

Chapter Outline

- 5.1 Energy: Some Basic Principles
- 5.2 Specific Heat Capacity: Heating and Cooling
- 5.3 Energy and Changes of State
- 5.4 The First Law of Thermodynamics
- 5.5 Enthalpy Changes for Chemical Reactions
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The importance of energy is evident in everyday life—in heating and cooling homes, in powering appliances, and in propelling vehicles, among other things. Most of the energy used for these purposes is obtained by conducting chemical reactions, largely by burning fossil fuels (natural gas, coal, and petroleum). Natural gas is used for heating, coal and natural gas are burned to provide electrical power, and fuels derived from petroleum are used in automobiles, trucks, and aircraft. In addition, energy is required for living things: Chemical reactions in our bodies provide energy for bodily functions, for movement, and to maintain body temperature.

Thermodynamics is the area of science that deals with energy and its relationship to quantities such as heat and work. Determining the energy changes that occur when chemical processes take place is an important factor in the study of chemical systems. In this chapter, you will learn how to measure energy changes for chemical processes, particularly those that result in heating and cooling, and how these can be used to explore chemical reactions more thoroughly.

5.1 Energy: Some Basic Principles

Goals for Section 5.1

- Recognize and use the language of thermodynamics: the system and its surroundings; exothermic and endothermic reactions.
- Describe the nature of energy transfers as heat.
- Understand the sign conventions of thermodynamics.

Energy is defined as the capacity to do work and can be divided into two basic categories: kinetic energy (the energy associated with motion) and potential energy (the energy that results from an object's position, composition, or state). Chemists often use the term **thermal energy** when referring to the kinetic energy of molecules.

◀ **The reaction of potassium and water.** This reaction involves the transfer of energy between the system and surroundings in the form of heat (thermal energy), work, and light.

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World Energy Consumption In 2021, burning fossil fuels provided about 84% of the total energy used by people on our planet. Nuclear power contributed about 5%. All other energy sources, including renewable sources (such as hydroelectric, solar, wind, biomass, and geothermal) provided about 12%.

Units of Energy The SI unit for energy (the joule) is discussed on page 37.

The Terminology of Thermodynamics

The definitions of terms (such as energy, heat, and work) used when discussing energy in chemistry are more precise than in everyday language.

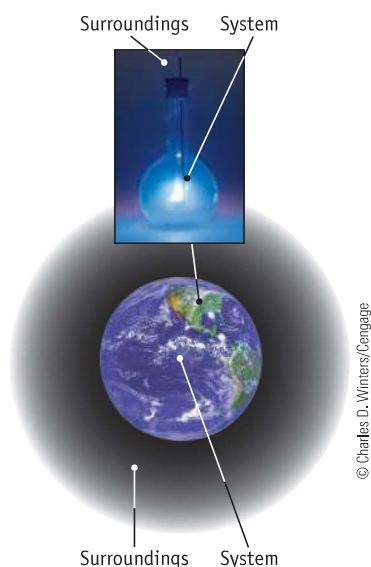


Figure 5.1 Systems and their surroundings. Earth can be considered a thermodynamic system, with the rest of the universe as its surroundings. A chemical reaction (here the reaction of S and O₂) occurring in a laboratory is also a system, with the flask and the laboratory as its surroundings.

Thermal Equilibrium A general feature of systems at equilibrium is that there is no change on a macroscopic level but that processes still occur at the particulate level. (Section 3.3, page 145.)

Chemical energy is one type of potential energy. It is the energy associated with the forces that hold atoms together as molecules or bind atoms and molecules together as solids or liquids. In a chemical reaction, chemical energy (potential energy) is converted to other forms of energy such as thermal energy or light (kinetic energy).

Although energy can be converted from one type into another, the total amount of energy is conserved. This is formally stated in the **law of conservation of energy**: Energy can neither be created nor destroyed. Or, stated differently, the total energy of the universe is constant. To understand the importance of this law, some new terminology must be introduced and the implications of a number of experiments must be considered.

