

PUZZLER

Biting into a hot piece of pizza can be either a pleasant experience or a painful one, depending on how it is done. Eating the crust doesn't usually cause a problem, but if you get a mouthful of hot cheese, you can be left with a burned palate. Why does it make so much difference whether your mouth touches the crust or the cheese when both are at the same temperature? (Charles D. Winters)



chapter

20

Heat and the First Law of Thermodynamics

Chapter Outline

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Until about 1850, the fields of thermodynamics and mechanics were considered two distinct branches of science, and the law of conservation of energy seemed to describe only certain kinds of mechanical systems. However, mid-19th century experiments performed by the Englishman James Joule and others showed that energy may be added to (or removed from) a system either by heat or by doing work on the system (or having the system do work). Today we know that internal energy, which we formally define in this chapter, can be transformed to mechanical energy. Once the concept of energy was broadened to include internal energy, the law of conservation of energy emerged as a universal law of nature.

This chapter focuses on the concept of internal energy, the processes by which energy is transferred, the first law of thermodynamics, and some of the important applications of the first law. The first law of thermodynamics is the law of conservation of energy. It describes systems in which the only energy change is that of internal energy, which is due to transfers of energy by heat or work. Furthermore, the first law makes no distinction between the results of heat and the results of work. According to the first law, a system's internal energy can be changed either by an energy transfer by heat to or from the system or by work done on or by the system.

20.1 HEAT AND INTERNAL ENERGY

10.3 At the outset, it is important that we make a major distinction between internal energy and heat. **Internal energy is all the energy of a system that is associated with its microscopic components—atoms and molecules—when viewed from a reference frame at rest with respect to the object.** The last part of this sentence ensures that any bulk kinetic energy of the system due to its motion through space is not included in internal energy. Internal energy includes kinetic energy of translation, rotation, and vibration of molecules, potential energy within molecules, and potential energy between molecules. It is useful to relate internal energy to the temperature of an object, but this relationship is limited—we shall find in Section 20.3 that internal energy changes can also occur in the absence of temperature changes.

As we shall see in Chapter 21, the internal energy of a monatomic ideal gas is associated with the translational motion of its atoms. This is the only type of energy available for the microscopic components of this system. In this special case, the internal energy is simply the total kinetic energy of the atoms of the gas; the higher the temperature of the gas, the greater the average kinetic energy of the atoms and the greater the internal energy of the gas. More generally, in solids, liquids, and molecular gases, internal energy includes other forms of molecular energy. For example, a diatomic molecule can have rotational kinetic energy, as well as vibrational kinetic and potential energy.

Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings. When you *heat* a substance, you are transferring energy into it by placing it in contact with surroundings that have a higher temperature. This is the case, for example, when you place a pan of cold water on a stove burner—the burner is at a higher temperature than the water, and so the water gains energy. We shall also use the term *heat* to represent the amount of energy transferred by this method.

Scientists used to think of heat as a fluid called *caloric*, which they believed was transferred between objects; thus, they defined heat in terms of the temperature changes produced in an object during heating. Today we recognize the distinct difference between internal energy and heat. Nevertheless, we refer to quantities



James Prescott Joule British physicist (1818–1889) Joule received some formal education in mathematics, philosophy, and chemistry but was in large part self-educated. His research led to the establishment of the principle of conservation of energy. His study of the quantitative relationship among electrical, mechanical, and chemical effects of heat culminated in his discovery in 1843 of the amount of work required to produce a unit of energy, called the mechanical equivalent of heat. (By kind permission of the President and Council of the Royal Society)

Heat

using names that do not quite correctly define the quantities but which have become entrenched in physics tradition based on these early ideas. Examples of such quantities are *latent heat* and *heat capacity*.

As an analogy to the distinction between heat and internal energy, consider the distinction between work and mechanical energy discussed in Chapter 7. The work done on a system is a measure of the amount of energy transferred to the system from its surroundings, whereas the mechanical energy of the system (kinetic or potential, or both) is a consequence of the motion and relative positions of the members of the system. Thus, when a person does work on a system, energy is transferred from the person to the system. It makes no sense to talk about the work *of* a system—one can refer only to the work done *on* or *by* a system when some process has occurred in which energy has been transferred to or from the system. Likewise, it makes no sense to talk about the heat *of* a system—one can refer to *heat* only when energy has been transferred as a result of a temperature difference. Both heat and work are ways of changing the energy of a system.

It is also important to recognize that the internal energy of a system can be changed even when no energy is transferred by heat. For example, when a gas is compressed by a piston, the gas is warmed and its internal energy increases, but no transfer of energy by heat from the surroundings to the gas has occurred. If the gas then expands rapidly, it cools and its internal energy decreases, but no transfer of energy by heat from it to the surroundings has taken place. The temperature changes in the gas are due not to a difference in temperature between the gas and its surroundings but rather to the compression and the expansion. In each case, energy is transferred to or from the gas by *work*, and the energy change within the system is an increase or decrease of internal energy. The changes in internal energy in these examples are evidenced by corresponding changes in the temperature of the gas.

Units of Heat

As we have mentioned, early studies of heat focused on the resultant increase in temperature of a substance, which was often water. The early notions of heat based on caloric suggested that the flow of this fluid from one body to another caused changes in temperature. From the name of this mythical fluid, we have an energy unit related to thermal processes, the **calorie (cal)**, which is defined as **the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C**.¹ (Note that the “Calorie,” written with a capital “C” and used in describing the energy content of foods, is actually a kilocalorie.) The unit of energy in the British system is the **British thermal unit (Btu)**, which is defined as **the amount of energy transfer required to raise the temperature of 1 lb of water from 63°F to 64°F**.

