons. In other words, the bonds of these molecular species must be broken in order for new bonds to be formed between oxygen and hydrogen atoms. Bond breaking is an endothermic process, and bond forming is exothermic. Even though the net process for forming water is exothermic, an initial input of energy is needed to overcome the repulsion forces that occur between reactant molecules when they are brought very close together. This initial energy input activates the reaction.

The Activated Complex

When molecules collide, some of their high kinetic energy is converted into internal potential energy within the colliding molecules. If enough

energy is converted, molecules with suitable orientation become activated. New bonds can then form. In this brief interval of bond breakage and bond formation, the collision complex is in a transition state. Some sort of partial bonding exists in this transitional structure. *A transitional structure that results from an effective collision and that persists while old bonds are breaking and new bonds are forming is called an **activated complex**.* The exact structure of this activated complex is not known.

Figure 17-11 graphically breaks down the reaction pathway of the formation of hydrogen iodide gas described on page 532 into three steps. Beginning with the reactants, H_2 and I_2 , we see that a certain amount of activation energy, E_{a1} , is needed to form the activated complex that leads to the formation of the intermediates H_2 and 2I . During the course of the reaction, more activation energy, E_{a2} , is needed to form the activated complex leading to the intermediates H_2I and I . In order to arrive at the final product, 2HI , another increase in activation energy is necessary, as seen by the highest peak labeled E_{a3} .

An activated complex is formed when an effective collision raises the internal energies of the reactants to their minimum level for reaction, as shown in Figure 17-10. Both forward and reverse reactions go through the same activated complex. A bond that is broken in the activated complex for the forward reaction must be re-formed in the activated complex for the reverse reaction. Observe that an activated complex occurs at a high-energy position along the reaction pathway. In this sense, the activated complex defines the activation energy for the system.

From the kinetic-molecular theory presented in Chapter 10, you know that the speeds and therefore the kinetic energies of the molecules increase as the temperature increases. An increase in speed causes more collisions, which can cause an increase in reactions. However, the increase in reactions depends on more than simply the number of collisions, as Figure 17-9 illustrates. The collisions between molecules must possess sufficient energy to form an activated complex or a reaction will not take place. Raising the temperature of a reaction provides more molecules with this activation energy, causing an increase in reactions.

In its brief existence, the activated complex has partial bonding that is characteristic of both reactant and product. In this state, it may re-form the original bonds and separate back into the reactant particles, or it may form new bonds and separate into product particles. Usually, the formation of products is just as likely as the formation of reactants. Do not confuse the activated complex with the relatively stable intermediate products of different steps of a reaction mechanism. The activated complex, unlike intermediate products, is a very short-lived molecular complex in which bonds are in the process of being broken and formed.

Activation Energy Peaks in the Formation of Activated Complexes

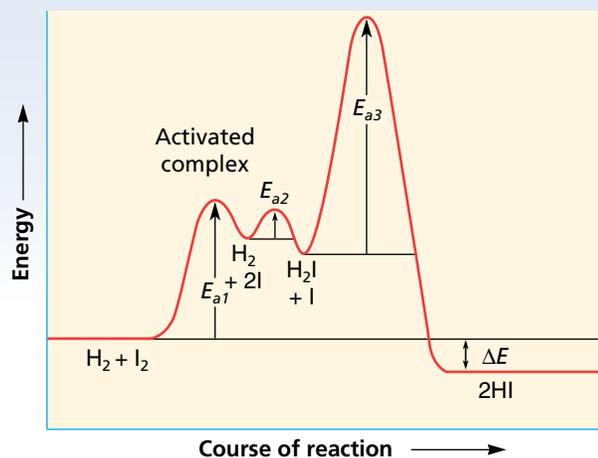
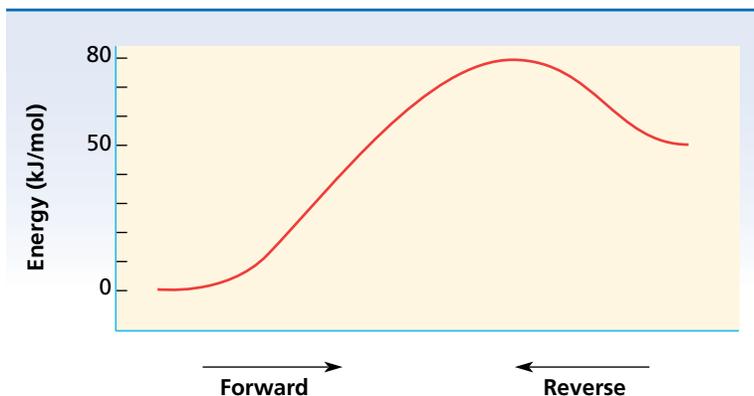


FIGURE 17-11 This energy profile graphically shows the formation of activated complexes during the gas-phase reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$.

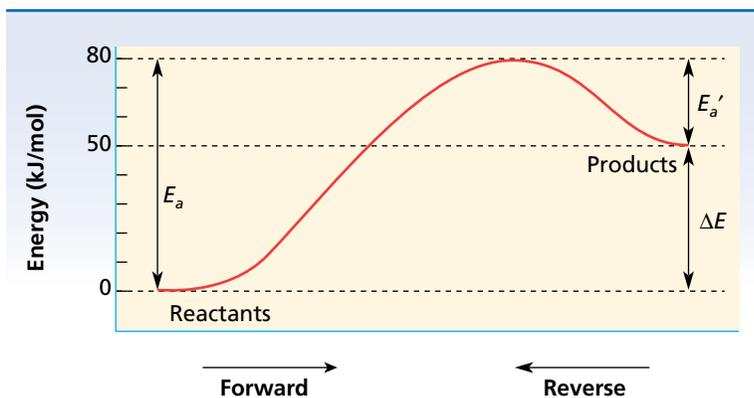
SAMPLE PROBLEM 17-5

Copy the energy diagram below, and label the reactants, products, ΔE , E_a , and E_a' . Determine the value of $\Delta E_{forward}$, $\Delta E_{reverse}$, E_a , and E_a' .