Systems and Surroundings

In thermodynamics, the terms *system* and *surroundings* have precise and important meanings. A **system** is defined as an object, or collection of objects, being studied (Figure 5.1). The **surroundings** include everything outside the system that can exchange energy and/or matter with the system. In the discussion that follows, systems will need to be defined precisely. If a chemical reaction is carried out in solution, for example, the system might be defined as the reactants, products, and solvent. The surroundings would be the reaction flask and the air in the room and anything else in contact with the flask with which it might exchange energy or matter. At the atomic level, the system could be a single atom or molecule, and the surroundings would be the atoms or molecules in its vicinity. This concept of a system and its surroundings applies to nonchemical situations as well. To study the energy balance on our planet, Earth might be defined as the system and outer space as the surroundings. On a cosmic level, the solar system might be defined as the system being studied, and the rest of the galaxy would be the surroundings. The treatment of experimental data is dependent upon the choices made for the system and surroundings.

Directionality and Extent of Transfer of Heat: Thermal Equilibrium

Energy can be transferred between a system and its surroundings or between different parts of the system. One way that energy can be transferred is as **heat**; this occurs when two objects at different temperatures are brought into contact. In Figure 5.2, for example, the beaker of water and the piece of metal being heated in a Bunsen burner flame have different temperatures. When the hot metal is plunged into the cold water, energy is transferred as heat from the metal to the water. The thermal energy (molecular motion) of the water molecules increases, and the thermal energy of the metal atoms decreases. Eventually, the two objects reach the same temperature, and the system has reached **thermal equilibrium**. The distinguishing feature of thermal equilibrium is that, on the macroscopic scale, no further temperature change occurs; both the metal and water are at the same temperature.



Figure 5.2 Energy transfer.

Energy transfer as heat occurs from the hotter metal cylinder to the cooler water. Eventually, the water and metal reach the same temperature and are said to be in thermal equilibrium.

What Is Heat?

Two hundred years ago, scientists characterized heat as a real substance called “caloric fluid.” The caloric hypothesis supposed that when a fuel burned and a pot of water was heated, for example, caloric fluid was transferred from the fuel to the water. Burning the fuel released caloric fluid, and the temperature of the water increased as the caloric fluid was absorbed.

However, the caloric-fluid concept was wrong. Experiments by James Joule (1818–1889) and Benjamin Thompson (1753–1814) that showed the interrelationship between heat and other forms of energy, such as mechanical energy, provided the key to disproving this idea. Even so, everyday language retains the influence of this early theory. For example, people often speak of heat “flowing” as if it were a fluid.

From the discussion so far, you know one thing that “heat” is not—but what is it? Heat is said to be a “process quantity.” It is the *process* by which energy is transferred across the boundary of a system owing to a difference in temperature between the two sides of the boundary. In this process, the energy of the object at

the lower temperature increases, and the energy of the object at the higher temperature decreases.

Heat is not the only process by which energy can be transferred. Another is work (as described in Section 5.4).

The idea of energy transfer by the processes of heat and work is embodied in the definition of thermodynamics: the science of heat and work.

A Rumford fireplace. Benjamin Thompson (1753–1814), also known as Count Rumford, established his scientific reputation through research on the explosive force of gunpowder. His experience with explosives led to an interest in heat, and he designed a classic experiment that showed the relationship between work and heat. He is also known for developing the Rumford fireplace, in which the back walls of the fire box are angled to reflect heat into the room and the chimney is better designed to carry away smoke. This design is still in use today.



Gregory_G/Shutterstock.com

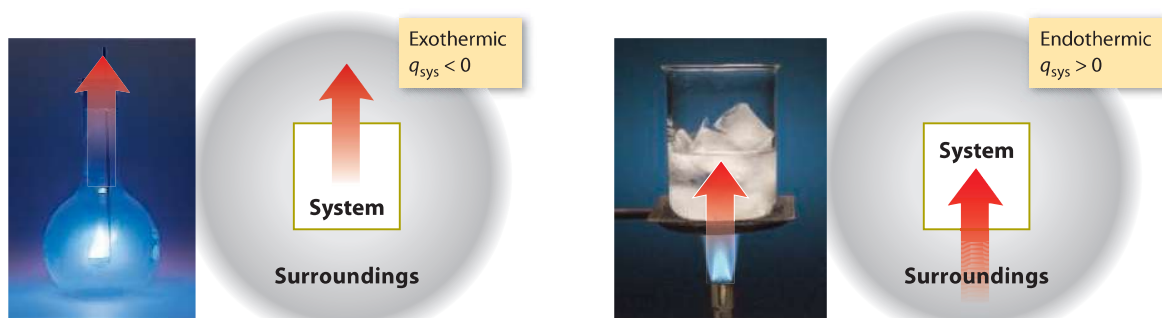
This experiment illustrates two important principles:

1. Energy transfer as heat occurs spontaneously from an object at a higher temperature to an object at a lower temperature; the object whose temperature increases gains thermal energy and the object whose temperature decreases loses thermal energy.
2. Transfer of energy as heat continues until both objects are at the same temperature and thermal equilibrium is achieved.

