

Sample Problem 11-2

To study the amount of heat released during a neutralization reaction (you will learn about neutralization in Chapter 21), 25.0 mL of water containing 0.025 mol HCl is added to 25.0 mL of water containing 0.025 mol NaOH in a foam cup calorimeter. At the start, the solutions and the calorimeter are all at 25.0 °C. During the reaction, the highest temperature observed is 32.0 °C. Calculate the heat (in kJ) released during this reaction. Assume the densities of the solutions are 1.00 g/mL.

1. ANALYZE List the knowns and the unknown.

Knowns:

HCl solution:

- $V_{\text{HCl}} = 25.0 \text{ mL}$
- solution contains 0.025 mol HCl

NaOH solution:

- $V_{\text{NaOH}} = 25.0 \text{ mL}$
- solution contains 0.025 mol NaOH
- $V_{\text{final}} = V_{\text{HCl}} + V_{\text{NaOH}}$
 $= 25.0 \text{ mL} + 25.0 \text{ mL} = 50.0 \text{ mL}$
- $T_i = 25.0 \text{ }^{\circ}\text{C}$
- $T_f = 32.0 \text{ }^{\circ}\text{C}$
- $C_{\text{water}} = 4.18 \text{ J/(g} \times ^{\circ}\text{C)}$
- $\text{Density}_{\text{solution}} = 1.00 \text{ g/mL}$

Unknown:

- $\Delta H = ? \text{ kJ}$

The equation requires the mass of the water used in the experiment, but the mass is not known. Use dimensional analysis to determine the mass of the water. ΔT must also be calculated. Once m , C , and ΔT are known, use $\Delta H = m \times C \times \Delta T$ to solve for ΔH of the water.

2. CALCULATE Solve for the unknown.

First, calculate the total mass of the water. Only the final volume of the solution (V_f) is needed to make the calculation.

$$m = (50.0 \text{ mL}) \times \left(\frac{1.00 \text{ g}}{\text{mL}} \right) = 50.0 \text{ g}$$

Now calculate ΔT .

$$\Delta T = T_f - T_i \quad \Delta T = 32.0 \text{ }^{\circ}\text{C} - 25.0 \text{ }^{\circ}\text{C} = 7.0 \text{ }^{\circ}\text{C}$$

Substitute the values for m , C_{water} , and ΔT into the equation and solve for the unknown (ΔH).

$$\begin{aligned} \Delta H &= m \times C \times \Delta T \\ &= (50.0 \text{ g})(4.18 \text{ J/(g} \times ^{\circ}\text{C)})(7.0 \text{ }^{\circ}\text{C}) \\ &= 1463 \text{ J} = 1.5 \times 10^3 \text{ J} \end{aligned}$$

Convert joules to kilojoules.

$$\Delta H = (1.5 \times 10^3 \text{ J}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 1.5 \text{ kJ}$$

Practice Problems

- A student mixed 50.0 mL of water containing 0.50 mol HCl at 22.5 °C with 50.0 mL of water containing 0.50 mol NaOH at 22.5 °C in a foam cup calorimeter. The temperature of the resulting solution increased to 26.0 °C. How much heat in kilojoules (kJ) was released by this reaction?
- A small pebble is heated and placed in a foam cup calorimeter containing 25.0 mL of water at 25.0 °C. The water reaches a maximum temperature of 26.4 °C. How many joules of heat were released by the pebble?

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Problem-Solving 12

Solve Problem 12 with the help of an interactive guided tutorial.



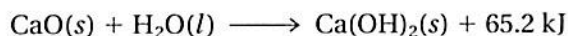
Sample Problem 11-2 (cont.)

3. **EVALUATE** Does the result make sense?

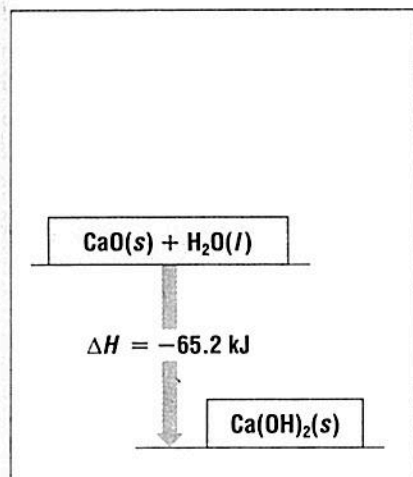
The sign of ΔH for the water is positive; the water absorbs 1.5 kJ of heat. Therefore, this neutralization reaction releases 1.5 kJ of heat into the water in the calorimeter, so the sign of ΔH for the reaction is negative. About 4 J of heat is required to raise the temperature of 1 g of water 1 °C. Thus it would take about 200 J to raise the temperature of 50 g of water 1 °C. Further, about 1400 J, or 1.4 kJ, is needed to raise the temperature of 50 g of water 7 °C. This estimated answer is very close to the calculated value of ΔH for the neutralization reaction.

Thermochemical Equations

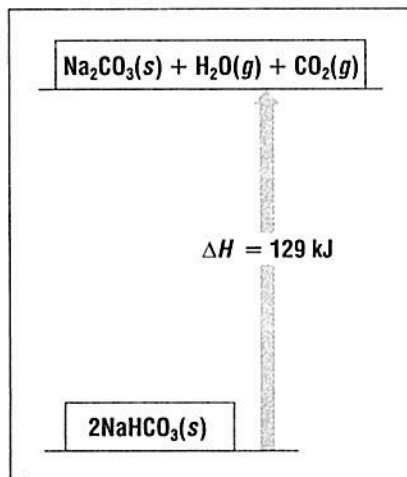
If you mix calcium oxide with water, an exothermic reaction takes place. The water in the mixture becomes warm. This reaction occurs when cement, which contains calcium oxide, is mixed to make concrete. When 1 mol of calcium oxide reacts with 1 mol of water, 1 mol of calcium hydroxide forms and 65.2 kJ of heat is released. You can show this in the chemical equation by including heat change as a product of the reaction. The diagram in Figure 11.11a shows the heat change that occurs in this exothermic reaction.



You can treat heat change in a chemical reaction like any other reactant or product in a chemical equation. An equation that includes the heat change is called a **thermochemical equation**. A **heat of reaction** is the heat change for the equation exactly as it is written. You will usually see heats of reaction reported as ΔH , which is the heat change at constant pressure. The physical state of the reactants and products must also be given. The standard conditions are that the reaction is carried out at 101.3 kPa (1 atmosphere) and that the reactants and products are in their usual physical states at 25 °C.



(a) Exothermic Reaction



(b) Endothermic Reaction

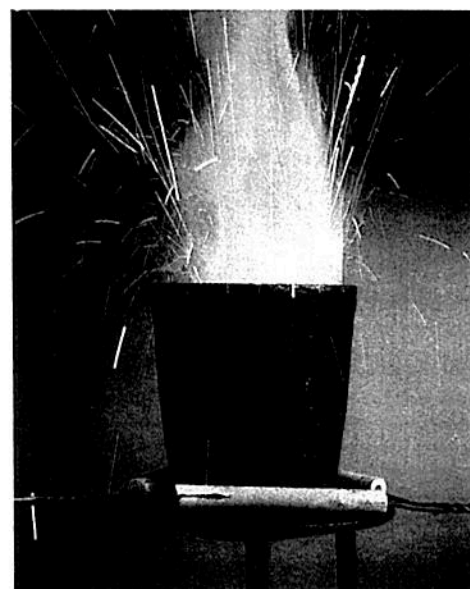


Figure 11.10

The reaction between iron(III) oxide and aluminum, called the thermite reaction, releases so much heat that the iron produced is in the molten state.