SOLUTION

The energy level of reactants is always at the left-hand end of such a curve, and the energy level of products is always at the right-hand end. The energy change in the reaction, ΔE , is the difference between these two energy levels. The activation energy differs in the forward and reverse directions. As E_a , it is the difference between the reactant energy level and the peak in the curve. As E_a' , it is the difference between the product energy level and the peak in the curve. It is the minimum energy needed to achieve effective reaction in either direction.



$$\Delta E_{forward} = \text{energy of products} - \text{energy of reactants}$$

$$\Delta E_{forward} = 50 \text{ kJ/mol} - 0 \text{ kJ/mol} = +50 \text{ kJ/mol}$$

$$\Delta E_{reverse} = \text{energy of reactants} - \text{energy of products}$$

$$\Delta E_{reverse} = 0 \text{ kJ/mol} - 50 \text{ kJ/mol} = -50 \text{ kJ/mol}$$

$$E_a = \text{energy of activated complex} - \text{energy of reactants}$$

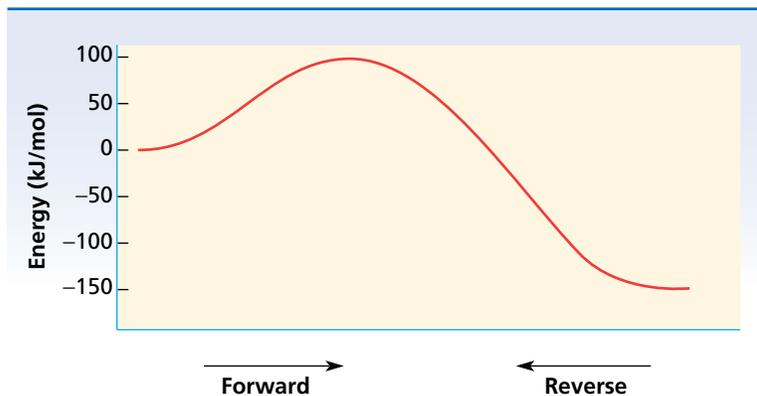
$$E_a = 80 \text{ kJ/mol} - 0 \text{ kJ/mol} = 80 \text{ kJ/mol}$$

$$E_a' = \text{energy of activated complex} - \text{energy of products}$$

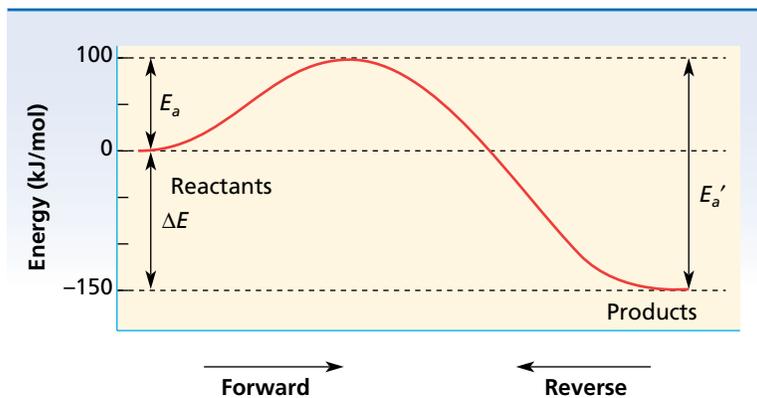
$$E_a' = 80 \text{ kJ/mol} - 50 \text{ kJ/mol} = 30 \text{ kJ/mol}$$

PRACTICE

1. Use the method shown in the sample problem to redraw and label the following energy diagram. Determine the value of $\Delta E_{\text{forward}}$, $\Delta E_{\text{reverse}}$, E_a , and E_a' .



Answer



$$\Delta E_{\text{forward}} = -150 \text{ kJ/mol}$$

$$\Delta E_{\text{reverse}} = +150 \text{ kJ/mol}$$

$$E_a = 100 \text{ kJ/mol}$$

$$E_a' = 250 \text{ kJ/mol}$$

SECTION REVIEW

1. What is meant by reaction mechanism?
2. What factors determine whether a molecular collision produces a reaction?
3. What is activation energy?
4. What is an activated complex?
5. How is activation energy related to the energy of reaction?

Reaction Rate

OBJECTIVES

- Define *chemical kinetics*, and explain the two conditions necessary for chemical reactions to occur.
- Discuss the five factors that influence reaction rate.
- Define *catalyst*, and discuss two different types.
- Explain and write rate laws for chemical reactions.

The change in concentration of reactants per unit time as a reaction proceeds is called the **reaction rate**. The study of reaction rates is concerned with the factors that affect the rate and with the mathematical expressions that reveal the specific dependencies of the rate on concentration. *The area of chemistry that is concerned with reaction rates and reaction mechanisms is called **chemical kinetics**.*

Rate-Influencing Factors

For reactions other than simple decompositions to occur, particles must come into contact in a favorable orientation and with enough energy for activation. Thus, the rate of a reaction depends on the collision frequency of the reactants and on the collision efficiency. Any change in reaction conditions that affects the collision frequency, the collision efficiency, or the collision energy affects the reaction rate. Five important factors influence the rate of a chemical reaction.

Nature of Reactants

Substances vary greatly in their tendencies to react. For example, hydrogen combines vigorously with chlorine under certain conditions. Under the same conditions, it may react only feebly with nitrogen. Sodium and oxygen combine much more rapidly than iron and oxygen under similar conditions. Bonds are broken and other bonds are formed in reactions. The rate of reaction depends on the particular reactants and bonds involved.

Surface Area

Gaseous mixtures and dissolved particles can mix and collide freely; therefore, reactions involving them can occur rapidly. In heterogeneous reactions, the reaction rate depends on the area of contact of the reaction substances. **Heterogeneous reactions** *involve reactants in two different phases*. These reactions can occur only when the two phases are in contact. Thus, the surface area of a solid reactant is an important factor in determining rate. An increase in surface area increases the rate of heterogeneous reactions.

Solid zinc reacts with aqueous hydrochloric acid to produce zinc chloride and hydrogen gas according to the following equation.