The calorie

Scientists are increasingly using the SI unit of energy, the *joule*, when describing thermal processes. In this textbook, heat and internal energy are usually measured in joules. (Note that both heat and work are measured in energy units. Do not confuse these two means of energy *transfer* with energy itself, which is also measured in joules.)

¹ Originally, the calorie was defined as the “heat” necessary to raise the temperature of 1 g of water by 1°C. However, careful measurements showed that the amount of energy required to produce a 1°C change depends somewhat on the initial temperature; hence, a more precise definition evolved.

The Mechanical Equivalent of Heat

In Chapters 7 and 8, we found that whenever friction is present in a mechanical system, some mechanical energy is lost—in other words, mechanical energy is not conserved in the presence of nonconservative forces. Various experiments show that this lost mechanical energy does not simply disappear but is transformed into internal energy. We can perform such an experiment at home by simply hammering a nail into a scrap piece of wood. What happens to all the kinetic energy of the hammer once we have finished? Some of it is now in the nail as internal energy, as demonstrated by the fact that the nail is measurably warmer. Although this connection between mechanical and internal energy was first suggested by Benjamin Thompson, it was Joule who established the equivalence of these two forms of energy.

A schematic diagram of Joule's most famous experiment is shown in Figure 20.1. The system of interest is the water in a thermally insulated container. Work is done on the water by a rotating paddle wheel, which is driven by heavy blocks falling at a constant speed. The stirred water is warmed due to the friction between it and the paddles. If the energy lost in the bearings and through the walls is neglected, then the loss in potential energy associated with the blocks equals the work done by the paddle wheel on the water. If the two blocks fall through a distance h , the loss in potential energy is $2mgh$, where m is the mass of one block; it is this energy that causes the temperature of the water to increase. By varying the conditions of the experiment, Joule found that the loss in mechanical energy $2mgh$ is proportional to the increase in water temperature ΔT . The proportionality constant was found to be approximately $4.18 \text{ J/g} \cdot ^\circ\text{C}$. Hence, 4.18 J of mechanical energy raises the temperature of 1 g of water by 1°C . More precise measurements taken later demonstrated the proportionality to be $4.186 \text{ J/g} \cdot ^\circ\text{C}$ when the temperature of the water was raised from 14.5°C to 15.5°C . We adopt this “15-degree calorie” value:

$$1 \text{ cal} \equiv 4.186 \text{ J} \quad (20.1)$$

This equality is known, for purely historical reasons, as the **mechanical equivalent of heat**.



Benjamin Thompson
(1753–1814).

Mechanical equivalent of heat

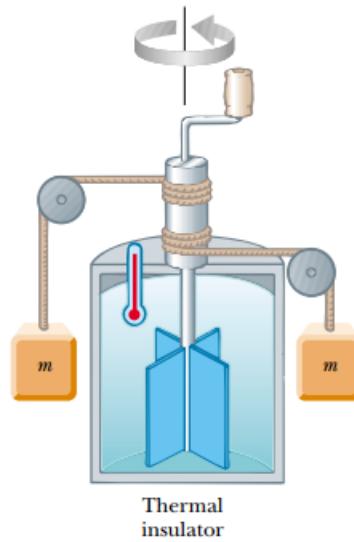


Figure 20.1 Joule's experiment for determining the mechanical equivalent of heat. The falling blocks rotate the paddles, causing the temperature of the water to increase.

EXAMPLE 20.1 Losing Weight the Hard Way

A student eats a dinner rated at 2 000 Calories. He wishes to do an equivalent amount of work in the gymnasium by lifting a 50.0-kg barbell. How many times must he raise the barbell to expend this much energy? Assume that he raises the barbell 2.00 m each time he lifts it and that he regains no energy when he drops the barbell to the floor.

Solution Because 1 Calorie = 1.00×10^3 cal, the work required is 2.00×10^6 cal. Converting this value to joules, we have for the total work required:

$$W = (2.00 \times 10^6 \text{ cal})(4.186 \text{ J/cal}) = 8.37 \times 10^6 \text{ J}$$

The work done in lifting the barbell a distance h is equal to mgh , and the work done in lifting it n times is $nmgh$. We equate this to the total work required:

$$W = nmgh = 8.37 \times 10^6 \text{ J}$$

$$n = \frac{8.37 \times 10^6 \text{ J}}{(50.0 \text{ kg})(9.80 \text{ m/s}^2)(2.00 \text{ m})} = 8.54 \times 10^3 \text{ times}$$

If the student is in good shape and lifts the barbell once every 5 s, it will take him about 12 h to perform this feat. Clearly, it is much easier for this student to lose weight by dieting.

20.2 HEAT CAPACITY AND SPECIFIC HEAT

 When energy is added to a substance and no work is done, the temperature of the substance usually rises. (An exception to this statement is the case in which a substance undergoes a change of state—also called a *phase transition*—as discussed in the next section.) The quantity of energy required to raise the temperature of a given mass of a substance by some amount varies from one substance to another. For example, the quantity of energy required to raise the temperature of 1 kg of water by 1°C is 4 186 J, but the quantity of energy required to raise the temperature of 1 kg of copper by 1°C is only 387 J. In the discussion that follows, we shall use heat as our example of energy transfer, but we shall keep in mind that we could change the temperature of our system by doing work on it.