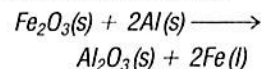
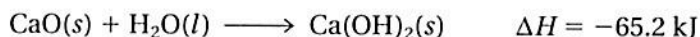


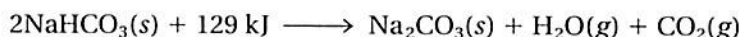
Figure 11.11

These enthalpy diagrams show exothermic and endothermic processes: (a) the reaction of calcium oxide and water and (b) the decomposition of sodium hydrogen carbonate. In which case is the enthalpy of the reactant(s) higher than that of the product(s)?

The heat of reaction, or ΔH , in the above example is -65.2 kJ. Each mole of calcium oxide and water that react to form calcium hydroxide produces 65.2 kJ of heat.



Other reactions absorb heat from the surroundings. For example, baking soda (sodium hydrogen carbonate) decomposes when it is heated, making it useful in baking. The carbon dioxide released in the reaction causes a cake to rise while baking. This process is endothermic, and the heat of reaction is 129 kJ.



Remember that ΔH is positive for endothermic reactions. Therefore, you can write the reaction as follows.



Sample Problem 11-3

Using the equation for the reaction above, calculate the kilojoules of heat required to decompose 2.24 mol $\text{NaHCO}_3(s)$.

1. ANALYZE List the knowns and the unknown.

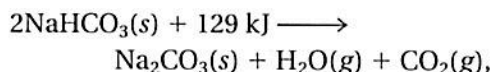
Knowns:

- 2.24 mol $\text{NaHCO}_3(s)$ decomposes • $\Delta H = 129 \text{ kJ}$

Unknown:

- $\Delta H = ? \text{ kJ}$

Use the thermochemical equation,



to write a conversion factor relating kilojoules of heat and moles of NaHCO_3 . Then use the conversion factor to determine ΔH for 2.24 mol NaHCO_3 .

2. CALCULATE Solve for the unknown.

The thermochemical equation indicates that 129 kJ are needed to decompose 2 mol $\text{NaHCO}_3(s)$. Using this relationship, the conversion factor is

$$\frac{129 \text{ kJ}}{2 \text{ mol NaHCO}_3(s)}$$

Using dimensional analysis, solve for ΔH .

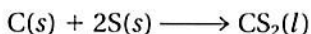
$$\begin{aligned} \Delta H &= 2.24 \text{ mol NaHCO}_3(s) \times \frac{129 \text{ kJ}}{2 \text{ mol NaHCO}_3(s)} \\ &= 144 \text{ kJ} \end{aligned}$$

3. EVALUATE Does the result make sense?

Because the ΔH of 129 kJ refers to the decomposition of 2 mol $\text{NaHCO}_3(s)$, the decomposition of 2.24 mol should absorb about 10% more heat than 129 kJ, or slightly more than 142 kJ. The answer of 144 kJ is consistent with this estimate.

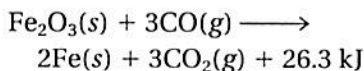
Practice Problems

13. When carbon disulfide is formed from its elements, heat is absorbed. Calculate the amount of heat (in kJ) absorbed when 5.66 g of carbon disulfide is formed.



$$\Delta H = 89.3 \text{ kJ}$$

14. The production of iron and carbon dioxide from iron(III) oxide and carbon monoxide is an exothermic reaction. How many kilojoules of heat are produced when 3.40 mol Fe_2O_3 reacts with an excess of CO ?



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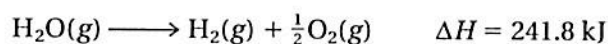
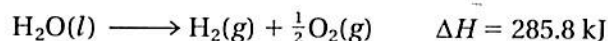
Problem-Solving 14

Solve Problem 14 with the help of an interactive guided tutorial.



Chemistry problems involving enthalpy changes are similar to stoichiometry problems. The amount of heat released or absorbed during a reaction depends on the number of moles of the reactants involved. The decomposition of 2 mol of sodium hydrogen carbonate, for example, requires 129 kJ of heat. Therefore, the decomposition of 4 mol of the same substance would require twice as much heat, or 258 kJ. Figure 11.11b on page 303 shows the heat changes for this reaction. In this and other endothermic processes, the potential energy of the product(s) is higher than the potential energy of the reactant(s).

The physical state of the reactants and products in a thermochemical reaction must also be stated. To see why, compare the following two equations for the decomposition of 1 mol of water.



$$\text{difference} = 44.0 \text{ kJ}$$

Although the two equations are very similar, the different physical states of the H_2O result in different ΔH values. In one case, the reactant is a liquid; in the other case, the reactant is a gas. The vaporization of 1 mole of liquid water to water vapor at 25 °C requires an extra 44.0 kJ of heat. Notice also that fractional coefficients are used here for O_2 because 1 mol H_2O is being decomposed.

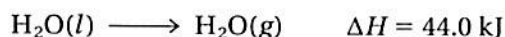


Table 11.4 lists heats of combustion for some common substances. The **heat of combustion** is the heat of reaction for the complete burning of one mole of a substance.

Table 11.4

Heats of Combustion at 25 °C		
Substance	Formula	ΔH (kJ/mol)
Hydrogen	$\text{H}_2(g)$	-286
Carbon	$\text{C}(s)$, graphite	-394
Carbon monoxide	$\text{CO}(g)$	-283
Methane	$\text{CH}_4(g)$	-890
Methanol	$\text{CH}_3\text{OH}(l)$	-726
Acetylene	$\text{C}_2\text{H}_2(g)$	-1300
Ethanol	$\text{C}_2\text{H}_5\text{OH}(l)$	-1368
Propane	$\text{C}_3\text{H}_8(g)$	-2220
Benzene	$\text{C}_6\text{H}_6(l)$	-3268
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(s)$	-2808
Octane	$\text{C}_8\text{H}_{18}(l)$	-5471
Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$	-5645

Link TO

BIOLOGY

Warmth from Fat

How do animals such as polar bears and seals survive the cold land and water temperatures where they live? A good coat of fur helps, but it is not enough to



keep them warm. These animals also have special fat cells that help generate heat. These special cells are in tissue called brown fat. The cells of brown fat are unlike other fat cells in the animal's body. Most other cells store chemical energy from the breakdown of carbohydrates and fatty acids in adenosine triphosphate (ATP). ATP acts as the central source of energy for the activities and growth of all animals. Heat is mostly a waste product in ATP-producing cells. The heat generated by the brown fat tissue, however, helps the animal keep relatively comfortable even at subzero temperatures.