TOPIC: Factors affecting rates
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This reaction occurs at the surface of the zinc solid. A cube of zinc measuring 1 cm on each edge presents only 6 cm^2 of contact area. The same amount of zinc in the form of a fine powder might provide a contact area thousands of times greater than the original area. Consequently, the reaction rate of the powdered solid is much higher.

A lump of coal burns slowly when kindled in air. The rate of burning can be increased by breaking the lump into smaller pieces, exposing more surface area. If the piece of coal is powdered and then ignited while suspended in air, it burns explosively. This is the cause of some explosions in coal mines.

Temperature

An increase in temperature increases the average kinetic energy of the particles in a substance; this can result in a greater number of effective collisions when the substance is allowed to react with another substance. If the number of effective collisions increases, the reaction rate will increase.

To be effective, the energy of the collisions must be equal to or greater than the activation energy. At higher temperatures, more particles possess enough energy to form the activated complex when collisions occur. Thus, a rise in temperature produces an increase in collision energy as well as in collision frequency.

Decreasing the temperature of a reaction system has the opposite effect. The average kinetic energy of the particles decreases, so they collide less frequently and with less energy, producing fewer effective collisions. Beginning near room temperature, the reaction rates of many common reactions roughly double with each 10 K (10°C) rise in temperature. This rule of thumb should be used with caution, however. The actual rate increase with a given rise in temperature must be determined experimentally.

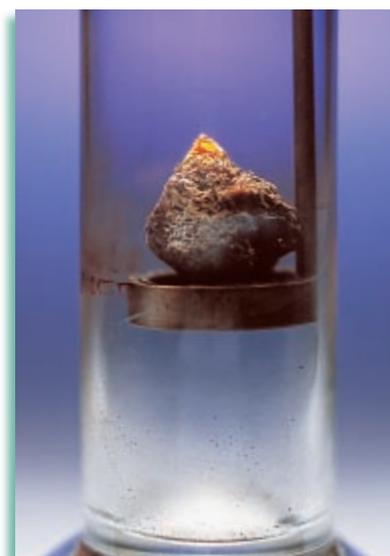
Concentration

Pure oxygen has five times the concentration of oxygen molecules that air has at the same pressure; consequently, a substance that oxidizes in air oxidizes more vigorously in pure oxygen. For example, in Figure 17-12, the light produced when the lump of charcoal is burned in pure oxygen is much more intense than the light produced when the charcoal lump is heated in air until combustion begins. The oxidation of charcoal is a heterogeneous reaction system in which one reactant is a gas. The reaction rate depends not only on the amount of exposed charcoal surface but also on the concentration of the reacting species, O_2 .

In homogeneous reaction systems, reaction rates depend on the concentration of the reactants. Predicting the mathematical relationship between rate and concentration is difficult because most chemical reactions occur in a series of steps, and only one of these steps determines the reaction rate. If the number of effective collisions increases, the rate



(a)



(b)

FIGURE 17-12 Carbon burns faster in pure oxygen (a) than in air (b) because the concentration of the reacting species, O_2 , is greater.

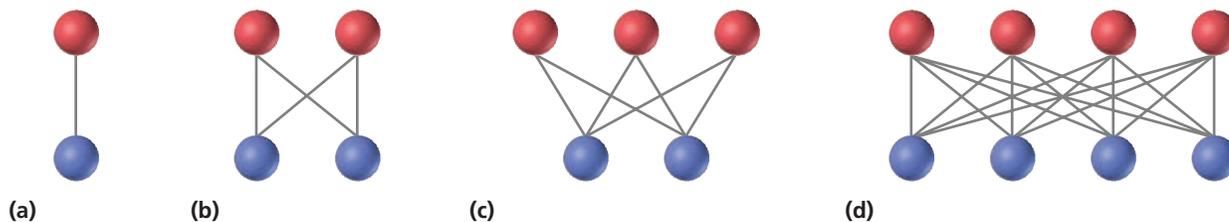


FIGURE 17-13 The concentration of reacting species affects the number of collisions and therefore the reaction rate.

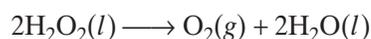
increases as well. In general, an increase in rate is expected if the concentration of one or more of the reactants is increased, as depicted by the model in Figure 17-13. In the system with only two molecules, shown in Figure 17-13(a), only one collision can possibly occur. When there are four molecules in the system, as in Figure 17-13(b), there can be four possible collisions. Under constant conditions, as the number of molecules in the system increases, so does the total number of possible collisions between them. Figure 17-13(c) and (d) show a five- and eight-molecule system, allowing six and sixteen possible collisions, respectively. Lowering the concentration should have the opposite effect. The actual effect of concentration changes on reaction rate, however, must be determined experimentally.



FIGURE 17-14 The reaction rate of the decomposition of hydrogen peroxide, H_2O_2 , can be increased by using a catalyst. The catalyst used here is manganese dioxide, MnO_2 , a black solid. A 30% H_2O_2 solution is added dropwise onto the MnO_2 in the beaker and rapidly decomposes to O_2 and H_2O . Both the oxygen and water appear as gases because the high heat of reaction causes the water to vaporize.

Presence of Catalysts

Some chemical reactions proceed quite slowly. Sometimes their reaction rates can be increased dramatically by the presence of a catalyst. A **catalyst** is a substance that changes the rate of a chemical reaction without itself being permanently consumed. The action of a catalyst is called **catalysis**. The catalysis of the decomposition reaction of hydrogen peroxide by manganese dioxide is shown in Figure 17-14. A catalyst provides an alternative energy pathway or reaction mechanism in which the potential-energy barrier between reactants and products is lowered. The catalyst may be effective in forming an alternative activated complex that requires a lower activation energy—as suggested in the energy profiles of the decomposition of hydrogen peroxide, H_2O_2 , shown in Figure 17-15—according to the following equation.



Catalysts do not appear among the final products of reactions they accelerate. They may participate in one step along a reaction pathway and be regenerated in a later step. In large-scale and cost-sensitive reaction systems, catalysts are recovered and reused. A catalyst that is in the same phase as all the reactants and products in a reaction system is called a **homogeneous catalyst**. When its phase is different from that of the reactants, it is called a **heterogeneous catalyst**. Metals are often used as heterogeneous catalysts. The catalysis of many reactions is promoted by adsorption of reactants on the metal surfaces, which has the effect of increasing the concentration of the reactants.

