section 11.1

THE FLOW OF ENERGY-HEAT

Lava flowing out of an erupting volcano is very hot. Its temperature ranges from 550 °C to 1400 °C. As lava flows down the side of a volcano, it loses heat and begins to cool slowly. In some instances, the lava may flow into the ocean

where it cools rapidly. Why does lava cool more quickly in water than on land?

Energy Transformations

Glowing campfires, the sun's rays, and rubbing your hands together all produce heat. However, other activities, such as melting ice and boiling water, absorb heat. Thermochemistry is concerned with the heat changes that occur during chemical reactions. In this chapter, you will examine heat and its effects on a number of chemical and physical processes. First, however, it is important to understand energy transformations.

When you buy gasoline, you are buying the stored potential energy it contains. This energy is used to do work, most often to propel a car. The controlled explosions of the gasoline in the car's engine transform the potential energy into useful work. Work is done when a force is used to move an object. Energy is the capacity for doing work or supplying heat. Unlike matter, energy is weightless, odorless, and tasteless. Energy is detected only because of its effects. Energy stored within the structural units of chemical substances is called **chemical potential energy**. Gasoline contains a significant amount of chemical potential energy. Different substances store different amounts of energy. The kinds of atoms and their arrangement in the substance determine the amount of energy stored in the substance.

Heat, represented by q, is energy that transfers from one object to another because of a temperature difference between them. Heat, itself, cannot be detected by the senses or by instruments. Only changes caused by heat can be detected. One of the effects of adding heat is a rise in the temperature of objects. It is the radiant heat of the sun's rays that makes a summer day hot. In this example, air is the object that absorbs heat and

objectives

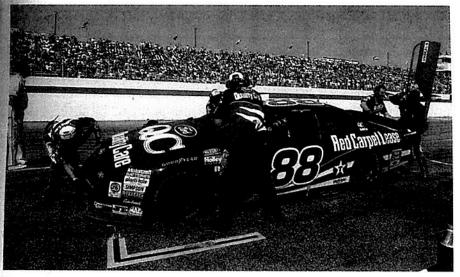
- Explain the relationship between energy and heat
- Distinguish between heat capacity and specific heat

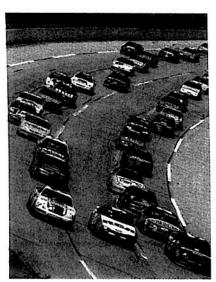
key terms

- ▶ thermochemistry
- ▶ energy
- chemical potential energy
- ▶ heat
- system
- surroundings
- universe
- law of conservation of energy
- endothermic process
- exothermic process
- ▶ calorie
- ▶ joule
- heat capacity
- specific heat capacity
- specific heat

Figure 11.1

Chemical potential energy is stored within the bonds of gasoline molecules (a). As the gasoline burns, the energy is released and is used to do work. In this example, the work is to propel race cars around the track (b).





(b)

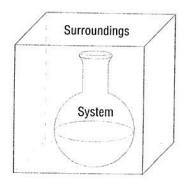


Figure 11.2

The part of the universe being studied is the system. What constitutes the surroundings?

There are two directions in which the heat of a system can flow. (a) In an endothermic process, heat flows into the system from the surroundings. The system

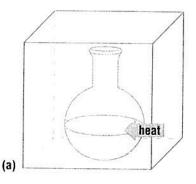
Figure 11.3

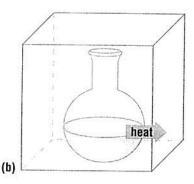
the surroundings. The system absorbs heat. (b) In an exothermic process, heat flows from the system to the surroundings. The system loses heat.

increases in temperature. Heat always flows from a warmer object to a cooler object. If two objects remain in contact, heat will flow from the warmer object to the cooler object until the temperature of both objects is the same.