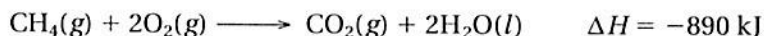
Figure 11.12

The combustion of natural gas is an exothermic reaction. As bonds in methane, the main component of natural gas, and oxygen are broken and bonds in carbon dioxide and water are formed, large amounts of energy are released. This energy powers the engine of automobiles. Natural gas is an alternative to gasoline because it substantially reduces air pollution while increasing engine life.

The combustion of natural gas, which is mostly methane, is an exothermic reaction used to heat many homes around the country.



This can also be written as follows.



Burning 1 mol of methane releases 890 kJ of heat. The heat of combustion (ΔH) for this reaction is -890 kJ per mole of carbon burned.

Like other heats of reaction, heats of combustion are reported as the enthalpy changes when the reactions are carried out at 101.3 kPa of pressure and the reactants and products are in their physical states at 25°C .

section review 11.2

- When 2 mol of solid magnesium (Mg) combines with 1 mole of oxygen gas (O_2), 2 mol of solid magnesium oxide (MgO) is formed and 1204 kJ of heat is released. Write the thermochemical equation for this combustion reaction.
- Gasohol contains ethanol ($\text{C}_2\text{H}_5\text{OH}(\text{l})$), which when burned reacts with oxygen to produce $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. How much heat is released when 12.5 g of ethanol burns?
- Explain the term heat of reaction.
- Hydrogen gas and fluorine gas react to produce hydrogen fluoride. Calculate the heat change (in kJ) for the conversion of 15.0 g of hydrogen gas to hydrogen fluoride gas at constant pressure.



- Why is it important to give the physical state of a substance in a thermochemical reaction?



Chem ASAP! Assessment 11.2 Check your understanding of the important ideas and concepts in Section 11.2.



HEAT IN CHANGES OF STATE

section 11.3

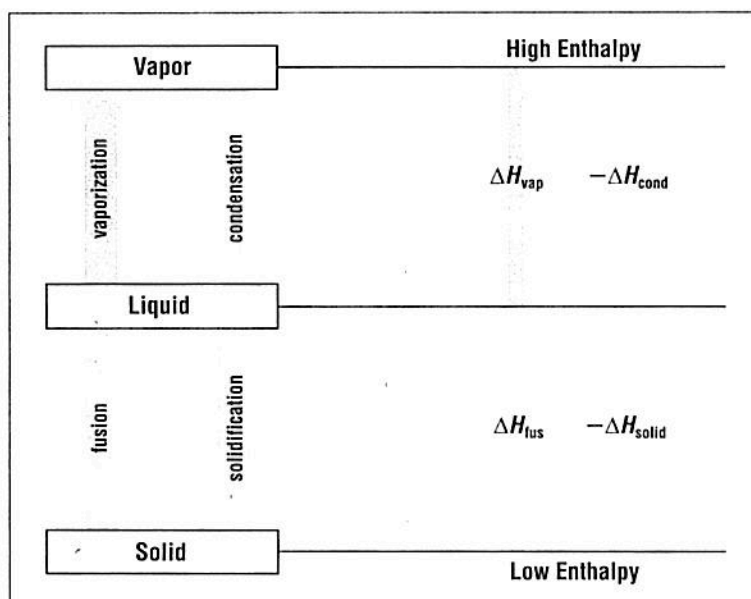
When your body heats up, you start to sweat. The evaporation of sweat is your body's way of cooling itself to a normal temperature. Why does the evaporation of sweat from your skin help to rid your body of excess heat?

Heats of Fusion and Solidification

What happens if you place an ice cube on a table in a warm room? The ice cube is the system, and the table and air around it are the surroundings. The ice absorbs heat from its surroundings and begins to melt. The temperature of the ice and the water produced remains at 0 °C until all of the ice has melted. The temperature of the water begins to increase only after all of the ice has melted. In this section you will learn about heat changes that occur during changes of state.

Like ice cubes, all solids absorb heat as they melt to become liquids. The heat absorbed by one mole of a substance in melting from a solid to a liquid at a constant temperature is the **molar heat of fusion** (ΔH_{fus}). The heat lost when one mole of a liquid solidifies at a constant temperature is the **molar heat of solidification** (ΔH_{solid}). The quantity of heat absorbed by a melting solid is exactly the same as the quantity of heat lost when the liquid solidifies; that is, $\Delta H_{\text{fus}} = -\Delta H_{\text{solid}}$, as shown in Figure 11.13. Why is this true? Table 11.5 on the following page gives heats of fusion of some substances.

The melting of 1 mol of ice at 0 °C to 1 mol of water at 0 °C requires the absorption of 6.01 kJ of heat. This quantity of heat is the molar heat of fusion. Likewise, the conversion of 1 mol of water at 0 °C to 1 mol of ice at 0 °C releases 6.01 kJ. This quantity of heat is the molar heat of solidification.



objectives

- ▶ Classify, by type, the heat changes that occur during melting, freezing, boiling, and condensing
- ▶ Calculate heat changes that occur during melting, freezing, boiling, and condensing

key terms

- ▶ molar heat of fusion
- ▶ molar heat of solidification
- ▶ molar heat of vaporization
- ▶ molar heat of condensation
- ▶ molar heat of solution

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Animation 12

Observe the phase changes as ice is converted to steam when heat is added.



Figure 11.13

Enthalpy changes accompany changes in state. Fusion and vaporization are endothermic processes. Solidification and condensation are exothermic processes.

Table 11.5

Heats of Physical Change					
Substance	Formula	Freezing point (K)	ΔH_{fus} (kJ/mol)	Boiling point (K)	ΔH_{vap} (kJ/mol)
Acetone	CH_3COCH_3	177.8	5.72	329.4	29.1
Ammonia	NH_3	195.3	5.65	239.7	23.4
Argon	Ar	83.8	1.2	87.3	6.5
Benzene	C_6H_6	278.7	9.87	353.3	30.8
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	158.7	4.60	351.5	43.5
Helium	He	3.5	0.02	4.22	0.08
Hydrogen	H_2	14.0	0.12	20.3	0.90
Methane	CH_4	90.7	0.94	111.7	8.2
Methanol	CH_3OH	175.5	3.16	337.2	35.3
Neon	Ne	24.5	0.33	27.1	1.76
Nitrogen	N_2	63.3	0.72	77.4	5.58
Oxygen	O_2	54.8	0.44	90.2	6.82
Water	H_2O	273.2	6.01	373.2	40.7

MINI LAB



Heat of Fusion of Ice

PURPOSE

To estimate the heat of fusion of ice.

MATERIALS

- ice
- foam cup
- graduated cylinder
- thermometer
- hot water
- temperature probe (optional)

PROCEDURE



Probe version available in the Probeware Lab Manual.

1. Fill a 100-mL graduated cylinder with hot tap water. Allow the filled cylinder to stand for 1 minute. Pour the water into the sink.
2. Use the graduated cylinder to measure 70 mL of hot water. Pour the water into the foam cup. Measure the temperature of the water.
3. Add a small ice cube to the cup of water and gently swirl the cup. Measure the temperature of the water immediately after the ice cube has completely melted.
4. Pour the water into the graduated cylinder and measure the volume.