Comparison of Pathways for the Decomposition of H_2O_2 by Various Catalysts

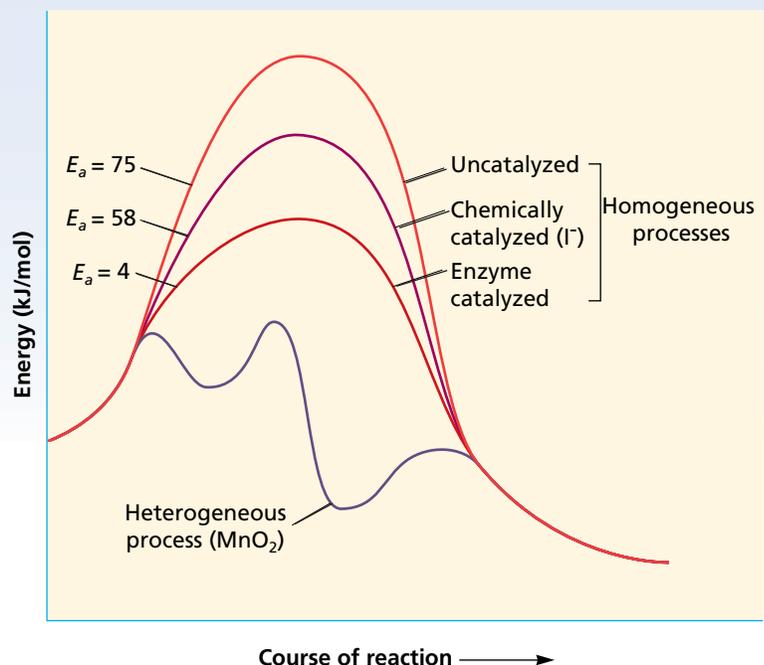


FIGURE 17-15 The activation energy for a chemical reaction can be reduced by adding an appropriate catalyst.

Rate Laws for Reactions

The relationship between the rate of a reaction and the concentration of one reactant is determined experimentally by first keeping the concentrations of other reactants and the temperature of the system constant. Then the reaction rate is measured for various concentrations of the reactant in question. A series of such experiments reveals how the concentration of each reactant affects the reaction rate.

Hydrogen gas reacts with nitrogen monoxide gas at constant volume and at an elevated constant temperature, according to the following equation.



Four moles of reactant gases produce three moles of product gases; thus, the pressure of the system diminishes as the reaction proceeds. The rate of the reaction can, therefore, be determined by measuring the change of pressure in the vessel with time.

Suppose a series of experiments is conducted using the same initial concentration of nitrogen monoxide but different initial concentrations of hydrogen. The initial reaction rate is found to vary directly with the hydrogen concentration: doubling the concentration of H_2 doubles the rate, and tripling the concentration of H_2 triples the rate. If R represents the reaction rate and $[\text{H}_2]$ is the concentration of hydrogen in moles per

liter, the mathematical relationship between rate and concentration can be expressed as follows.

$$R \propto [\text{H}_2]$$

The \propto is a symbol that is read “is proportional to.”

Now suppose the same initial concentration of hydrogen is used but the initial concentration of nitrogen monoxide is varied. The initial reaction rate is found to increase fourfold when the NO concentration is doubled and ninefold when the concentration of NO is tripled. Thus, the reaction rate varies directly with the square of the nitrogen monoxide concentration, as described by the following proportion.

$$R \propto [\text{NO}]^2$$

Because R is proportional to $[\text{H}_2]$ and to $[\text{NO}]^2$, it is proportional to their product.

$$R \propto [\text{H}_2][\text{NO}]^2$$

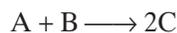
By introduction of an appropriate proportionality constant, k , the expression becomes an equality.

$$R = k[\text{H}_2][\text{NO}]^2$$

*An equation that relates reaction rate and concentrations of reactants is called the **rate law** for the reaction.* It is applicable for a specific reaction at a given temperature. A rise in temperature increases the reaction rates of most reactions. The value of k usually increases as the temperature increases, but the relationship between reaction rate and concentration almost always remains unchanged.

Rate Laws and Reaction Pathway

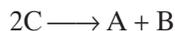
The form of the rate law depends on the reaction mechanism. For a reaction that occurs in a *single step*, the reaction rate of that step is proportional to the product of the reactant concentrations, each of which is raised to its stoichiometric coefficient. For example, suppose one molecule of gas A collides with one molecule of gas B to form two molecules of substance C, according to the following equation.



One particle of each reactant is involved in each collision. Thus, doubling the concentration of either reactant will double the collision frequency. It will also double the reaction rate *for this step*. Therefore, the rate for this step is directly proportional to the concentration of A and B. The rate law for this one-step reaction follows.

$$R = k[\text{A}][\text{B}]$$

Now suppose the reaction is reversible. In the reverse step, two molecules of C must decompose to form one molecule of A and one of B.



Thus, the reaction rate for this reverse step is directly proportional to $[C] \times [C]$. The rate law for the step is as follows.

$$R = k[C]^2$$

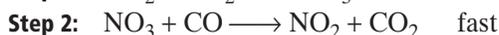
The power to which the molar concentration of each reactant is raised in the rate laws above corresponds to the coefficient for the reactant in the balanced chemical equation. Such a relationship holds *only* if the reaction follows a simple one-step path, that is, if the reaction occurs at the molecular level exactly as written in the chemical equation.

If a chemical reaction proceeds in a sequence of steps, the rate law is determined from the slowest step because it has the lowest rate. *This slowest-rate step is called the **rate-determining step** for the chemical reaction.*

Consider the reaction of nitrogen dioxide and carbon monoxide.



The reaction is believed to be a two-step process represented by the following mechanism.



In the first step, two molecules of NO_2 collide, forming the intermediate species NO_3 . This structure then collides with one molecule of CO and reacts quickly to produce one molecule each of NO_2 and CO_2 . The first step is the slower of the two and is therefore the rate-determining step. We can write the rate law from this rate-determining step.