Exothermic and Endothermic Processes

Essentially all chemical reactions and changes in physical state involve either the release or the absorption of heat. In studying heat changes, it is useful to define a system as the part of the universe on which you focus your attention. The surroundings include everything else in the universe. In thermochemical experiments, it is a good approximation to consider the region in the immediate vicinity of the system as the surroundings. In Figure 11.2, for example, the mixture of chemicals undergoing a reaction is the system, and everything else is the surroundings. Together, the system and its surroundings constitute the universe. A major goal of studying thermochemistry is to examine the flow of heat from the system to its surroundings, or the flow of heat from the surroundings to the system. The law of conservation of energy states that in any chemical or physical process, energy is neither created nor destroyed. All of the energy involved in a process can be accounted for as work, stored energy, or heat.

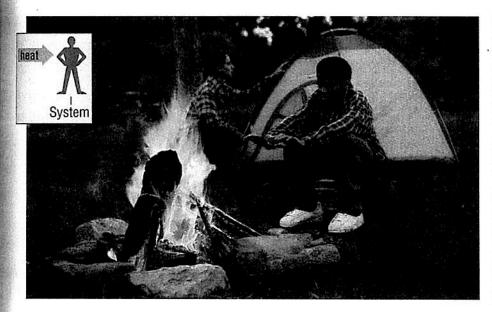




In thermochemical calculations the direction of the heat flow is given from the point of view of the system. Look at Figure 11.3a. Heat flowing into a system from its surroundings is defined as positive; q has a positive value. A process that absorbs heat from the surroundings is called an endothermic process. In an endothermic process, the system gains heat as the surroundings cool down. In Figure 11.3b, heat flows out of the system into its surroundings. This type of heat flow is given a negative value; q is negative because the system is losing heat. A process that releases heat to its surroundings is called an exothermic process. In an exothermic process, the system loses heat as the surroundings heat up. Table 11.1 explains the sign convention for heat changes.

Table 11.1

Heat Change Sign Convention				
Direction of heat flow	Sign Reaction type			
Heat flows out of the system	Heat change < 0 (negative)	Exothermic		
Heat flows into the system	Heat change > 0 (positive)	Endothermi		



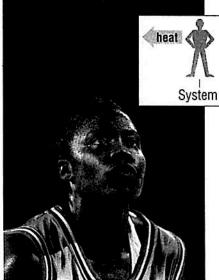


Figure 11.4

A fire helps keep you warm when you are out in the cold. If your body is the system, what is the fire? The human body cools itself by giving off heat when perspiration evaporates. What is the system here? Which of these processes is exothermic and which is endothermic?

In the photograph on the left in Figure 11.4, the system (the people) gains heat from its surroundings (the fire). As shown in the inset illustration, heat flows into the system from its surroundings. What kind of process is this? In the photograph on the right, the system (the body) cools as perspiration evaporates from the skin and heat flows to the surroundings. What kind of process is shown in this illustration?

Heat Capacity and Specific Heat

You have probably heard of someone exercising to burn off fat and calories. What does it mean to "burn calories"? During exercise your body generates heat, and this heat is measured in units called calories. The heat is generated as your body breaks down sugars and fats into carbon dioxide and water. Although there is not an actual fire burning the sugars and fats within your body, chemical reactions accomplish the same result. In breaking down 10 g of sugar, for example, your body generates a certain amount of heat. The same amount of heat would be produced if 10 g of sugar were completely burned in a fire, producing carbon dioxide and water.

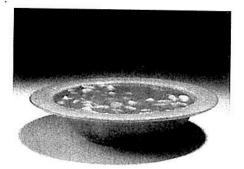
A **calorie** is defined as the quantity of heat needed to raise the temperature of 1 g of pure water 1 °C. There is an important difference, however, between a calorie and a Calorie. The calorie, written with a small c, is defined above and is used except when referring to the energy contained in food. The dietary Calorie, written with a capital C, always refers to the energy in food. One dietary Calorie is actually equal to one kilocalorie, or 1000 calories.

1 Calorie = 1 kilocalorie = 1000 calories

The statement "10 g of sugar has 41 Calories" means that 10 g of sugar releases 41 kilocalories of heat when completely burned to produce carbon dioxide and water.