The **heat capacity** C of a particular sample of a substance is defined as the amount of energy needed to raise the temperature of that sample by 1°C . From this definition, we see that if heat Q produces a change ΔT in the temperature of a substance, then

Heat capacity

$$Q = C\Delta T \quad (20.2)$$

The **specific heat** c of a substance is the heat capacity per unit mass. Thus, if energy Q transferred by heat to mass m of a substance changes the temperature of the sample by ΔT , then the specific heat of the substance is

Specific heat

$$c = \frac{Q}{m\Delta T} \quad (20.3)$$

Specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy. The greater a material's specific heat, the more energy must be added to a given mass of the material to cause a particular temperature change. Table 20.1 lists representative specific heats.

From this definition, we can express the energy Q transferred by heat between a sample of mass m of a material and its surroundings for a temperature change ΔT as

$$Q = mc\Delta T \quad (20.4)$$

For example, the energy required to raise the temperature of 0.500 kg of water by 3.00°C is $(0.500 \text{ kg})(4 186 \text{ J/kg}\cdot{}^\circ\text{C})(3.00^\circ\text{C}) = 6.28 \times 10^3 \text{ J}$. Note that when the temperature increases, Q and ΔT are taken to be positive, and energy flows into

TABLE 20.1 Specific Heats of Some Substances at 25°C and Atmospheric Pressure

Substance		Specific Heat <i>c</i>	
	J/kg · °C	cal/g · °C	
Elemental Solids			
Aluminum	900	0.215	
Beryllium	1 830	0.436	
Cadmium	230	0.055	
Copper	387	0.092 4	
Germanium	322	0.077	
Gold	129	0.030 8	
Iron	448	0.107	
Lead	128	0.030 5	
Silicon	703	0.168	
Silver	234	0.056	
Other Solids			
Brass	380	0.092	
Glass	837	0.200	
Ice (-5°C)	2 090	0.50	
Marble	860	0.21	
Wood	1 700	0.41	
Liquids			
Alcohol (ethyl)	2 400	0.58	
Mercury	140	0.033	
Water (15°C)	4 186	1.00	
Gas			
Steam (100°C)	2 010	0.48	

the system. When the temperature decreases, Q and ΔT are negative, and energy flows out of the system.

Specific heat varies with temperature. However, if temperature intervals are not too great, the temperature variation can be ignored and c can be treated as a constant.² For example, the specific heat of water varies by only about 1% from 0°C to 100°C at atmospheric pressure. Unless stated otherwise, we shall neglect such variations.

Measured values of specific heats are found to depend on the conditions of the experiment. In general, measurements made at constant pressure are different from those made at constant volume. For solids and liquids, the difference between the two values is usually no greater than a few percent and is often neglected. Most of the values given in Table 20.1 were measured at atmospheric pressure and room temperature. As we shall see in Chapter 21, the specific heats for

² The definition given by Equation 20.3 assumes that the specific heat does not vary with temperature over the interval $\Delta T = T_f - T_i$. In general, if c varies with temperature over the interval, then the correct expression for Q is

$$Q = m \int_{T_i}^{T_f} c \, dT$$

gases measured at constant pressure are quite different from values measured at constant volume.

Quick Quiz 20.1

Imagine you have 1 kg each of iron, glass, and water, and that all three samples are at 10°C.

- (a) Rank the samples from lowest to highest temperature after 100 J of energy is added to each. (b) Rank them from least to greatest amount of energy transferred by heat if each increases in temperature by 20°C.

QuickLab

In an open area, such as a parking lot, use the flame from a match to pop an air-filled balloon. Now try the same thing with a water-filled balloon. Why doesn't the water-filled balloon pop?

It is interesting to note from Table 20.1 that water has the highest specific heat of common materials. This high specific heat is responsible, in part, for the moderate temperatures found near large bodies of water. As the temperature of a body of water decreases during the winter, energy is transferred from the cooling water to the air by heat, increasing the internal energy of the air. Because of the high specific heat of water, a relatively large amount of energy is transferred to the air for even modest temperature changes of the water. The air carries this internal energy landward when prevailing winds are favorable. For example, the prevailing winds on the West Coast of the United States are toward the land (eastward). Hence, the energy liberated by the Pacific Ocean as it cools keeps coastal areas much warmer than they would otherwise be. This explains why the western coastal states generally have more favorable winter weather than the eastern coastal states, where the prevailing winds do not tend to carry the energy toward land.



A difference in specific heats causes the cheese topping on a slice of pizza to burn you more than a mouthful of crust at the same temperature. Both crust and cheese undergo the same change in temperature, starting at a high straight-from-the-oven value and ending at the temperature of the inside of your mouth, which is about 37°C. Because the cheese is much more likely to burn you, it must release much more energy as it cools than does the crust. If we assume roughly the same mass for both cheese and crust, then Equation 20.3 indicates that the specific heat of the cheese, which is mostly water, is greater than that of the crust, which is mostly air.