5. Calculate the heat of fusion of ice (kJ/mol) by dividing the heat given up from the water by the moles of ice melted. *Hint:* The mass of ice melted is the same as the increase in the volume of the water: 1 g H_2O = 1 mL H_2O .

ANALYSIS AND CONCLUSIONS

1. Compare your experimental value for the heat of fusion of ice with the accepted value of 6.01 kJ/mol. Account for any error in your value.
2. Suggest some changes in this procedure that would improve the accuracy of the results.



Figure 11.14

Ice is commonly used to refrigerate perishable foods. What happens to the temperature of the ice as it begins to melt?

Sample Problem 11-4

How many grams of ice at 0 °C and 101.3 kPa could be melted by the addition of 2.25 kJ of heat?

1. ANALYZE List the knowns and the unknown.

Knowns:

- Initial conditions are 0 °C and 101.3 kPa.
- $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$
- $\Delta H = 2.25 \text{ kJ}$

Unknown:

- $m_{\text{ice}} = ? \text{ g}$

The conditions 0 °C and 101.3 kPa indicate that the standard conditions for the fusion of ice have been met. Use the chemical equation $\text{H}_2\text{O}(s) + 6.01 \text{ kJ} \rightarrow \text{H}_2\text{O}(l)$ to find the number of moles of ice that can be melted by the addition of 2.25 kJ of heat. Convert moles of ice to grams of ice.

2. CALCULATE Solve for the unknown.

The required conversion factors come from ΔH_{fus} and the molar mass of ice. The conversion factors are

$$\frac{1 \text{ mol ice}}{6.01 \text{ kJ}} \quad \text{and} \quad \frac{18.0 \text{ g ice}}{1 \text{ mol ice}}$$

Multiply the known heat change (2.25 kJ) by the conversion factors

$$\begin{aligned} m_{\text{ice}} &= 2.25 \text{ kJ} \times \frac{1 \text{ mol ice}}{6.01 \text{ kJ}} \times \frac{18.0 \text{ g ice}}{1 \text{ mol ice}} \\ &= 6.74 \text{ g ice} \end{aligned}$$

3. EVALUATE Does the result make sense?

6.01 kJ is required to melt 1 mol of ice. Because only about one-third of this amount of heat (roughly 2 kJ) is available, only about one-third mol of ice, or $\frac{18.0 \text{ g}}{3} = 6 \text{ g}$, should melt. This estimate and the calculated answer are similar.

Practice Problems

- 20.** How many grams of ice at 0 °C and 101.3 kPa could be melted by the addition of 0.400 kJ of heat?
- 21.** How many kilojoules of heat are required to melt a 10.0 g popsicle at 0 °C and 101.3 kPa? Assume the popsicle has the same molar mass and heat capacity as water.

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Problem-Solving 21

Solve Problem 21 with the help of an interactive guided tutorial.



Heats of Vaporization and Condensation

When liquids absorb heat at their boiling points, they become vapors. Vaporization of a liquid, through boiling or evaporation, cools the environment around the liquid as heat flows from the surroundings to the liquid. The amount of heat necessary to vaporize one mole of a given liquid is called its **molar heat of vaporization**. Table 11.5 on page 308 gives some values of molar heats of vaporization for various compounds. The values are derived at standard conditions: the reactions are carried out at one atmosphere pressure and the reactants and products are in their usual physical states at the same temperature.

The molar heat of vaporization of water is 40.7 kJ/mol. This means that in order to vaporize 1 mol of water, 40.7 kJ of energy must be supplied. This energy converts 1 mol of water molecules in the liquid state to 1 mol of water molecules in the vapor state, given the same temperature and 1 atm pressure. This process is described in the thermochemical equation below.



Diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$) is a low-boiling-point liquid (bp = 34.6 °C) that is a good solvent and was formerly used as an anesthetic. If diethyl ether is poured into a beaker on a warm, humid day, the ether will absorb heat from the beaker walls and evaporate very rapidly. If the beaker loses enough heat, the water vapor in the air may condense and freeze on the beaker walls. If so, a coating of frost will form on the outside of the beaker. Diethyl ether has a molar heat of vaporization (ΔH_{vap}) of 15.7 kJ/mol. Is this an endothermic or an exothermic process?

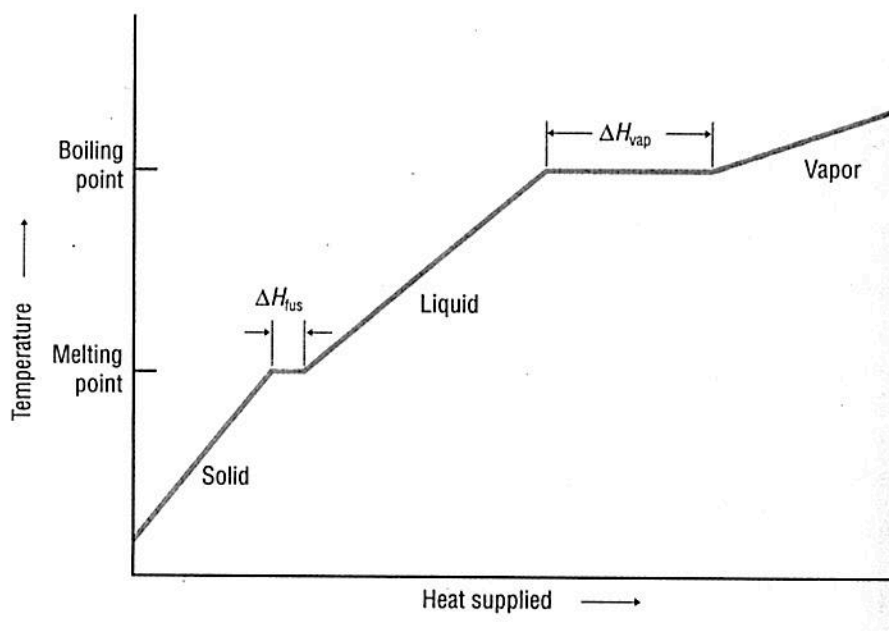
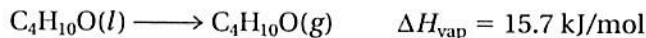


Figure 11.15

This graph shows the heating curve for water. Notice that the temperature remains constant during melting and vaporization. Notice also that it requires much more energy to vaporize liquid water than it does to melt the same mass of ice.

Condensation is the exact opposite of vaporization. Therefore, the amount of heat released when 1 mol of vapor condenses is called its **molar heat of condensation** (ΔH_{cond}). This value is numerically the same as the corresponding molar heat of vaporization, however the value has the opposite sign. Because energy is conserved in a physical change, $\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$. Figure 11.15 summarizes the heat changes that occur as a solid is heated to a liquid and then to a gas. You should be able to identify certain trends regarding the temperature during changes of state and the energy requirements that accompany these changes from the graph. The large values for ΔH_{vap} and ΔH_{cond} are the reason hot vapors such as steam can be very dangerous. You can receive a scalding burn from steam when the heat of condensation is released as it touches your skin.



Sample Problem 11-5

How much heat (in kJ) is absorbed when 24.8 g $\text{H}_2\text{O}(l)$ at 100 °C is converted to steam at 100 °C?