Figure 11.5

Which food will warm you up more when you are cold: a bowl of hot soup, or two slices of hot buttered toast? Why?







PHYSIOLOGY

Dietary Calories

Your proper caloric intake depends on your level of physical activity. In an eight-hour day at a desk, you burn about 800 Calories. This is about the number of Calories in two helpings of spaghetti. When exercising, however, you become a relative biochemical blast furnace. In vigorous activities such as running and jumping, you expend 7-10 Calories per minute, or 420-600 Calories per hour. At these rates, a runner who covers a 26-mile marathon course in 3 hours might expend 1800 Calories, or the equivalent of 4.5 helpings of spaghetti.

The calorie is also related to the **joule**, the SI unit of heat and energy named after the English physicist James Prescott Joule (1818–1889). A joule is slightly less than one-fourth of a calorie. One joule of heat raises the temperature of 1 g of pure water 0.2390 °C. You can convert between calories and joules using the following relationships.

$$1 J = 0.2390 \text{ cal}$$
 $4.184 J = 1 \text{ cal}$

The amount of heat needed to increase the temperature of an object exactly 1 °C is the heat capacity of that object. The heat capacity of an object depends on its mass as well as its chemical composition. The greater the mass of the object, the greater its heat capacity. A massive steel girder, for example, requires much more heat to raise its temperature 1 °C than a small steel nail does. Similarly, a cup of water has a much greater heat capacity than a drop of water. Besides varying with mass, the heat capacity of an object also depends on its chemical composition. It follows that different substances with the same mass may have different heat capacities.

On a sunny day, a 20 kg puddle of water may be cool, while a nearby 20 kg iron sewer cover may be too hot to touch. This situation illustrates how different heat capacities affect the temperature of objects. Assuming that both the water and the iron absorb the same amount of radiant energy from the sun, the temperature of the water changes less than the temperature of the iron because the specific heat capacity of water is larger.

Table 11.2

	Specific h	Specific heat capacity	
Substance	J/(g × °C)	$cal/(g \times ^{\circ}C)$	
Water	4.18	1.00	
Grain alcohol	2.4	0.58	
Ice	2.1	0.50	
Steam	1.7	0.40	
Chloroform	0.96	0.23	
Aluminum	0.90	0.21	
Glass	0.50	0.12	
Iron	0.46	0.11	
Silver	0.24	€ 0.057	
Mercury	0.14	0.033	

The specific heat capacity, or simply the specific heat, of a substance is the amount of heat it takes to raise the temperature of 1 g of the substance 1°C. What is the relationship between specific heat and heat capacity? Table 11.2 gives specific heats for some common substances. Water has a very high specific heat compared with the other substances in the table. You can see from the table that one calorie of heat raises the temperature of 1 g of water 1 °C. Metals, however, have low specific heats. One calorie of heat raises the temperature of 1 g of iron 9 °C. Thus water has a specific heat nine times that of iron. Heat affects the temperature of objects with a high specific heat much less than the temperature of those with a low specific heat. Just as it takes a lot of heat to raise the temperature of water, water also releases a lot of heat as it cools. Water in lakes and oceans absorbs heat from the air on hot days and releases it back into the air on cool days. As illustrated in Figure 11.6, this property of water is responsible for moderate climates in coastal areas. The specific heat of water is often used by farmers to protect their crops. In freezing weather, citrus crops are often sprayed with water to protect the fruit from damage. As the water freezes, it releases heat, which helps to prevent the fruit from freezing. The results of this procedure are shown in Figure 11.7.

To calculate the specific heat of a substance, you divide the heat input by the temperature change times the mass of the substance. The equation for specific heat (C) follows, where q is heat and m is mass. The symbol ΔT (read "delta T") in the equation represents the change in temperature. ΔT is calculated from the equation $\Delta T = T_{\rm f} - T_{\rm i}$, where $T_{\rm f}$ is the final temperature and $T_{\rm i}$ is the initial temperature.

$$C = \frac{q}{m \times \Delta T} = \frac{\text{heat (joules or calories)}}{\text{mass (g)} \times \text{change in temperature (°C)}}$$

As you can see from this equation, specific heat may be expressed in terms of joules or calories. Therefore, the units of specific heat are either $J/(g \times {}^{\circ}C)$ or cal/ $(g \times {}^{\circ}C)$.