For the specific case where energy is transferred only as heat within an **isolated system** (that is, a system that cannot transfer either energy or matter with its surroundings), the quantity of energy lost as heat by the hotter object and the quantity of energy gained as heat by the cooler object are numerically equal. This is required by the law of conservation of energy.

When energy is transferred as heat between a system and its surroundings, the directionality of this transfer is described as **exothermic** or **endothermic** (Figure 5.3).

- In an **exothermic process**, energy is transferred as heat from a system to its surroundings. The energy of the system decreases and the energy of the surroundings increases. The energy transferred as heat is designated by the symbol q . Because the system ends up with less energy than it started with, $q_{\text{sys}} < 0$ (where the subscript sys refers to the system).
- An **endothermic process** is the opposite of an exothermic process. Energy is transferred as heat from the surroundings to the system, increasing the energy of the system and decreasing the energy of the surroundings. For an endothermic process, $q_{\text{sys}} > 0$ because the system ends up with more energy than it started with.



Exothermic: energy transferred from system to surroundings

Endothermic: energy transferred from surroundings to system

Figure 5.3 Exothermic and endothermic processes. The symbol q represents the energy transferred as heat, and the subscript sys refers to the system.

5.2 Specific Heat Capacity: Heating and Cooling

Goal for Section 5.2

- Use specific heat capacity in calculations of energy transfers as heat involving temperature changes.

Change of State A change of state (such as melting or boiling) is a change of an object's physical state (solid, liquid, or gas).

When an object is heated or cooled without a change in its physical state, the object's change in temperature is proportional to the quantity of thermal energy gained or lost by the object. The energy gained or lost as heat (q , in joules) is described by Equation 5.1.

$$q = C \times \Delta T \quad (5.1)$$

Heat capacity Heat capacity is defined as the energy required to change the temperature of an object by 1 kelvin. Common units for heat capacity are joules per kelvin (J/K).

The constant, C , is called the **heat capacity**. This constant, usually reported in units of J/K, has a unique value for every object. The change in temperature, ΔT , is calculated as the final temperature minus the initial temperature.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} \quad (5.2)$$

For many calculations the **specific heat capacity** (c) is used. This is defined as the energy transferred as heat that is required to raise the temperature of one gram of a substance or a mixture by one kelvin. It is often reported in units of joules per gram per kelvin (J/g · K). A few specific heat capacities are listed in Figure 5.4, and a longer list is given in Appendix D (Table D.2).

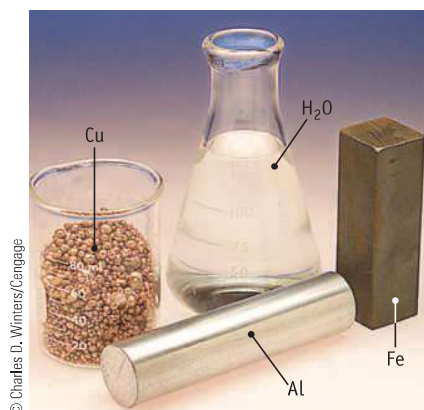
The energy gained or lost as heat when a given mass of a substance is warmed or cooled can be calculated using Equation 5.3.

$$q = c \times m \times \Delta T \quad (5.3)$$

Here, q is the energy gained or lost as heat by a given mass of substance (m), c is the specific heat capacity, and ΔT is the change in temperature.

Heat capacity can also be expressed on a per-mole basis. The amount of energy that is transferred as heat in raising the temperature of one mole of a substance by one kelvin is the **molar heat capacity**. For water, the molar heat capacity is 75.4 J/mol · K. The molar heat capacity of metals at room temperature is always near 25 J/mol · K.

Calculating a value of q using Equation 5.3 gives a result with an algebraic sign that indicates the direction of energy transfer. This depends on whether the value of ΔT calculated using Equation 5.2 is positive or negative. A positive q indicates that the energy of the system increases, while a negative q indicates that the energy of the system decreases. For example, you can use the specific heat capacity of copper, 0.385 J/g · K, to calculate the energy that must be transferred from the surroundings to a 10.0-g sample of copper if the metal's temperature is raised from 298 K (25 °C) to 598 K (325 °C).