1. ANALYZE List the knowns and the unknown.

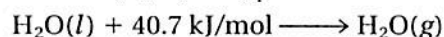
Knowns:

- mass of water converted to steam = 24.8 g
- $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$

Unknown:

- $\Delta H = ? \text{ kJ}$

The ΔH_{vap} in the following equation is given in kJ/mol, but the quantity of water is given in grams. Thus the first steps in the problem solution are to convert grams of water to moles of water and then multiply by ΔH_{vap} .



2. CALCULATE Solve for the unknown.

The required conversion factors come from ΔH_{vap} and the molar mass of water.

$$\frac{1 \text{ mol H}_2\text{O}(l)}{18.0 \text{ g H}_2\text{O}(l)} \quad \text{and} \quad \frac{40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}(l)}$$

Multiply the known mass of water in grams by the conversion factors.

$$\begin{aligned} \Delta H &= 24.8 \text{ g H}_2\text{O}(l) \times \frac{1 \text{ mol H}_2\text{O}(l)}{18.0 \text{ g H}_2\text{O}(l)} \times \frac{40.7 \text{ kJ}}{1 \text{ mol H}_2\text{O}(l)} \\ &= 56.1 \text{ kJ} \end{aligned}$$

3. EVALUATE Does the result make sense?

Knowing the molar mass of water is 18.0 g/mol, 24.8 g $\text{H}_2\text{O}(l)$ can be estimated to be somewhat less than 1.5 mol H_2O . Thus the calculated heat change should be somewhat less than $1.5 \text{ mol} \times 40 \text{ kJ/mol} = 60 \text{ kJ}$, and it is.

Practice Problems

- How much heat (in kJ) is absorbed when 63.7 g $\text{H}_2\text{O}(l)$ at 100 °C is converted to steam at 100 °C?
- How many kilojoules of heat are absorbed when 0.46 g of chloroethane ($\text{C}_2\text{H}_5\text{Cl}$, bp 12.3 °C) vaporizes at its boiling point? The molar heat of vaporization of chloroethane is 26.4 kJ/mol.

Chem ASAP!

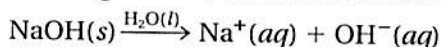
Problem-Solving 23

Solve Problem 23 with the help of an interactive guided tutorial.



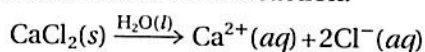
Heat of Solution

Heat changes can also occur when a solute dissolves in a solvent. The heat change caused by dissolution of one mole of substance is the **molar heat of solution** (ΔH_{soln}). Sodium hydroxide provides a good example of an exothermic molar heat of solution. When 1 mol of sodium hydroxide ($\text{NaOH}(s)$) is dissolved in water, the solution can become so hot that it steams. The heat from this process is released as the sodium ions and the hydroxide ions separate and interact with the water. The temperature of the solution increases, releasing 445.1 kJ of heat as the molar heat of solution.



$$\Delta H_{\text{soln}} = -445.1 \text{ kJ/mol}$$

A practical application of an exothermic reaction is how a hot pack works. A hot pack mixes calcium chloride (CaCl_2) and water, which produces the heat characteristic of an exothermic reaction.



$$\Delta H_{\text{soln}} = -82.8 \text{ kJ/mol}$$

The dissolution of ammonium nitrate ($\text{NH}_4\text{NO}_3(s)$) is an example of an endothermic process. When ammonium nitrate dissolves in water, the solution becomes so cold that frost may form on the outside of the container. Is heat absorbed or released as the ammonium and nitrate ions separate and interact with the water? Heat is released from the water and the temperature of the solution decreases. The cold pack allows water and ammonium nitrate (NH_4NO_3) to mix, producing an endothermic reaction.



$$\Delta H_{\text{soln}} = 25.7 \text{ kJ/mol}$$

Figure 11.16 illustrates a practical application of heats of solution.

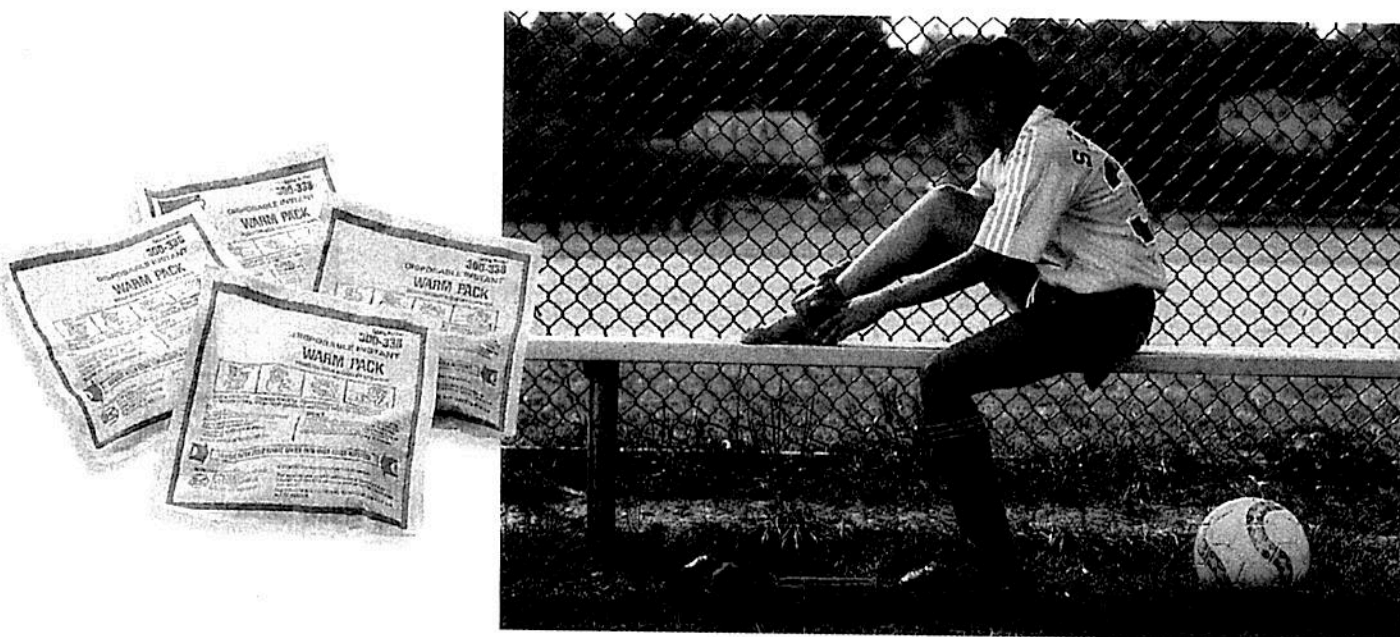


Figure 11.16

Cold packs and hot packs are available for a variety of medical uses.

Sample Problem 11-6

How much heat (in kJ) is released when 2.500 mol NaOH(s) is dissolved in water?