Conservation of Energy: Calorimetry

One technique for measuring specific heat involves heating a sample to some known temperature T_x , placing it in a vessel containing water of known mass and temperature $T_w < T_x$, and measuring the temperature of the water after equilibrium has been reached. Because a negligible amount of mechanical work is done in the process, the law of the conservation of energy requires that the amount of energy that leaves the sample (of unknown specific heat) equal the amount of energy that enters the water.³ This technique is called **calorimetry**, and devices in which this energy transfer occurs are called **calorimeters**.

Conservation of energy allows us to write the equation

$$Q_{\text{cold}} = -Q_{\text{hot}} \quad (20.5)$$

which simply states that the energy leaving the hot part of the system by heat is equal to that entering the cold part of the system. The negative sign in the equation is necessary to maintain consistency with our sign convention for heat. The

³ For precise measurements, the water container should be included in our calculations because it also exchanges energy with the sample. However, doing so would require a knowledge of its mass and composition. If the mass of the water is much greater than that of the container, we can neglect the effects of the container.

heat Q_{hot} is negative because energy is leaving the hot sample. The negative sign in the equation ensures that the right-hand side is positive and thus consistent with the left-hand side, which is positive because energy is entering the cold water.

Suppose m_x is the mass of a sample of some substance whose specific heat we wish to determine. Let us call its specific heat c_x and its initial temperature T_x . Likewise, let m_w , c_w , and T_w represent corresponding values for the water. If T_f is the final equilibrium temperature after everything is mixed, then from Equation 20.4, we find that the energy transfer for the water is $m_w c_w (T_f - T_w)$, which is positive because $T_f > T_w$, and that the energy transfer for the sample of unknown specific heat is $m_x c_x (T_f - T_x)$, which is negative. Substituting these expressions into Equation 20.5 gives

$$m_w c_w (T_f - T_w) = -m_x c_x (T_f - T_x)$$

Solving for c_x gives

$$c_x = \frac{m_w c_w (T_f - T_w)}{m_x (T_x - T_f)}$$

EXAMPLE 20.2 Cooling a Hot Ingot

A 0.050 0-kg ingot of metal is heated to 200.0°C and then dropped into a beaker containing 0.400 kg of water initially at 20.0°C. If the final equilibrium temperature of the mixed system is 22.4°C, find the specific heat of the metal.

Solution According to Equation 20.5, we can write

$$\begin{aligned} m_w c_w (T_f - T_w) &= -m_x c_x (T_f - T_x) \\ (0.400 \text{ kg}) (4186 \text{ J/kg}\cdot^\circ\text{C}) (22.4^\circ\text{C} - 20.0^\circ\text{C}) &= \\ &\quad - (0.050 0 \text{ kg}) (c_x) (22.4^\circ\text{C} - 200.0^\circ\text{C}) \end{aligned}$$

From this we find that

$$c_x = 453 \text{ J/kg}\cdot^\circ\text{C}$$

The ingot is most likely iron, as we can see by comparing this result with the data given in Table 20.1. Note that the temperature of the ingot is initially above the steam point. Thus, some of the water may vaporize when we drop the ingot into the water. We assume that we have a sealed system and thus that this steam cannot escape. Because the final equilibrium temperature is lower than the steam point, any steam that does result recondenses back into water.

Exercise What is the amount of energy transferred to the water as the ingot is cooled?

Answer 4 020 J.

EXAMPLE 20.3 Fun Time for a Cowboy

A cowboy fires a silver bullet with a mass of 2.00 g and with a muzzle speed of 200 m/s into the pine wall of a saloon. Assume that all the internal energy generated by the impact remains with the bullet. What is the temperature change of the bullet?

Solution The kinetic energy of the bullet is

$$\frac{1}{2}mv^2 = \frac{1}{2}(2.00 \times 10^{-3} \text{ kg})(200 \text{ m/s})^2 = 40.0 \text{ J}$$

Because nothing in the environment is hotter than the bullet, the bullet gains no energy by heat. Its temperature increases because the 40.0 J of kinetic energy becomes 40.0 J of extra internal energy. The temperature change is the same as that which would take place if 40.0 J of energy were transferred by

heat from a stove to the bullet. If we imagine this latter process taking place, we can calculate ΔT from Equation 20.4. Using 234 J/kg·°C as the specific heat of silver (see Table 20.1), we obtain

$$\Delta T = \frac{Q}{mc} = \frac{40.0 \text{ J}}{(2.00 \times 10^{-3} \text{ kg})(234 \text{ J/kg}\cdot^\circ\text{C})} = 85.5^\circ\text{C}$$

Exercise Suppose that the cowboy runs out of silver bullets and fires a lead bullet of the same mass and at the same speed into the wall. What is the temperature change of the bullet?

Answer 156°C.

20.3 LATENT HEAT

A substance often undergoes a change in temperature when energy is transferred between it and its surroundings. There are situations, however, in which the transfer of energy does not result in a change in temperature. This is the case whenever the physical characteristics of the substance change from one form to another; such a change is commonly referred to as a **phase change**. Two common phase changes are from solid to liquid (melting) and from liquid to gas (boiling); another is a change in the crystalline structure of a solid. All such phase changes involve a change in internal energy but no change in temperature. The increase in internal energy in boiling, for example, is represented by the breaking of bonds between molecules in the liquid state; this bond breaking allows the molecules to move farther apart in the gaseous state, with a corresponding increase in intermolecular potential energy.