Specific Heat Capacities of Some Elements and Compounds

Substances	Specific Heat Capacity (J/g · K)	Molar Heat Capacity (J/mol · K)
Al, aluminum	0.897	24.2
Fe, iron	0.449	25.1
Cu, copper	0.385	24.5
Au, gold	0.129	25.4
Water (liquid)	4.184	75.4
Water (ice)	2.06	37.1
Water (steam)	1.86	33.6
HOCH ₂ CH ₂ OH(ℓ), ethylene glycol (antifreeze)	2.39	14.8

All metals have molar heat capacities near 25 J/mol · K

Figure 5.4 Specific heat capacity. Metals have different values of specific heat capacity. However, their molar heat capacities are all near 25 J/mol · K.

$$q = \left(0.385 \frac{\text{J}}{\text{g} \cdot \text{K}} \right) (10.0 \text{ g}) (598 \text{ K} - 298 \text{ K}) = +1160 \text{ J}$$

\uparrow \uparrow
 T_{final} T_{initial}
 Final temp. Initial temp.

Notice that the answer has a positive sign. This indicates that the energy of the sample of copper has *increased* by 1160 J, which is in accord with energy being transferred as heat to the copper (the system) from the surroundings.

The relationship between energy, mass, and specific heat capacity has numerous implications. The high specific heat capacity of liquid water, 4.184 J/g · K, is a major reason that large bodies of water have a profound influence on climate. In spring, lakes warm up more slowly than the air. In autumn, the energy transferred by a large lake as it cools moderates the drop in air temperature. The relevance of specific heat capacity is also illustrated when food is wrapped in aluminum foil (specific heat capacity 0.897 J/g · K) and heated in an oven. You can remove the foil with your fingers after taking the food from the oven. The small mass of aluminum foil used and its low specific heat capacity result in only a small quantity of energy being transferred to your fingers (which have a larger mass and a higher specific heat capacity).



A practical example of knowing about specific heat capacity. If you are careful, it is possible to remove the salmon from the grill by grasping the edges of the aluminum foil with unprotected hands. Due to the small quantity of aluminum and its low specific heat capacity, only a small quantity of energy is transferred.

Example 5.1

Specific Heat Capacity

Problem How much energy must be transferred to raise the temperature of a cup of coffee (250 mL) from 20.5 °C (293.7 K) to 95.6 °C (368.8 K)? Assume that water and coffee have the same density (1.00 g/mL) and specific heat capacity (4.184 J/g · K).

What Do You Know? The energy required to warm a substance is related to its specific heat capacity (c), the mass of the substance, and the temperature change (Equation 5.3). The mass of coffee, initial and final temperatures, and the value for c are given in the problem.

Strategy You can calculate the mass of coffee from the volume and density (mass = volume \times density) and the temperature change from the initial and final temperatures ($\Delta T = T_{\text{final}} - T_{\text{initial}}$). Use Equation 5.3 to solve for q .

Solution Mass of coffee = (250 mL)(1.00 g/mL) = 250 g
 $\Delta T = T_{\text{final}} - T_{\text{initial}} = 368.8 \text{ K} - 293.7 \text{ K} = 75.1 \text{ K}$
 $q = c \times m \times \Delta T$
 $q = (4.184 \text{ J/g} \cdot \text{K})(250 \text{ g})(75.1 \text{ K})$
 $q = 79,000 \text{ J (or 79 kJ)}$

Think about Your Answer The positive value for the answer indicates that energy has been transferred to the coffee. The thermal energy of the coffee is now higher.

Check Your Understanding

An experiment showed that 59.8 J was required to raise the temperature of 25.0 g of ethylene glycol (a compound used as antifreeze in automobile engines) by 1.00 K. Calculate the specific heat capacity of ethylene glycol from these data.

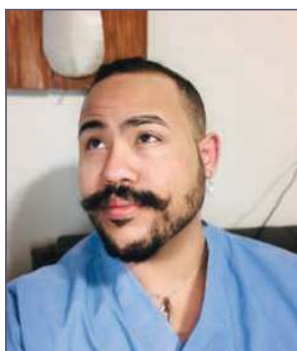
Quantitative Aspects of Energy Transferred as Heat

Specific heat capacity is a characteristic intensive property of a pure substance. It can be determined experimentally by accurately measuring temperature changes that occur when energy is transferred as heat from the substance to a known quantity of water (whose specific heat capacity is known).