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

This tells us that two molecules of NO_2 are the reactants in the slower, rate-determining step. CO does not appear in the rate law because it reacts after the rate-determining step, so the reaction rate will not depend on $[\text{CO}]$.

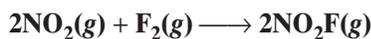
The general form for the rate law is given by the following equation.

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

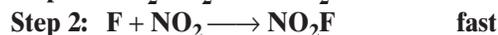
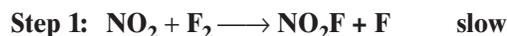
The reaction rate is represented by R , k is the rate constant, and $[\text{A}]$ and $[\text{B}] \dots$ represent the molar concentrations of reactants. The n and m are the respective powers to which the concentrations are raised. They must be determined from *experimental data*.

SAMPLE PROBLEM 17-6

Nitrogen dioxide and fluorine react in the gas phase according to the following equation.



A proposed mechanism for this reaction follows.



Identify the rate-determining step and write an acceptable rate law.

SOLUTION

If we combine these two steps, the intermediate, F, cancels out and we are left with the original equation. The first step is the slower step, and is considered the rate-determining step. We can write the rate law from this rate-determining step.

$$R = k [\text{NO}_2][\text{F}_2]$$

SAMPLE PROBLEM 17-7

A reaction involving reactants X and Y was found to occur by a one-step mechanism: $\text{X} + 2\text{Y} \longrightarrow \text{XY}_2$. Write the rate law for this reaction, and then determine the effect of each of the following on the reaction rate:

- doubling the concentration of X
- doubling the concentration of Y
- using one-third the concentration of Y

SOLUTION

Because the equation represents a single-step mechanism, the rate law can be written from the equation (otherwise, it could not be). The rate will vary directly with the concentration of X, which has an implied coefficient of 1 in the equation, and will vary directly with the square of the concentration of Y, which has the coefficient of 2: $R = k[\text{X}][\text{Y}]^2$.

- Doubling the concentration of X will double the rate ($R = k[2\text{X}][\text{Y}]^2$).
- Doubling the concentration of Y will increase the rate fourfold ($R = k[\text{X}][2\text{Y}]^2$).
- Using one-third the concentration of Y will reduce the rate to one-ninth of its original value ($R = k[\text{X}][\frac{1}{3}\text{Y}]^2$).

PRACTICE

- The rate of a reaction involving L, M, and N is found to double if the concentration of L is doubled, to increase eightfold if the concentration of M is doubled, and to double if the concentration of N is doubled. Write the rate law for this reaction.
- At temperatures below 498 K, the following reaction takes place.



Doubling the concentration of NO_2 quadruples the rate of CO_2 being formed if the CO concentration is held constant. However, doubling the concentration of CO has no effect on the rate of CO_2 formation. Write a rate-law expression for this reaction.

Answer
 $R = k[\text{L}][\text{M}]^3[\text{N}]$

Answer
 $R = k[\text{NO}_2]^2$



Factors Influencing Reaction Rate

Wear Safety Goggles and an Apron.



Materials

- Bunsen burner
- paper ash
- copper foil strip
- graduated cylinder, 10 mL
- magnesium ribbon
- matches
- paper clip
- sandpaper
- steel wool
- 2 sugar cubes
- white vinegar
- zinc strip
- 6 test tubes, 16 × 150 mm
- tongs

Question

How do the type of reactants, surface area of reactants, concentration of reactants, and catalysts affect the rates of chemical reactions?

Procedure

Remove all combustible material from the work area. Wear safety goggles and an apron. Record all your results in a data table.

1. Add 10 mL of vinegar to each of three test tubes. To one test tube, add a 3 cm piece of magnesium ribbon; to a second, add a 3 cm zinc strip; and to a third, add a 3 cm copper strip. (All metals should be the same width.) If necessary, sandpaper the metals until they are shiny.
2. Using tongs, hold a paper clip in the hottest part of the burner flame for 30 s. Repeat with a ball of steel wool 2 cm in diameter.

3. To one test tube, add 10 mL of vinegar; to a second, add 5 mL of vinegar plus 5 mL of water; and to a third, add 2.5 mL of vinegar plus 7.5 mL of water. To each of the three test tubes, add a 3 cm piece of magnesium ribbon.

4. Using tongs, hold a sugar cube and try to ignite it with a match. Then try to ignite it in a burner flame. Rub paper ash on a second cube, and try to ignite it with a match.

Discussion

1. What are the rate-influencing factors in each step of the procedure?
2. What were the results from each step of the procedure? How do you interpret each result?

SECTION REVIEW

1. What is studied in the branch of chemistry that is known as chemical kinetics?
2. List the five important factors that influence the rate of chemical reactions.
3. What is a catalyst? Explain the effect of a catalyst on the rate of chemical reactions. How does a catalyst influence the activation energy required by a particular reaction?
4. What is meant by a rate law for a chemical reaction? Explain the conditions under which a rate law can be written from a chemical equation. When can a rate law not be written from a single step?

CHAPTER 17 REVIEW

CHAPTER SUMMARY

- 17-1**
- Thermochemistry is the study of the changes in energy that accompany chemical reactions and physical changes.
 - A thermochemical equation is an equation that includes the quantity of energy released or absorbed as heat during the reaction as written.
 - The heat of reaction is the quantity of energy released or absorbed as heat during a chemical reaction.
 - An enthalpy change is the amount of energy absorbed or lost as heat by a system in a process carried out at constant pressure.
 - The heat of reaction is negative for exothermic reactions and positive for endothermic reactions.
 - Compounds with highly negative heats of formation tend to be stable; compounds with highly positive or only slightly negative heats of formation tend to be unstable.
 - The standard molar heat of formation is the energy absorbed or released as heat in the formation of one mole of a compound from its elements in their standard states at 25°C.
 - The energy released as heat in a combustion reaction is called the heat of combustion.
 - Heats of reaction can be calculated by using heats of formation of reactants and products.