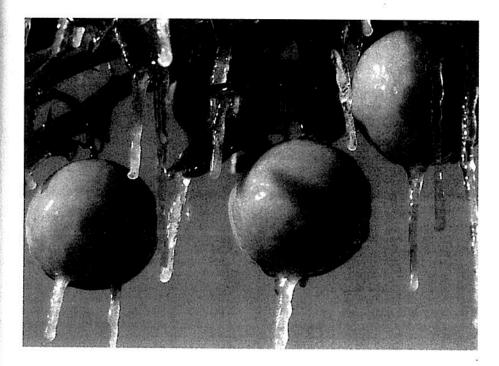




Figure 11.6

San Francisco is located on the Pacific coast. The high specific heat of the ocean helps keep the temperature in San Francisco much more moderate than that of towns and cities farther inland.

Figure 11.1

Water must give off a lot of heat in order to freeze. Sometimes farmers use water's high specific heat capacity to their advantage. In freezing weather, orange groves are often sprayed with water to protect the fruit from frost damage.

CHEMath

REVIEW OF SIGNIFICANT FIGURES

This page offers you a chance to refresh your knowledge of significant figures before beginning this chapter—a chapter which involves solving problems containing numerous numerical values. As you learned in Section 3.2, a value in science must be reported using the correct number of significant figures (or digits). Answers cannot be more precise than the given data, as they would be misleading.

The rules for determining significant figures are summarized below. (Note that this list is a condensed version of the rules listed in Chapter 3.)

- 1. Nonzero digits are always significant.
- 2. A zero is significant only if it is
 - a. at the right end of a number and after a decimal
 - b. between digits that are significant according to rule 1 or 2a.

Zeros to the left of nonzero digits or at the end of a quantity written as a whole number are "placeholders" and are not significant.

3. If a quantity is known to be exact, it has an unlimited number of significant figures.

4. If a quantity is written in scientific notation, all digits of the coefficient are significant.

For example, the significant digits in each number below are shown in blue.

30 400	3 significant figures
150.0	4 significant figures
2401	4 significant figures
168.030	6 significant figures
0.0058	2 significant figures
3.010×10^{8}	4 significant figures

When working with significant digits, round up the final significant digit only if the next digit is 5 or greater. When you do a calculation, round your final answer (not the intermediate steps) according to these rules:

Addition and Subtraction Round the result to the same number of decimal places as the measurement with the fewest decimal places.

Multiplication and Division Round the result to the same number of significant figures as the measurement with the fewest significant figures.

Example 1

Evaluate 2.34 + 1.2 and express the answer with the correct number of significant figures.

2.34 has 2 decimal places and 1.2 has 1 decimal place. So, the answer should be rounded to 1 decimal place.

Without rounding, 2.34 + 1.2 = 3.54.

After rounding 3.54 to 1 decimal place, the final answer is 3.5.

Example 2

Use the formula $C = \frac{q}{m \times \Delta T}$ to calculate C, the specific heat capacity, if q = 516 J, m = 6.4 g, and $\Delta T = 25.80 \, ^{\circ}\text{C}.$

Because 6.4 g has only 2 significant figures, the answer should be rounded to 2 significant figures.

$$C = \frac{516 \text{ J}}{6.4 \text{ g} \times 25.80 \text{ °C}} = 3.125 \frac{\text{J}}{\text{g} \times \text{°C}} = 3.1 \frac{\text{J}}{\text{g} \times \text{°C}}$$

Practice Problems

Find the number of significant figures in each quantity.

A. 1340

B. 0.06

c. 3.400×10^4

D. 0.00350

E. 16.0

Round each answer to the appropriate number of significant figures.