Suppose a 55.0-g piece of metal is heated in boiling water to 99.8 °C and then dropped into cool water in an insulated beaker (Figure 5.5). Assume the beaker contains 225 g of water and its initial temperature (before the metal was dropped in) was 21.0 °C. The final temperature of the metal and water is 23.1 °C. What is the specific heat capacity of the metal? Here are the important aspects of this experiment.

- The system in this experiment includes the metal and the water; the surroundings include the beaker and the environment.
- Energy is transferred *only within the system*. (This means that energy is not transferred between the system and the surroundings. This assumption is good, but not perfect; for a more accurate result, any energy transfer to the surroundings must also be measured.)

Chemistry in Your Career



Randy Santos

Randy Santos

Randy Santos uses chemistry daily in his job at an urgent care veterinary facility, where he is a veterinary technician. There he works alongside veterinarians to triage, stabilize, diagnose, and treat his animal patients.

Santos draws on his chemistry education (with degrees in veterinary nursing and health science) to understand the fundamental principles behind medications and diagnostic testing. Knowing how different drugs affect the body or react with another substance or medication is

extremely important. "When mixing drugs in a singular syringe, I'm always very observant of different reactions such as heat production, color change/discolorations, or even precipitation." When administering anesthesia or sedatives, Santos must calculate the duration of drug action based on how the body breaks down molecules.

Santos finds it rewarding to see his patients recover and come back happy and healthy. He adds, "I also really enjoy mastering my technical skills and taking on the challenges the day brings."

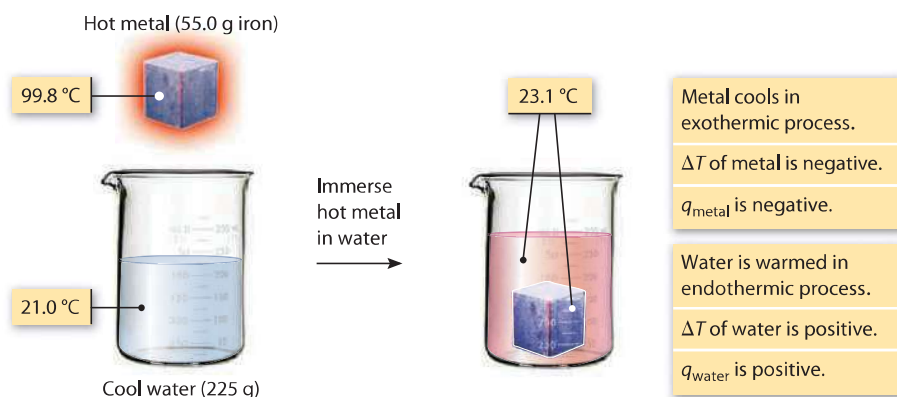


Figure 5.5 Transfer of energy as heat. When energy is transferred as heat from a hot metal to cool water, the thermal energy of the metal decreases and that of the water increases. The value of q_{metal} is thus negative and the value of q_{water} is positive.

- Energy is transferred *only as heat* within the system.
- The water and the metal end with the same temperature. (T_{final} is the same for both.)
- The energy transferred as heat from the metal to the water, q_{metal} , has a negative value because the temperature of the metal decreases. Conversely, q_{water} has a positive value because its temperature increases.
- The values of q_{metal} and q_{water} are numerically equal but have opposite signs.

Because of the law of conservation of energy, **in an isolated system the sum of the energy changes within the system must be zero.** If energy is transferred only as heat, then

$$q_1 + q_2 + q_3 + \dots = 0 \quad (5.4)$$

where the quantities q_1 , q_2 , and so on represent the energies transferred as heat for the individual parts of the system. For this specific problem, there are thermal energy changes associated with the two components of the system, water and metal, q_{water} and q_{metal} ; thus

$$q_{\text{water}} + q_{\text{metal}} = 0$$

Each of these quantities is related individually to specific heat capacities, masses, and changes of temperature, as defined by Equation 5.3. Thus

$$[c_{\text{water}} \times m_{\text{water}} \times (T_{\text{final}} - T_{\text{initial, water}})] + [c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{final}} - T_{\text{initial, metal}})] = 0$$

The specific heat capacity of the metal, c_{metal} , is the unknown in this example. Using the specific heat capacity of water (4.184 J/g · K) and converting Celsius to kelvin temperatures gives

$$[(4.184 \text{ J/g} \cdot \text{K})(225 \text{ g})(296.3 \text{ K} - 294.2 \text{ K})] + [(c_{\text{metal}})(55.0 \text{ g})(296.3 \text{ K} - 373.0 \text{ K})] = 0$$

$$c_{\text{metal}} = 0.47 \text{ J/g} \cdot \text{K}$$

Celsius to Kelvin Unit

Conversions Conversions are not necessary when measuring changes in temperature because a change of 1° C is also a change of 1 K. (See Problem Solving Tip 5.1.)