Vocabulary

| | | | |
|-----------------------|--------------------------|-------------------------------|-------------------------------|
| calorimeter (511) | heat of combustion (519) | joule (511) | temperature (511) |
| enthalpy change (516) | heat of reaction (514) | molar heat of formation (517) | thermochemical equation (515) |
| heat (512) | Hess's law (519) | specific heat (512) | thermochemistry (511) |

- 17-2**
- The tendency throughout nature is for a reaction to proceed in the direction that leads to a lower energy state.
 - Entropy is a measure of the disorder of a system.
 - Free-energy change combines the effects of entropy and enthalpy changes and temperature of a system, and it is a measure of the overall tendency toward natural change.
 - A reaction can occur spontaneously if it is accompanied by a decrease in free energy. It cannot occur spontaneously if there is an increase in free energy.

Vocabulary

| | | |
|---------------|-------------------|--------------------------|
| entropy (527) | free energy (528) | free-energy change (528) |
|---------------|-------------------|--------------------------|

- 17-3**
- The step-by-step process by which an overall chemical reaction occurs is called the reaction mechanism.
 - In order for chemical reactions to occur, the particles of the reactants must collide.
 - Activation energy is needed to merge valence electrons and loosen bonds sufficiently for molecules to react.
 - An activated complex is formed when an effective collision between molecules of reactants raises the internal energy to the minimum level necessary for a reaction to occur.

Vocabulary

| | | | |
|-------------------------|------------------------|----------------------------|--------------------------|
| activated complex (535) | collision theory (532) | homogeneous reaction (532) | intermediates (532) |
| activation energy (534) | | | reaction mechanism (531) |

CHAPTER SUMMARY (continued)

- 17-4** • The rate of reaction is influenced by the following factors: nature of reactants, surface area, temperature, concentration of reactants, and the presence of catalysts and inhibitors.
- The rates at which chemical reactions occur can sometimes be experimentally measured and expressed in terms of mathematical equations called rate laws.

Vocabulary

| | | | |
|-----------------|-------------------------------|-----------------------------|---------------------|
| catalysis (540) | heterogeneous catalyst (540) | homogeneous catalyst (540) | rate law (542) |
| catalyst (540) | heterogeneous reactions (538) | rate-determining step (543) | reaction rate (538) |

REVIEWING CONCEPTS

- How does the energy of the products of a reaction system compare with the energy of the reactants when the reaction is
 - endothermic?
 - exothermic? (17-1)
- Distinguish between heats of reaction, formation, and combustion.
 - On what basis are heats of formation and combustion defined? (17-1)
- Write the equation that can be used to calculate the heat of reaction from heats of formation. (17-1)
- What factors affect the value of ΔH in a reaction system? (17-1)
- Would entropy increase or decrease for phase changes in which the reactant is a gas or liquid and the product is a solid? What sign would the entropy change have? (17-2)
- How does an increase in temperature affect the entropy of a system? (17-2)
- What combination of ΔH and ΔS values always produces a negative free-energy change? (17-2)
- Explain the relationship between temperature and the tendency for reactions to occur spontaneously. (17-2)
- What is the collision theory?
 - According to this theory, what two conditions must be met in order for a collision between reactant molecules to be effective in producing new chemical species? (17-3)
- What condition must be met in order for an activated complex to result from the collision of reactant particles?
 - Where, in terms of energy, does the activated complex occur along a typical reaction pathway? (17-3)
- In a reversible reaction, how does the activation energy required for the exothermic change compare with the activation energy required for the endothermic change? (17-3)
- Would you expect the following equation to represent the mechanism by which ethane (C_2H_6) burns? Why or why not? (17-3)
$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$
- The decomposition of nitrogen dioxide $2NO_2 \longrightarrow 2NO + O_2$ occurs in a two-step sequence at elevated temperatures. The first step is $NO_2 \longrightarrow NO + O$. Predict a possible second step that, when combined with the first step, gives the complete reaction. (17-3)
- What is meant by the rate-determining step for a chemical reaction? (17-4)
- Write the general equation for the rate law, and label the various factors. (17-4)

PROBLEMS

Specific Heat

16. How much heat energy is needed to raise the temperature of a 55 g sample of aluminum from 22.4°C to 94.6°C? Refer to Table 17-1 for the specific heat of aluminum. (Hint: See Sample Problem 17-1.)
17. 3.5 kJ of heat are added to a 28.2 g sample of iron at 20°C. What is the final temperature of the iron in kelvins? Refer to Table 17-1 for the specific heat of iron.

Reaction Heat

18. For each equation listed below, determine the ΔH and type of reaction (endothermic or exothermic).
- $\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 393.51 \text{ kJ}$
 - $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) + 890.31 \text{ kJ}$
 - $\text{CaCO}_3(s) + 176 \text{ kJ} \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
 - $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l) + 44.02 \text{ kJ}$
19. Rewrite each equation below with the ΔH value included with either the reactants or the products, and identify the reaction as endothermic or exothermic.
- $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l);$
 $\Delta H^\circ = -285.83 \text{ kJ/mol}$
 - $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s);$
 $\Delta H^\circ = -1200 \text{ kJ/mol}$
 - $\text{I}_2(s) \longrightarrow \text{I}_2(g); \Delta H^\circ = +62.4 \text{ kJ/mol}$
 - $3\text{CO}(g) + \text{Fe}_2\text{O}_3(s) \longrightarrow 2\text{Fe}(s) + 3\text{CO}_2(g);$
 $\Delta H^\circ = -24.7 \text{ kJ/mol}$
20. Use Appendix Table A-14 to write the reaction illustrating the formation of each of the following compounds from its elements. Write the ΔH as part of each equation, and indicate the ΔH for the reverse reaction.
- $\text{CaCl}_2(s)$
 - $\text{C}_2\text{H}_2(g)$ (ethyne or acetylene)
 - $\text{SO}_2(g)$

21. Use heat-of-formation data given in Appendix Table A-14 (page 902) to calculate the heat of reaction for each of the following. Solve each by combining the known thermochemical equations. Verify each result by using the general equation

for finding heats of reaction from heats of formation. (Hint: See Sample Problem 17-2.)