1. ANALYZE List the knowns and the unknown.

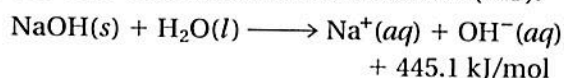
Knowns:

- $\Delta H_{\text{soln}} = -445.1 \text{ kJ/mol}$
- amount of NaOH(s) dissolved: 2.500 mol

Unknown:

- $\Delta H = ? \text{ kJ}$

Use the heat of solution from the following chemical equation to solve for the amount of heat released (ΔH).



2. CALCULATE Solve for the unknown.

Multiplying the number of mol NaOH and ΔH_{soln} will yield the value of the unknown (ΔH).

$$\Delta H = 2.500 \text{ mol NaOH(s)} \times \frac{-445.1 \text{ kJ}}{1 \text{ mol NaOH(aq)}} = -1113 \text{ kJ}$$

3. EVALUATE Does the result make sense?

By inspection, ΔH is 2.5 times greater than ΔH_{soln} , as it should be. Also, the heat of solution in the answer is negative, indicating an exothermic reaction. This is consistent with the heat of solution of sodium hydroxide discussed earlier in the text.

Practice Problems

24. How much heat (in kJ) is released when 0.677 mol NaOH(s) is dissolved in water?
25. How many moles of $\text{NH}_4\text{NO}_3(\text{s})$ must be dissolved in water so that 88.0 kJ of heat is released from the water?

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Problem-Solving 25

Solve Problem 25 with the help of an interactive guided tutorial.



section review 11.3

26. Identify each heat change by name and classify each change as exothermic or endothermic.
- 1 mol $\text{C}_3\text{H}_8(\text{l}) \longrightarrow 1 \text{ mol C}_3\text{H}_8(\text{g})$
 - 1 mol $\text{NaCl(s)} + 3.88 \text{ kJ/mol} \longrightarrow 1 \text{ mol NaCl(aq)}$
 - 1 mol $\text{NaCl(s)} \longrightarrow 1 \text{ mol NaCl(l)}$
 - 1 mol $\text{NH}_3(\text{g}) \longrightarrow 1 \text{ mol NH}_3(\text{l})$
 - 1 mol $\text{Hg(l)} \longrightarrow 1 \text{ mol Hg(s)}$
27. Heavy water, in which the hydrogens are hydrogen-2 instead of the more common hydrogen-1, is called deuterium oxide (D_2O). Solid D_2O melts at 3.78°C . The molar heat of fusion of $\text{D}_2\text{O(s)}$ is 6.34 kJ/mol . How much heat is released when $8.46 \text{ g D}_2\text{O(l)}$ solidifies at its melting point?
28. Why is a burn from steam potentially far more serious than a burn from very hot water?
29. Why does an ice cube melt at room temperature?



Chem ASAP! Assessment 11.3 Check your understanding of the important ideas and concepts in Section 11.3.

CALCULATING HEAT CHANGES



objectives

- ▶ Apply Hess's law of heat summation to find heat changes for chemical and physical processes
- ▶ Calculate heat changes using standard heats of formation

key terms

- ▶ Hess's law of heat summation
- ▶ standard heat of formation

Emeralds are beautiful gemstones composed of the elements chromium, aluminum, silicon, oxygen, and beryllium. If you were interested in the heat changes that occur when an emerald is converted to its elements, it is more than likely that you would not want to destroy the emerald by measuring the heat changes directly. Is there a way to determine the heat of reaction without actually performing the reaction?

Hess's Law

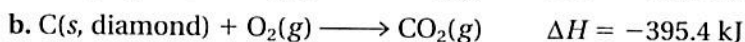
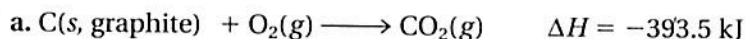
It is possible to talk in general terms about the heat changes that take place in chemical reactions. However, most reactions occur in a series of steps. Suppose, for example, you need to know the heat of reaction for an intermediate step, but it is impossible for you to obtain the value directly. Fortunately, Hess's law makes it possible to measure a heat of reaction indirectly. Thus even when a direct measurement cannot be made, the heat of reaction can still be determined.

Elemental carbon exists as both graphite and diamond at 25 °C. Because graphite is more stable than diamond, you would expect the following process to take place.

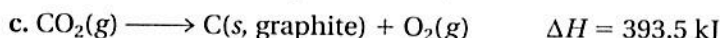


Fortunately for people who own diamonds, the conversion of diamond to graphite takes millions and millions of years. This enthalpy change cannot be measured directly because the reaction is far too slow. Hess's law, however, provides a way to calculate the heat of reaction. Hess's law is expressed by a simple rule: If you add two or more thermochemical equations to give a final equation, then you can also add the heats of reaction to give the final heat of reaction. This rule is **Hess's law of heat summation**.

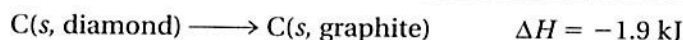
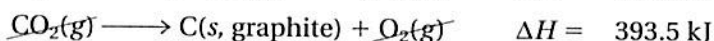
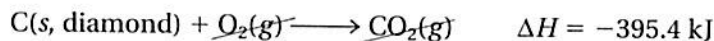
You can use Hess's law to find the enthalpy changes for the conversion of diamond to graphite by using the following combustion reactions and Figure 11.17.



Write equation a in reverse to give:



When you write a reverse reaction, you must also change the sign of ΔH . If you now add equations b and c, you get the equation for the conversion of diamond to graphite. The $\text{CO}_2(\text{g})$ and $\text{O}_2(\text{g})$ terms on both sides of the summed equations cancel, just as they do in algebra. Now if you also add the values of ΔH for equations b and c, you get the heat of reaction for this conversion.



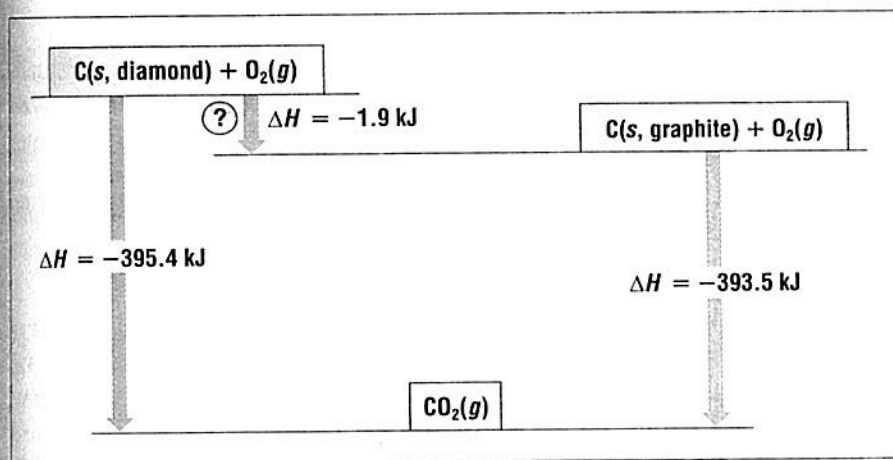
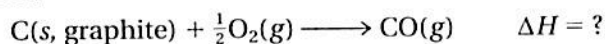


Figure 11.17

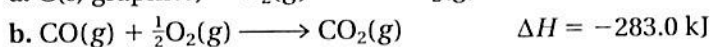
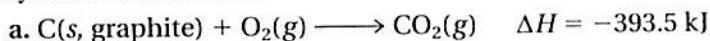
Hess's law is used to determine the enthalpy change of a very slow chemical process.