Problem Solving Tip 5.1 Calculating ΔT

Virtually all calculations that involve temperature in chemistry require expressing temperature in kelvins. In calculating ΔT , however, you can use Celsius temperatures

because a kelvin and a Celsius degree are the same size. That is, the difference between two temperatures is the same on both scales. For example, the difference

between the boiling and freezing points of water is

$$\Delta T, \text{ Celsius} = 100^\circ \text{C} - 0^\circ \text{C} = 100^\circ \text{C}$$

$$\Delta T, \text{ kelvin} = 373 \text{ K} - 273 \text{ K} = 100 \text{ K}$$

Example 5.2

Using Specific Heat Capacity

Problem In an experiment like that shown in Figure 5.5, an 88.5-g piece of iron whose temperature is 78.8 °C (352.0 K) is placed in a beaker containing 244 g of water at 18.8 °C (292.0 K). When thermal equilibrium is reached, what is the final temperature? (Assume no energy is transferred to warm the beaker and its surroundings.)

What Do You Know? Iron cools and the water warms until thermal equilibrium is reached. The energies associated with the two changes are determined by the specific heat capacities, masses, and temperature changes for each species. If iron and water are defined as the system, the sum of these two energy quantities will be zero due to the law of conservation of energy. The final temperature is the unknown in this problem. Masses and initial temperatures are given; the specific heat capacities of iron and water can be found in Appendix D or Figure 5.4.

Strategy The sum of the two energy quantities, q_{water} and q_{Fe} , is zero ($q_{\text{water}} + q_{\text{Fe}} = 0$). Each energy quantity is defined using Equation 5.3; the value of ΔT in each is $T_{\text{final}} - T_{\text{initial}}$. You can use either kelvin or Celsius temperatures (Problem Solving Tip 5.1). Substitute the given information into Equation 5.4 and solve.

Solution

$$q_{\text{water}} + q_{\text{Fe}} = 0$$

$$\begin{aligned} [c_{\text{water}} \times m_{\text{water}} \times (T_{\text{final}} - T_{\text{initial, water}})] + [c_{\text{Fe}} \times m_{\text{Fe}} \times (T_{\text{final}} - T_{\text{initial, Fe}})] &= 0 \\ [(4.184 \text{ J/g} \cdot \text{K})(244 \text{ g})(T_{\text{final}} - 292.0 \text{ K})] + [(0.449 \text{ J/g} \cdot \text{K})(88.5 \text{ g})(T_{\text{final}} - 352.0 \text{ K})] &= 0 \\ (1021 \text{ J/K})T_{\text{final}} - 298100 \text{ J} + (39.74 \text{ J/K})T_{\text{final}} - 13990 \text{ J} &= 0 \\ (1061 \text{ J/K})T_{\text{final}} - 312100 \text{ J} &= 0 \\ (1061 \text{ J/K})T_{\text{final}} &= 312100 \text{ J} \\ T_{\text{final}} &= 294 \text{ K (21 °C)} \end{aligned}$$

Think about Your Answer Be sure to notice that T_{initial} for the metal and T_{initial} for the water in this problem have different values. Also, the low specific heat capacity and smaller quantity of iron result in the temperature of iron being reduced by about 60 degrees; in contrast, the temperature of the water has been raised by only a few degrees. Finally, as expected, T_{final} (294 K) is between $T_{\text{initial, Fe}}$ and $T_{\text{initial, water}}$.

Check Your Understanding

A 15.5-g piece of chromium, heated to 100.0 °C, is dropped into 55.5 g of water at 16.5 °C. The final temperature of the metal and the water is 18.9 °C. What is the specific heat capacity of chromium? (Assume no energy is lost to the container or to the surrounding air.)

5.3 Energy and Changes of State

Goal for Section 5.3

- Use heat of fusion and heat of vaporization to calculate the energy transferred as heat in changes of state.

A *change of state* refers to changes (such as melting or boiling) between the three states of matter: solid, liquid, and gas. When a solid melts, its atoms, molecules, or