As you might expect, different substances respond differently to the addition or removal of energy as they change phase because their internal molecular arrangements vary. Also, the amount of energy transferred during a phase change depends on the amount of substance involved. (It takes less energy to melt an ice cube than it does to thaw a frozen lake.) If a quantity Q of energy transfer is required to change the phase of a mass m of a substance, the ratio $L \equiv Q/m$ characterizes an important thermal property of that substance. Because this added or removed energy does not result in a temperature change, the quantity L is called the **latent heat** (literally, the “hidden” heat) of the substance. The value of L for a substance depends on the nature of the phase change, as well as on the properties of the substance.

From the definition of latent heat, and again choosing heat as our energy transfer mechanism, we find that the energy required to change the phase of a given mass m of a pure substance is

$$Q = mL \quad (20.6)$$

Latent heat of fusion L_f is the term used when the phase change is from solid to liquid (*to fuse* means “to combine by melting”), and **latent heat of vaporization**

TABLE 20.2 Latent Heats of Fusion and Vaporization

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	-269.65	5.23×10^3	-268.93	2.09×10^4
Nitrogen	-209.97	2.55×10^4	-195.81	2.01×10^5
Oxygen	-218.79	1.38×10^4	-182.97	2.13×10^5
Ethyl alcohol	-114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

L_v is the term used when the phase change is from liquid to gas (the liquid “vaporizes”).⁴ The latent heats of various substances vary considerably, as data in Table 20.2 show.

Quick Quiz 20.2

Which is more likely to cause a serious burn, 100°C liquid water or an equal mass of 100°C steam?

To understand the role of latent heat in phase changes, consider the energy required to convert a 1.00-g block of ice at -30.0°C to steam at 120.0°C . Figure 20.2 indicates the experimental results obtained when energy is gradually added to the ice. Let us examine each portion of the red curve.

Part A. On this portion of the curve, the temperature of the ice changes from -30.0°C to 0.0°C . Because the specific heat of ice is $2\,090\,\text{J/kg}\cdot{}^\circ\text{C}$, we can calculate the amount of energy added by using Equation 20.4:

$$Q = m_i c_i \Delta T = (1.00 \times 10^{-3} \text{ kg})(2\,090 \text{ J/kg}\cdot{}^\circ\text{C})(30.0^\circ\text{C}) = 62.7 \text{ J}$$

Part B. When the temperature of the ice reaches 0.0°C , the ice–water mixture remains at this temperature—even though energy is being added—until all the ice melts. The energy required to melt 1.00 g of ice at 0.0°C is, from Equation 20.6,

$$Q = mL_f = (1.00 \times 10^{-3} \text{ kg})(3.33 \times 10^5 \text{ J/kg}) = 333 \text{ J}$$

Thus, we have moved to the 396 J ($= 62.7 \text{ J} + 333 \text{ J}$) mark on the energy axis.

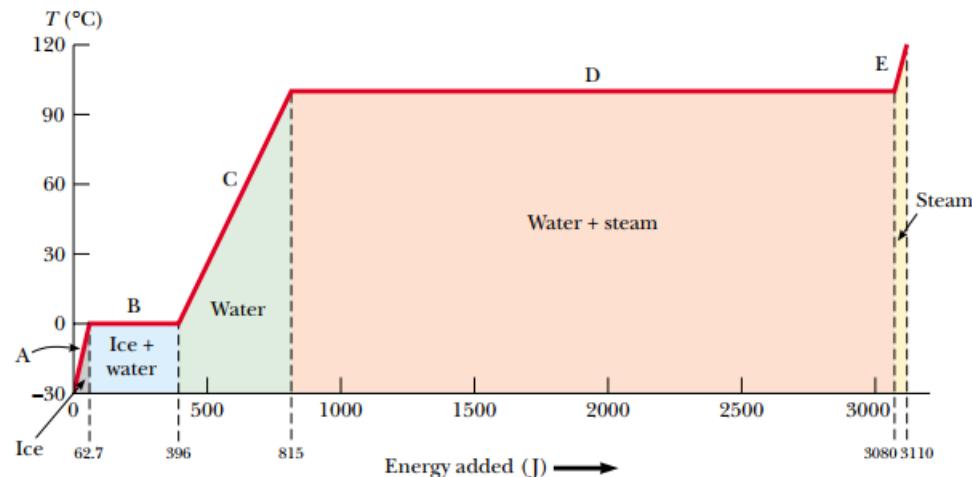


Figure 20.2 A plot of temperature versus energy added when 1.00 g of ice initially at -30.0°C is converted to steam at 120.0°C .

⁴ When a gas cools, it eventually *condenses*—that is, it returns to the liquid phase. The energy given up per unit mass is called the *latent heat of condensation* and is numerically equal to the latent heat of vaporization. Likewise, when a liquid cools, it eventually solidifies, and the *latent heat of solidification* is numerically equal to the latent heat of fusion.