- $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
 - $\text{Ca}(\text{OH})_2(s) \longrightarrow \text{CaO}(s) + \text{H}_2\text{O}(g)$
 - $\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \longrightarrow 2\text{Fe}(s) + 3\text{CO}_2(g)$
22. Calculate the standard heats of reaction for combustion reactions in which ethane, C_2H_6 , and benzene, C_6H_6 , are the respective reactants and $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are the products in each. Solve each by combining the known thermochemical equations using the ΔH_f° values in Appendix Table A-14 (page 902). Verify the result by using the general equation for finding heats of reaction from heats of formation.
- $\text{C}_2\text{H}_6(g) + \text{O}_2(g) \longrightarrow$
 - $\text{C}_6\text{H}_6(l) + \text{O}_2(g) \longrightarrow$
23. The heat of formation of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is -277.0 kJ/mol at 298.15 K. Calculate the heat of combustion of one mole of ethanol, assuming that the products are $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. (Hint: See Sample Problem 17-3.)

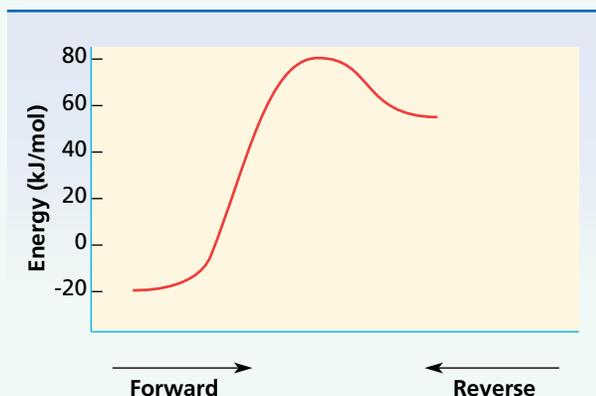
Entropy and Free Energy

24. Based on the following values, compute ΔG values for each reaction and predict whether the reaction will occur spontaneously. (Hint: See Sample Problem 17-4.)
- $\Delta H = +125 \frac{\text{kJ}}{\text{mol}}, T = 293 \text{ K},$
 $\Delta S = 0.0350 \frac{\text{kJ}}{(\text{mol}\cdot\text{K})}$
 - $\Delta H = -85.2 \frac{\text{kJ}}{\text{mol}}, T = 127^\circ\text{C},$
 $\Delta S = 0.125 \frac{\text{kJ}}{(\text{mol}\cdot\text{K})}$
 - $\Delta H = -275 \frac{\text{kJ}}{\text{mol}}, T = 773 \text{ K},$
 $\Delta S = 0.450 \frac{\text{kJ}}{(\text{mol}\cdot\text{K})}$
25. The ΔS° for the reaction shown, at 298.15 K, is $0.00300 \text{ kJ}/(\text{mol}\cdot\text{K})$. Calculate the ΔG° for this reaction, and determine whether it will occur spontaneously at 298.15 K.
- $$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) + 393.51 \text{ kJ}$$

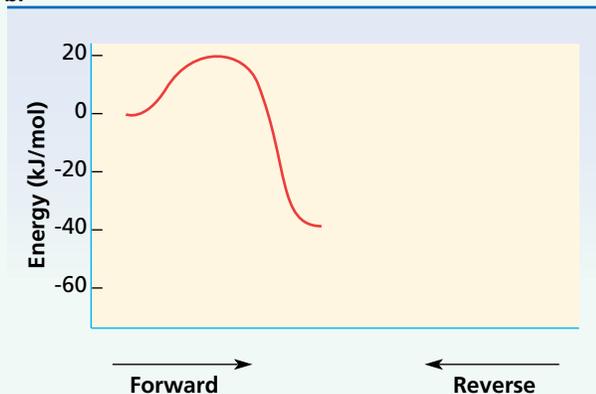
Reaction Diagrams

26. For each of the energy diagrams provided below, label the reactants, products, ΔE , E_a , and E_a' . Also determine the values of ΔE for the forward and reverse reactions, and the values of E_a and E_a' . (Hint: See Sample Problem 17-5.)

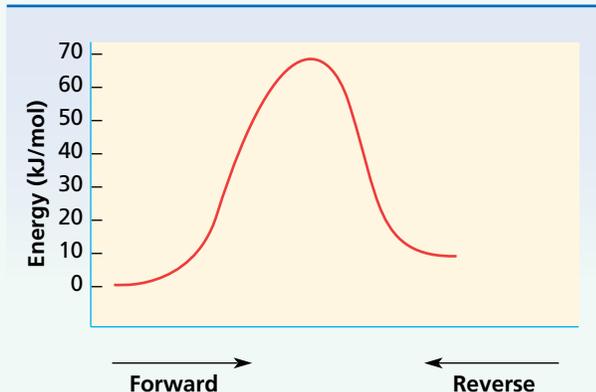
a.



b.



c.



27. Draw and label energy diagrams depicting the following reactions, and determine all remaining values. Place the reactants at energy level zero.
- $\Delta E_{\text{forward}} = -10 \text{ kJ/mol}$ $E_a' = 40 \text{ kJ/mol}$
 - $\Delta E_{\text{forward}} = -95 \text{ kJ/mol}$ $E_a = 20 \text{ kJ/mol}$
 - $\Delta E_{\text{reverse}} = -40 \text{ kJ/mol}$ $E_a' = 30 \text{ kJ/mol}$

Rate Law

28. Determine the overall balanced equation for a reaction having the following proposed mechanism and write an acceptable rate law. (Hint: See Sample Problem 17-6.)
- Step 1:** $\text{B}_2 + \text{B}_2 \longrightarrow \text{E}_3 + \text{D}$ slow
Step 2: $\text{E}_3 + \text{A} \longrightarrow \text{B}_2 + \text{C}_2$ fast
29. A reaction involving reactants A and B is found to occur in the one-step mechanism:
 $2\text{A} + \text{B} \longrightarrow \text{A}_2\text{B}$. Write the rate law for this reaction, and predict the effect of doubling the concentration of either reactant on the overall reaction rate. (Hint: See Sample Problem 17-7.)
30. A chemical reaction is expressed by the balanced chemical equation $\text{A} + 2\text{B} \longrightarrow \text{C}$. Using the data below, answer the following:
- Determine the rate law for the reaction.
 - Calculate the value of the specific rate constant.
 - If the initial concentrations of both A and B are 0.30 M, at what initial rate is C formed?