F. 16.382 + 17.5

1. 317.04 ÷ 18.7

G. 1.4×6.03 H. 128.0 - 64.37

 $\dot{\mathbf{K}}$. $(3.0 \times 10^{15}) \div (2.19 \times 10^4)$

Sample Problem 11-1

The temperature of a piece of copper with a mass of 95.4 g increases from 25.0 °C to 48.0 °C when the metal absorbs 849 J of heat. What is the specific heat of copper?

1. ANALYZE List the knowns and the unknown.

Knowns:

- $m_{\rm Cu} = 95.4 {\rm g}$
- $\Delta T = (48.0 \, ^{\circ}\text{C} 25.0 \, ^{\circ}\text{C}) = 23.0 \, ^{\circ}\text{C}$
- q = 849 J

Unknown:

•
$$C_{\text{Cu}} = ? \frac{J}{g \times {}^{\circ}\text{C}}$$

Use the known values and the definition of specific heat,

$$C = \frac{q}{m \times \Delta T}$$
, to calculate the unknown value C_{Cu} .

2. CALCULATE Solve for the unknown.

Substitute the known values into the equation for the specific heat and solve.

$$C_{\text{Cu}} = \frac{q}{m \times \Delta T}$$

$$C_{\text{Cu}} = \frac{849 \text{ J}}{95.4 \text{ g} \times 23.0 \text{ °C}} = 0.387 \frac{\text{J}}{\text{g} \times \text{°C}}$$

3. EVALUATE Does the result make sense?

Remember that water has a very high specific heat $(4.18 \text{ J/(g} \times ^{\circ}\text{C}))$. Metals, however, have low specific heats—values less than $4.18 \text{ J/(g} \times ^{\circ}\text{C})$. Thus the calculated value of $0.387 \text{ J/(g} \times ^{\circ}\text{C})$ seems reasonable.

Practice Problems

- When 435 J of heat is added to 3.4 g of olive oil at 21 °C, the temperature increases to 85 °C. What is the specific heat of olive oil?
- 2. A 1.55-g piece of stainless steel absorbs 141 J of heat when its temperature increases by 178 °C. What is the specific heat of the stainless steel?
- 3. How much heat is required to raise the temperature of 250.0 g of mercury 52 °C?

Chem ASAP!

Problem-Solving 3

Solve Problem 3 with the help of an interactive guided tutorial.



section review 11.1

- 4. Define energy and explain how energy and heat are related.
- 5. Explain the difference between heat capacity and specific heat.
- 6. Will the specific heat of 50 g of a substance be the same as, or greater than, the specific heat of 10 g of the same substance?
- 7. On a sunny day, why does the concrete deck around an outdoor swimming pool become hot, while the water stays cool?
- 8. Using calories, calculate how much heat 32.0 g of water absorbs when it is heated from 25.0 °C to 80.0 °C. How many joules is this?
- 9. A chunk of silver has a heat capacity of 42.8 J/°C. If the silver has a mass of 181 g, calculate the specific heat of silver.
- 10. How many kilojoules of heat are absorbed when 1.00 L of water is heated from 18 °C to 85 °C?
- Chem ASAP! Assessment 11.1 Check your understanding of the important ideas and concepts in Section 11.1.

section 11.2

objectives

- Construct equations that show the heat changes for chemical and physical processes
- Calculate heat changes in chemical and physical processes

key terms

- calorimetry
- ▶ calorimeter
- enthalpy (H)
- thermochemical equation
- heat of reaction
- heat of combustion

MEASURING AND EXPRESSING HEAT CHANGES

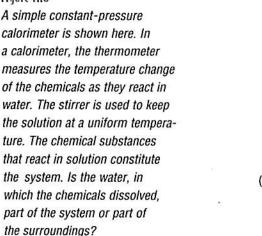
As you know, a burning match gives off heat. When you strike a match, heat is released to the surroundings in all directions. As you have learned, heat cannot be detected by the senses or by instruments. Is there a way to measure exactly how much heat is released from a burning match?