Part C. Between 0.0°C and 100.0°C, nothing surprising happens. No phase change occurs, and so all energy added to the water is used to increase its temperature. The amount of energy necessary to increase the temperature from 0.0°C to 100.0°C is

$$Q = m_w c_w \Delta T = (1.00 \times 10^{-3} \text{ kg})(4.19 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C})(100.0^\circ\text{C}) = 419 \text{ J}$$

Part D. At 100.0°C, another phase change occurs as the water changes from water at 100.0°C to steam at 100.0°C. Similar to the ice–water mixture in part B, the water–steam mixture remains at 100.0°C—even though energy is being added—until all of the liquid has been converted to steam. The energy required to convert 1.00 g of water to steam at 100.0°C is

$$Q = mL_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2.26 \times 10^3 \text{ J}$$

Part E. On this portion of the curve, as in parts A and C, no phase change occurs; thus, all energy added is used to increase the temperature of the steam. The energy that must be added to raise the temperature of the steam from 100.0°C to 120.0°C is

$$Q = m_s c_s \Delta T = (1.00 \times 10^{-3} \text{ kg})(2.01 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C})(20.0^\circ\text{C}) = 40.2 \text{ J}$$

The total amount of energy that must be added to change 1 g of ice at –30.0°C to steam at 120.0°C is the sum of the results from all five parts of the curve, which is $3.11 \times 10^3 \text{ J}$. Conversely, to cool 1 g of steam at 120.0°C to ice at –30.0°C, we must remove $3.11 \times 10^3 \text{ J}$ of energy.

We can describe phase changes in terms of a rearrangement of molecules when energy is added to or removed from a substance. (For elemental substances in which the atoms do not combine to form molecules, the following discussion should be interpreted in terms of atoms. We use the general term *molecules* to refer to both molecular substances and elemental substances.) Consider first the liquid-to-gas phase change. The molecules in a liquid are close together, and the forces between them are stronger than those between the more widely separated molecules of a gas. Therefore, work must be done on the liquid against these attractive molecular forces if the molecules are to separate. The latent heat of vaporization is the amount of energy per unit mass that must be added to the liquid to accomplish this separation.

Similarly, for a solid, we imagine that the addition of energy causes the amplitude of vibration of the molecules about their equilibrium positions to become greater as the temperature increases. At the melting point of the solid, the amplitude is great enough to break the bonds between molecules and to allow molecules to move to new positions. The molecules in the liquid also are bound to each other, but less strongly than those in the solid phase. The latent heat of fusion is equal to the energy required per unit mass to transform the bonds among all molecules from the solid-type bond to the liquid-type bond.

As you can see from Table 20.2, the latent heat of vaporization for a given substance is usually somewhat higher than the latent heat of fusion. This is not surprising if we consider that the average distance between molecules in the gas phase is much greater than that in either the liquid or the solid phase. In the solid-to-liquid phase change, we transform solid-type bonds between molecules into liquid-type bonds between molecules, which are only slightly less strong. In the liquid-to-gas phase change, however, we break liquid-type bonds and create a situation in which the molecules of the gas essentially are not bonded to each

other. Therefore, it is not surprising that more energy is required to vaporize a given mass of substance than is required to melt it.

Quick Quiz 20.3

Calculate the slopes for the A, C, and E portions of Figure 20.2. Rank the slopes from least to greatest and explain what this ordering means.

Problem-Solving Hints

Calorimetry Problems

If you are having difficulty in solving calorimetry problems, be sure to consider the following points:

- Units of measure must be consistent. For instance, if you are using specific heats measured in cal/g·°C, be sure that masses are in grams and temperatures are in Celsius degrees.
- Transfers of energy are given by the equation $Q = mc\Delta T$ only for those processes in which no phase changes occur. Use the equations $Q = mL_f$ and $Q = mL_v$ only when phase changes are taking place.
- Often, errors in sign are made when the equation $Q_{\text{cold}} = -Q_{\text{hot}}$ is used. Make sure that you use the negative sign in the equation, and remember that ΔT is always the final temperature minus the initial temperature.

EXAMPLE 20.4 Cooling the Steam

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

Solution The steam loses energy in three stages. In the first stage, the steam is cooled to 100°C. The energy transfer in the process is

$$\begin{aligned} Q_1 &= m_s c_s \Delta T = m_s (2.01 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C}) (-30.0^\circ\text{C}) \\ &= -m_s (6.03 \times 10^4 \text{ J/kg}) \end{aligned}$$

where m_s is the unknown mass of the steam.

In the second stage, the steam is converted to water. To find the energy transfer during this phase change, we use $Q = -mL_v$, where the negative sign indicates that energy is leaving the steam:

$$Q_2 = -m_s (2.26 \times 10^6 \text{ J/kg})$$

In the third stage, the temperature of the water created from the steam is reduced to 50.0°C. This change requires an energy transfer of

$$\begin{aligned} Q_3 &= m_s c_w \Delta T = m_s (4.19 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C}) (-50.0^\circ\text{C}) \\ &= -m_s (2.09 \times 10^5 \text{ J/kg}) \end{aligned}$$

Adding the energy transfers in these three stages, we obtain

$$\begin{aligned} Q_{\text{hot}} &= Q_1 + Q_2 + Q_3 \\ &= -m_s (6.03 \times 10^4 \text{ J/kg} + 2.26 \times 10^6 \text{ J/kg} \\ &\quad + 2.09 \times 10^5 \text{ J/kg}) \\ &= -m_s (2.53 \times 10^6 \text{ J/kg}) \end{aligned}$$

Now, we turn our attention to the temperature increase of the water and the glass. Using Equation 20.4, we find that

$$\begin{aligned} Q_{\text{cold}} &= (0.200 \text{ kg}) (4.19 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C}) (30.0^\circ\text{C}) \\ &\quad + (0.100 \text{ kg}) (837 \text{ J/kg} \cdot ^\circ\text{C}) (30.0^\circ\text{C}) \\ &= 2.77 \times 10^4 \text{ J} \end{aligned}$$