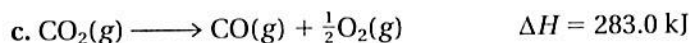
Thus the conversion of diamond to graphite is an exothermic process; its heat of reaction has a negative sign. Conversely, the change of graphite to diamond is an endothermic process. Some reactions give other products in addition to the product of interest. Suppose you want to determine the enthalpy change for the formation of carbon monoxide from its elements. The reaction is:



Although it is easy to write the equation, carrying out the reaction in the laboratory as written is virtually impossible. Carbon dioxide (a "side product") is produced along with carbon monoxide (the "desired product"). Therefore, any measured heat of reaction is related to the formation of both CO(g) and $\text{CO}_2(\text{g})$, and not CO(g) alone. You can solve the problem, however, using Hess's law and two reactions that can be carried out in the laboratory. The reactions are:



Writing the reverse of equation b and changing the sign of ΔH yields equation c.



As shown on the following page, adding equations a and c gives the expression for the formation of CO(g) from its elements. Notice that only $\frac{1}{2}\text{O}_2(\text{g})$ cancels in the final equation. See Figure 11.18.

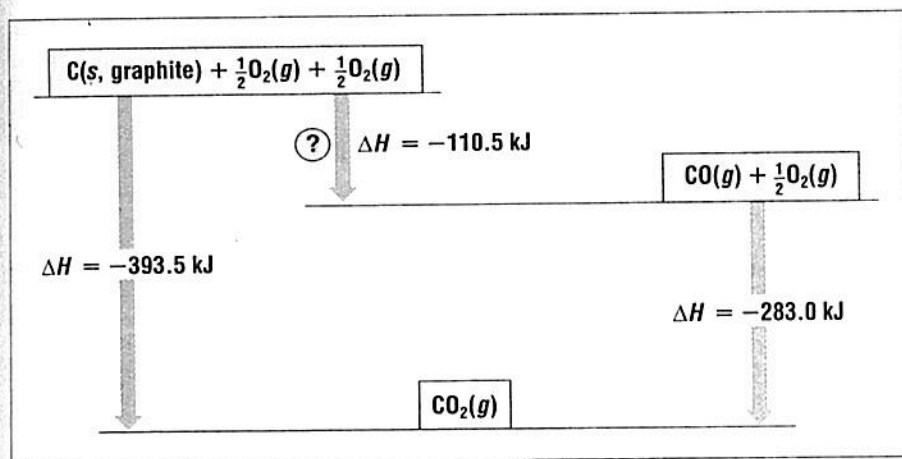
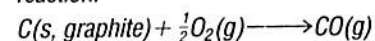
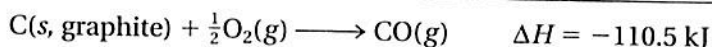
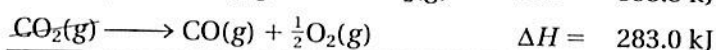
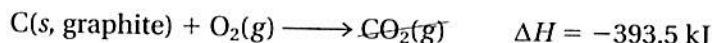


Figure 11.18

Hess's law is used to determine the enthalpy change for the reaction:





The formation of $\text{CO}(\text{g})$ is exothermic; 110.5 kJ of heat is given off when 1 mol $\text{CO}(\text{g})$ is formed from its elements.

Standard Heats of Formation

Sometimes it is hard to measure the heat change for a reaction. What are some examples where this might be the case? In such cases you can calculate the heat of reaction from standard heats of formation. The **standard heat of formation** (ΔH_f°) of a compound is the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states at 25 °C.

The ΔH_f° of a free element in its standard state is arbitrarily set at zero. For example, $\Delta H_f^\circ = 0$ for the diatomic molecules $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{F}_2(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{Br}_2(\text{l})$, and $\text{I}_2(\text{s})$. Similarly, $\Delta H_f^\circ = 0$ for the graphite form of carbon, $\text{C}(\text{s, graphite})$.

Many values of ΔH_f° have been measured. Table 11.6 lists ΔH_f° values for some common substances. Standard heats of formation of compounds are handy for calculating heats of reaction at standard conditions. The standard heat of reaction (ΔH°) is the difference between the standard heats of formation of all the reactants and products. This relationship can be expressed by the following equation.

$$\Delta H^\circ = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants})$$

Table 11.6

Standard Heats of Formation (ΔH_f°) at 25 °C and 101.3 kPa					
Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$\text{Al}_2\text{O}_3(\text{s})$	-1676.0	$\text{Fe}(\text{s})$	0.0	$\text{NO}(\text{g})$	90.37
$\text{Br}_2(\text{g})$	30.91	$\text{Fe}_2\text{O}_3(\text{s})$	-822.1	$\text{NO}_2(\text{g})$	33.85
$\text{Br}_2(\text{l})$	0.0	$\text{H}_2(\text{g})$	0.0	$\text{Na}_2\text{CO}_3(\text{s})$	-1131.1
$\text{C}(\text{s, diamond})$	1.9	$\text{H}_2\text{O}(\text{g})$	-241.8	$\text{NaCl}(\text{s})$	-411.2
$\text{C}(\text{s, graphite})$	0.0	$\text{H}_2\text{O}(\text{l})$	-285.8	$\text{O}_2(\text{g})$	0.0
$\text{CH}_4(\text{g})$	-74.86	$\text{H}_2\text{O}_2(\text{l})$	-187.8	$\text{O}_3(\text{g})$	142.0
$\text{CO}(\text{g})$	-110.5	$\text{HCl}(\text{g})$	-92.31	$\text{P}(\text{s, white})$	0.0
$\text{CO}_2(\text{g})$	-393.5	$\text{H}_2\text{S}(\text{g})$	-20.1	$\text{P}(\text{s, red})$	-18.4
$\text{CaCO}_3(\text{s})$	-1207.0	$\text{I}_2(\text{g})$	62.4	$\text{S}(\text{s, rhombic})$	0.0
$\text{CaO}(\text{s})$	-635.1	$\text{I}_2(\text{s})$	0.0	$\text{S}(\text{s, monoclinic})$	0.30
$\text{Cl}_2(\text{g})$	0.0	$\text{N}_2(\text{g})$	0.0	$\text{SO}_2(\text{g})$	-296.8
$\text{F}_2(\text{g})$	0.0	$\text{NH}_3(\text{g})$	-46.19	$\text{SO}_3(\text{g})$	-395.7

Figure 11.19 is a diagram similar to others you have seen, except that it displays the standard heats of formation of the reactants hydrogen and oxygen and the product water. The heat difference between the reactants and products, -285.8 kJ/mol , is the standard heat of formation of liquid water from the gases hydrogen and oxygen. Does water have a lower or higher enthalpy than the elements from which it is formed? On what other basis can you account for your answer?