Three reaction-rate experiments yield the following data.

| Experiment number | Initial [A] | Initial [B] | Initial rate of formation of C |
|-------------------|-------------|-------------|------------------------------------|
| 1 | 0.20 M | 0.20 M | $2.0 \times 10^{-4} \text{ M/min}$ |
| 2 | 0.20 M | 0.40 M | $8.0 \times 10^{-4} \text{ M/min}$ |
| 3 | 0.40 M | 0.40 M | $1.6 \times 10^{-3} \text{ M/min}$ |

MIXED REVIEW

31. When graphite reacts with hydrogen at 300 K, ΔH is -74.8 kJ/mol and ΔS is $-0.0809 \text{ kJ/(mol}\cdot\text{K)}$. Will this reaction occur spontaneously?
32. How might you change reaction conditions to induce an endothermic reaction that does not occur naturally?

33. The standard heat of formation for sulfur dioxide gas is $-296.8 \text{ J}/(\text{mol}\cdot\text{K})$. Calculate the amount of energy given off in kJ when 30.0 g of $\text{SO}_2(\text{g})$ is formed from its elements.
34. The thermite reaction used in some welding applications has the following enthalpy and entropy changes at 298.15 K. Assuming ΔS and ΔH are constant, calculate ΔG at 448 K.
 $\text{Fe}_2\text{O}_3 + 2\text{Al}(\text{s}) \longrightarrow 2\text{Fe}(\text{s}) + \text{Al}_2\text{O}_3(\text{s})$
 $\Delta H^\circ = -851.5 \text{ kJ/mol}$ $\Delta S^\circ = -38.5 \text{ J}/(\text{mol}\cdot\text{K})$
35. Draw and label energy diagrams depicting the following reactions, and determine all remaining values. Place the reactants at energy level zero.
- $\Delta E = +30 \text{ kJ/mol}$ $E_a' = 20 \text{ kJ/mol}$
 - $\Delta E = -30 \text{ kJ/mol}$ $E_a = 20 \text{ kJ/mol}$
36. A particular reaction is found to have the following rate law.

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

How is the rate affected by each of the following changes?

- the initial concentration of A is cut in half
 - the initial concentration of B is tripled
 - the concentration of A is doubled, but the concentration of B is cut in half
 - a catalyst is added
37. Rewrite each equation below with the ΔH value included in either the reactants or products, and identify the reaction as endothermic or exothermic.
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g}); \Delta H = -197.8 \text{ kJ/mol}$
 - $2\text{NO}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g}); \Delta H = +114.2 \text{ kJ/mol}$
 - $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta H = -1411.0 \text{ kJ/mol}$
38. For each of the following pairs, choose the substance or process you would expect to react more rapidly.
- granulated sugar or powdered sugar
 - zinc in HCl at 298.15 K or zinc in HCl at 410 K
 - 5 g of thick platinum wire or 5 g of thin platinum wire
39. Calculate the change in enthalpy for the following reaction.
- $$4\text{FeO}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{Fe}_2\text{O}_3(\text{s})$$

Use the heat-of-formation data listed in Appendix Table A-14.

CRITICAL THINKING

40. **Predicting Outcomes** The balanced equation for a rapid homogeneous reaction between two gases is as follows: $4\text{A} + \text{B} \longrightarrow 2\text{C} + 2\text{D}$. Since the simultaneous collision of four molecules of one reactant with one molecule of the other reactant is extremely improbable, what would you predict about the nature of the reaction mechanism for this reaction system?
41. **Evaluating Ideas**
- How can you justify calling the reaction pathway that is shown in Figure 17-10 the minimum-energy pathway for reaction?
 - What significance is associated with the maximum-energy region of this minimum-energy pathway?
42. **Applying Models** Explain why there is a danger of explosion in places such as coal mines, saw mills, and grain elevators, where large amounts of dry, powdered combustible materials are present.
43. **Evaluating Methods** What property would you measure in order to determine the reaction rate for the following reaction? Justify your choice.



TECHNOLOGY & LEARNING

44. **Graphing Calculator** Calculating the Free-Energy Change

The graphing calculator can run a program that calculates the free-energy change, given the temperature, T , change in enthalpy, ΔH , and change in entropy, ΔS . Given that the temperature is 298 K, the change in enthalpy is 131.3 kJ/mol, and the change in entropy is 0.134 kJ/(mol·K), you can calculate free-energy change in kJ/mol. Then use the program to make calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

- What is the free energy change given a temperature of 300 K, a change in enthalpy of 132 kJ/mol, and a change in entropy of 0.086 kJ/(mol•K)?
- What is the free energy change given a temperature of 288 K, a change in enthalpy of 115 kJ/mol, and a change in entropy of 0.113 kJ/(mol•K)?
- What is the free energy change given a temperature of 298 K, a change in enthalpy of 181 kJ/mol, and a change in entropy of 0.135 kJ/(mol•K)?

RESEARCH & WRITING

- Obtain information on alternative units of measure used to express values of heat and other forms of energy. Also, find out how the quantities relate to SI metric units. Include information specifically on English units, such as the British Thermal Unit (BTU), and on typical BTU ratings of household appliances. Calculate how these ratings would be expressed in joules instead.
- Look for situations around your house in which processes are speeded up by an increase in temperature or slowed down by a decrease in temperature. Make a list, and discuss the different processes.

ALTERNATIVE ASSESSMENT

- Performance** Design a simple calorimeter investigation to determine the molar heat of fusion of water. Use the following materials: a large plastic-foam cup with cover, a thermometer, a balance, water at room temperature, and an ice cube. Allow your teacher to review your design. Then carry out the investigation, and write a laboratory report including your calculations and a comparison of your quantitative results with known values. Try to account for any disagreements between the experimental and actual values.