Using Equation 20.5, we can solve for the unknown mass:

$$\begin{aligned} Q_{\text{cold}} &= -Q_{\text{hot}} \\ 2.77 \times 10^4 \text{ J} &= -[-m_s (2.53 \times 10^6 \text{ J/kg})] \\ m_s &= 1.09 \times 10^{-2} \text{ kg} = 10.9 \text{ g} \end{aligned}$$

EXAMPLE 20.5 Boiling Liquid Helium

Liquid helium has a very low boiling point, 4.2 K, and a very low latent heat of vaporization, $2.09 \times 10^4 \text{ J/kg}$. If energy is transferred to a container of boiling liquid helium from an immersed electric heater at a rate of 10.0 W, how long does it take to boil away 1.00 kg of the liquid?

Solution Because $L_v = 2.09 \times 10^4 \text{ J/kg}$, we must supply $2.09 \times 10^4 \text{ J}$ of energy to boil away 1.00 kg. Because $10.0 \text{ W} = 10.0 \text{ J/s}$, 10.0 J of energy is transferred to the helium each second. Therefore, the time it takes to transfer $2.09 \times 10^4 \text{ J}$

of energy is

$$t = \frac{2.09 \times 10^4 \text{ J}}{10.0 \text{ J/s}} = 2.09 \times 10^3 \text{ s} \approx 35 \text{ min}$$

Exercise If 10.0 W of power is supplied to 1.00 kg of water at 100°C , how long does it take for the water to completely boil away?

Answer 62.8 h.

20.4 WORK AND HEAT IN THERMODYNAMIC PROCESSES

10.6 In the macroscopic approach to thermodynamics, we describe the *state* of a system using such variables as pressure, volume, temperature, and internal energy. The number of macroscopic variables needed to characterize a system depends on the nature of the system. For a homogeneous system, such as a gas containing only one type of molecule, usually only two variables are needed. However, it is important to note that a *macroscopic state* of an isolated system can be specified only if the system is in thermal equilibrium internally. In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature.

Consider a gas contained in a cylinder fitted with a movable piston (Fig. 20.3). At equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder's walls and on the piston. If the piston has a cross-sectional area A , the

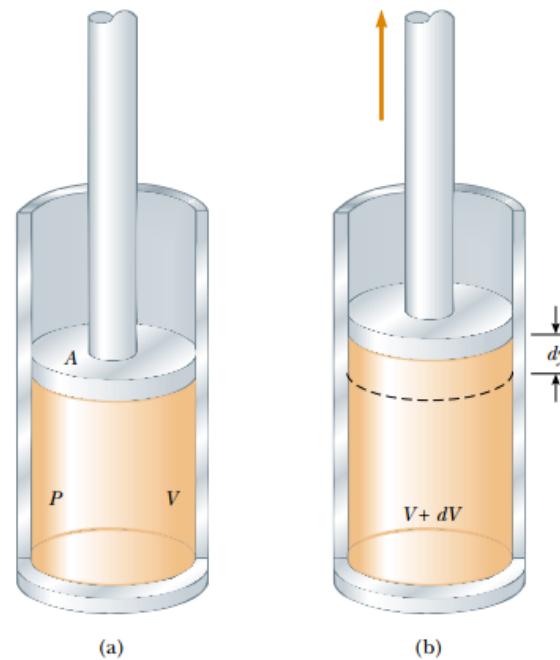


Figure 20.3 Gas contained in a cylinder at a pressure P does work on a moving piston as the system expands from a volume V to a volume $V + dV$.

force exerted by the gas on the piston is $F = PA$. Now let us assume that the gas expands **quasi-statically**, that is, slowly enough to allow the system to remain essentially in thermal equilibrium at all times. As the piston moves up a distance dy , the work done by the gas on the piston is

$$dW = F dy = PA dy$$

Because $A dy$ is the increase in volume of the gas dV , we can express the work done by the gas as

$$dW = P dV \quad (20.7)$$

Because the gas expands, dV is positive, and so the work done by the gas is positive. If the gas were compressed, dV would be negative, indicating that the work done by the gas (which can be interpreted as work done *on* the gas) was negative.

In the thermodynamics problems that we shall solve, we shall identify the system of interest as a substance that is exchanging energy with the environment. In many problems, this will be a gas contained in a vessel; however, we will also consider problems involving liquids and solids. It is an unfortunate fact that, because of the separate historical development of thermodynamics and mechanics, positive work for a thermodynamic system is commonly defined as the work done *by* the system, rather than that done *on* the system. This is the reverse of the case for our study of work in mechanics. Thus, **in thermodynamics, positive work represents a transfer of energy out of the system**. We will use this convention to be consistent with common treatments of thermodynamics.

The total work done by the gas as its volume changes from V_i to V_f is given by the integral of Equation 20.7:

$$W = \int_{V_i}^{V_f} P dV \quad (20.8)$$

To evaluate this integral, it is not enough that we know only the initial and final values of the pressure. We must also know the pressure at every instant during the expansion; we would know this if we had a functional dependence of P with respect to V . This important point is true for any process—the expansion we are discussing here, or any other. To fully specify a process, we must know the values of the thermodynamic variables at every state through which the system passes between the initial and final states. In the expansion we are considering here, we can plot the pressure and volume at each instant to create a PV diagram like the one shown in Figure 20.4. The value of the integral in Equation 20.8 is the area bounded by such a curve. Thus, we can say that

the work done by a gas in the expansion from an initial state to a final state is the area under the curve connecting the states in a PV diagram.