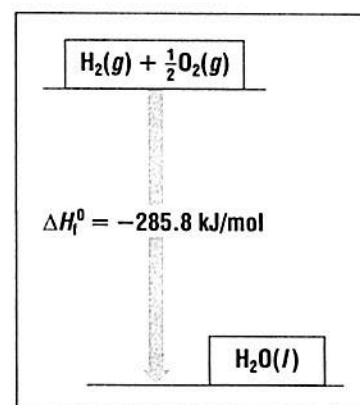


Figure 11.19
This enthalpy diagram shows the standard heat of formation of water.

Sample Problem 11-7

What is the standard heat of reaction (ΔH°) for the reaction of gaseous carbon monoxide with oxygen to form gaseous carbon dioxide?

1. ANALYZE List the knowns and the unknown.

Knowns (from Table 11.6):

- $\Delta H_f^\circ \text{O}_2(\text{g}) = 0 \text{ kJ/mol}$ (free element)
- $\Delta H_f^\circ \text{CO}(\text{g}) = -110.5 \text{ kJ/mol}$
- $\Delta H_f^\circ \text{CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$

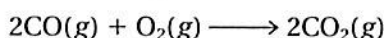
Unknown:

- $\Delta H^\circ = ? \text{ kJ}$

Balance the equation of the reaction of $\text{CO}(\text{g})$ with $\text{O}_2(\text{g})$ to form $\text{CO}_2(\text{g})$. Then determine ΔH° using the standard heats of formation of the reactants and products.

2. CALCULATE Solve for the unknown.

First, write the balanced equation.



Next, find and sum the ΔH_f° of all of the reactants, taking into account the number of moles of each.

$$\begin{aligned} \Delta H_f^\circ(\text{reactants}) &= 2 \text{ mol CO}(\text{g}) \times \frac{-110.5 \text{ kJ}}{1 \text{ mol CO}(\text{g})} \\ &\quad + 1 \text{ mol O}_2(\text{g}) \times \frac{0 \text{ kJ}}{1 \text{ mol O}_2(\text{g})} \\ &= -221.0 \text{ kJ} \end{aligned}$$

Then, find the ΔH_f° of the product in a similar way.

$$\begin{aligned} \Delta H_f^\circ(\text{product}) &= 2 \text{ mol CO}_2(\text{g}) \times \frac{-393.5 \text{ kJ}}{1 \text{ mol CO}_2(\text{g})} \\ &= -787.0 \text{ kJ} \end{aligned}$$

Finally, find the difference between $\Delta H_f^\circ(\text{products})$ and $\Delta H_f^\circ(\text{reactants})$.

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants}) \\ \Delta H^\circ &= (-787.0 \text{ kJ}) - (-221.0 \text{ kJ}) \\ \Delta H^\circ &= -566.0 \text{ kJ} \end{aligned}$$

Practice Problems

- 30.** Use the standard heats of formation to calculate the standard heats of reaction (ΔH°) for these reactions.
- $\text{Br}_2(\text{g}) \longrightarrow \text{Br}_2(\text{l})$
 - $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
- 31.** With one exception, the standard heats of formation of $\text{Na}(\text{s})$, $\text{O}_2(\text{g})$, $\text{Br}_2(\text{l})$, $\text{CO}(\text{g})$, $\text{Fe}(\text{s})$, and $\text{He}(\text{g})$ are identical. What is the exception? Explain.

Chem ASAP!

Problem-Solving 30

Solve Problem 30 with the help of an interactive guided tutorial.



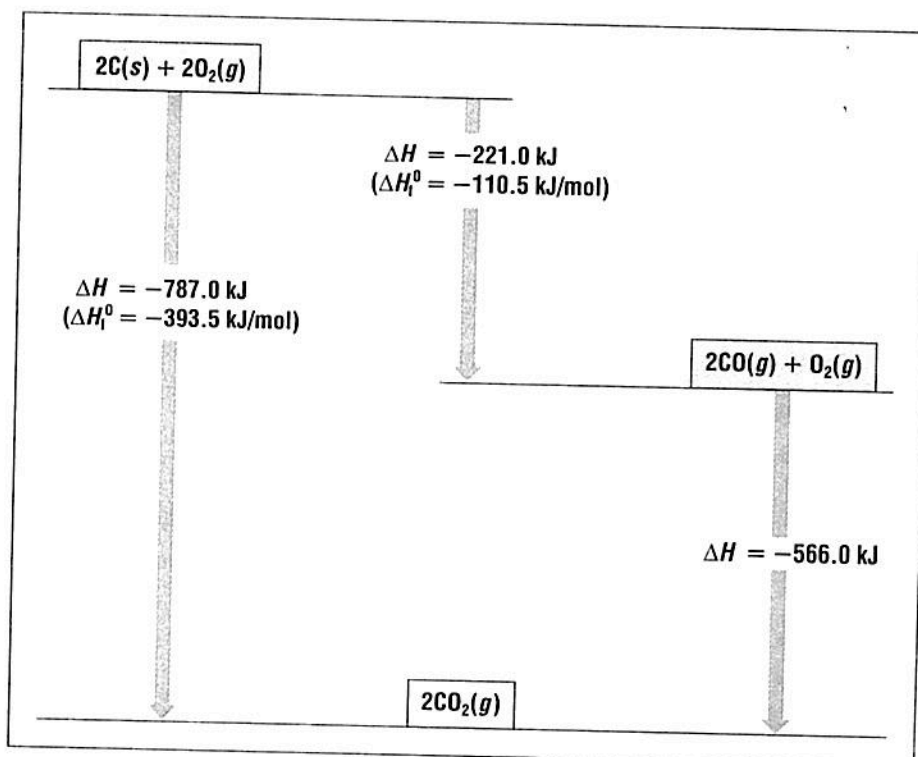
Sample Problem 11-7 (cont.)

 3. **EVALUATE** Does the result make sense?

The ΔH° is negative. Therefore, the reaction is exothermic, as illustrated in Figure 11.20. This makes sense because the oxidation of carbon monoxide is a combustion reaction. Combustion reactions always release heat.

Figure 11.20

Hess's law is used to determine the enthalpy change for the reaction of carbon monoxide and oxygen.

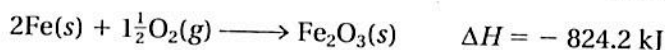
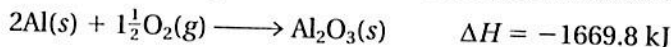
$$2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$$


section review 11.4

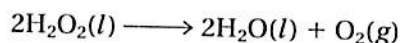
32. Calculate the enthalpy change (ΔH) in kJ for the following reaction.



Use the enthalpy changes for the combustion of aluminum and iron:



33. What is the standard heat of reaction (ΔH°) for the decomposition of hydrogen peroxide?



34. State Hess's law of heat summation in your own words. Explain its usefulness.

35. What happens to the sign of ΔH when the reverse of a chemical reaction is written? Why?



Chem ASAP! Assessment 11.4 Check your understanding of the important ideas and concepts in Section 11.4.

portfolio project

Some chefs use heavy cast iron skillets; others use lightweight stainless steel. Use what you have learned about heat capacity to list the advantages and drawbacks of these skillets. Write an advertisement for each skillet stressing only its positive features.