Calorimetry

Energy changes occur in many systems, from the inner workings of a clock, to the eruption of volcanoes, to the formation of the solar system. Most chemical and physical changes you will encounter occur at constant atmospheric pressure. For example, a reaction in an open beaker, the formation of ice in a lake, and the reactions in many living organisms all occur at constant atmospheric pressure. By defining a thermodynamic variable called enthalpy—a variable that takes constant pressure into account—you can measure the energy changes that accompany chemical and physical processes.

Heat that is released or absorbed during many chemical reactions can be measured by calorimetry. Calorimetry is the accurate and precise measurement of heat change for chemical and physical processes. In calorimetry, the heat released by the system is equal to the heat absorbed by its surroundings. What law describes this relationship? To measure heat changes accurately and precisely, the processes must be carried out in an insulated container. The insulated device used to measure the absorption or release of heat in chemical or physical processes is called a calorimeter.

Foam cups, which keep hot drinks hot and cold drinks cold, are excellent heat insulators. Because they do not let much heat in or out, they can be used as simple calorimeters. In fact, the heat change for many chemical reactions can be measured in a constant-pressure calorimeter similar to the one shown in Figure 11.8. Because most chemical reactions and physical



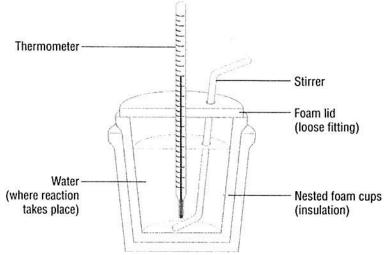


Figure 11.8

Table 11.3

Enthalpy Sign Convention		
Exothermic reaction	ΔH is negative ($\Delta H < 0$)	
Endothermic reaction	ΔH is positive ($\Delta H > 0$)	

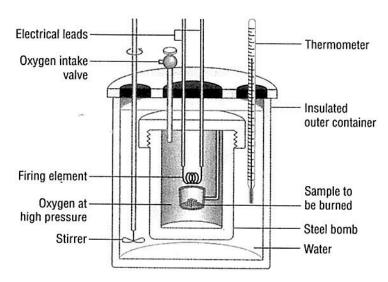
changes carried out in the laboratory are open to the atmosphere, these changes occur at constant pressure. For systems at constant pressure, the heat content is the same as a property called the **enthalpy** (H) of the system. Heat changes for reactions carried out at constant pressure are the same as changes in enthalpy, symbolized as ΔH (read "delta H"). Because the reactions presented in this textbook occur at constant pressure, the terms heat and enthalpy are used interchangeably. In other words, $q = \Delta H$. Recalling the equation for specific heat, we can write the following relationship for the heat change in a chemical reaction carried out in aqueous solution.

$$q = \Delta H = m \times C \times \Delta T$$

 ΔH is the heat change; m is the mass of the water; C is the specific heat capacity of water; and $\Delta T = T_{\rm f} - T_{\rm i}$. The sign of ΔH is negative for an exothermic reaction and positive for an endothermic reaction. Table 11.3 summarizes the sign convention for enthalpy.

To measure the heat change for a reaction in aqueous solution in a foam cup calorimeter, you dissolve the reacting chemicals (the system) in known volumes of water (the surroundings). Then measure the initial temperature of each solution and mix the solutions in the foam cup. After the reaction is complete, measure the final temperature of the mixed solutions. Because you know the initial and final temperatures and the heat capacity of water, you can calculate the heat released or absorbed in the reaction using the equation for specific heat.

Calorimetry experiments can also be performed at constant volume using a device called a bomb calorimeter. A bomb calorimeter, similar to the one shown in Figure 11.9, measures the heat released from burning a compound. The calorimeter is a closed system; that is, the mass of the system is constant.



Chem ASAP!

Simulation 8 Simulate a combustion reaction and compare the ΔH results for several compounds.

Figure 11.9

In a bomb calorimeter, a sample is burned in a constant-volume chamber in the presence of oxygen at high pressure. The heat that is released warms the water surrounding the chamber. By measuring the temperature increase of the water, it is possible to calculate the quantity of heat released during the combustion reaction.