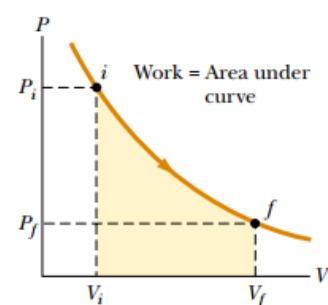


Figure 20.4 A gas expands quasi-statically (slowly) from state i to state f . The work done by the gas equals the area under the PV curve.

As Figure 20.4 shows, the work done in the expansion from the initial state i to the final state f depends on the path taken between these two states, where the *path* on a PV diagram is a description of the thermodynamic process through which the system is taken. To illustrate this important point, consider several paths connecting i and f (Fig. 20.5). In the process depicted in Figure 20.5a, the pressure of the gas is first reduced from P_i to P_f by cooling at constant volume V_i . The gas then expands from V_i to V_f at constant pressure P_f . The value of the work done along this path is equal to the area of the shaded rectangle, which is equal to

Work equals area under the curve in a PV diagram.

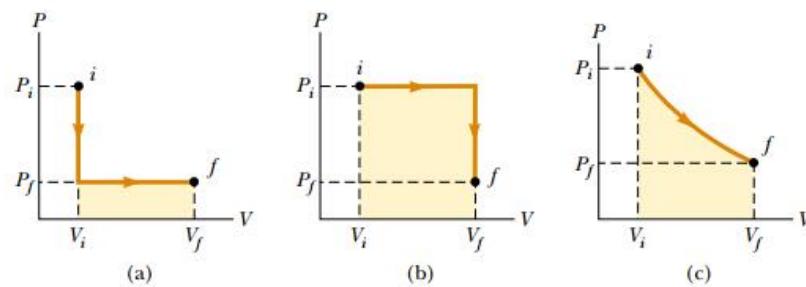


Figure 20.5 The work done by a gas as it is taken from an initial state to a final state depends on the path between these states.

$P_f(V_f - V_i)$. In Figure 20.5b, the gas first expands from V_i to V_f at constant pressure P_i . Then, its pressure is reduced to P_f at constant volume V_f . The value of the work done along this path is $P_i(V_f - V_i)$, which is greater than that for the process described in Figure 20.5a. Finally, for the process described in Figure 20.5c, where both P and V change continuously, the work done has some value intermediate between the values obtained in the first two processes. Therefore, we see that **the work done by a system depends on the initial and final states and on the path followed by the system between these states**.

Work done depends on the path between the initial and final states.

The energy transfer by heat Q into or out of a system also depends on the process. Consider the situations depicted in Figure 20.6. In each case, the gas has the same initial volume, temperature, and pressure and is assumed to be ideal. In Figure 20.6a, the gas is thermally insulated from its surroundings except at the bottom of the gas-filled region, where it is in thermal contact with an energy reservoir. An *energy reservoir* is a source of energy that is considered to be so great that a finite transfer of energy from the reservoir does not change its temperature. The piston is held at its initial position by an external agent—a hand, for instance. When the force with which the piston is held is reduced slightly, the piston rises very slowly to its final position. Because the piston is moving upward, the gas is doing work on

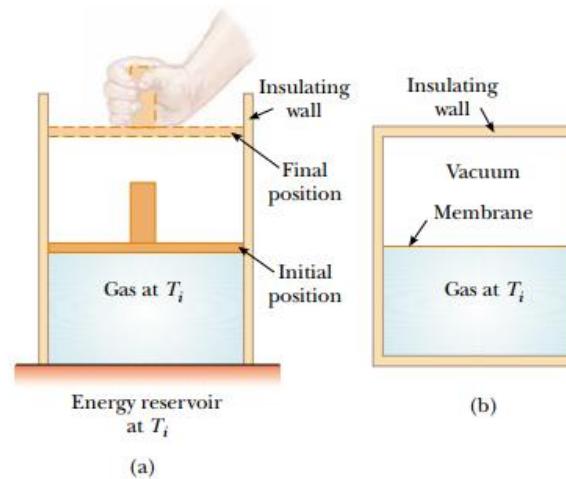


Figure 20.6 (a) A gas at temperature T_i expands slowly while absorbing energy from a reservoir in order to maintain a constant temperature. (b) A gas expands rapidly into an evacuated region after a membrane is broken.

the piston. During this expansion to the final volume V_f , just enough energy is transferred by heat from the reservoir to the gas to maintain a constant temperature T_i .

Now consider the completely thermally insulated system shown in Figure 20.6b. When the membrane is broken, the gas expands rapidly into the vacuum until it occupies a volume V_f and is at a pressure P_f . In this case, the gas does no work because there is no movable piston on which the gas applies a force. Furthermore, no energy is transferred by heat through the insulating wall.

The initial and final states of the ideal gas in Figure 20.6a are identical to the initial and final states in Figure 20.6b, but the paths are different. In the first case, the gas does work on the piston, and energy is transferred slowly to the gas. In the second case, no energy is transferred, and the value of the work done is zero. Therefore, we conclude that **energy transfer by heat, like work done, depends on the initial, final, and intermediate states of the system**. In other words, because heat and work depend on the path, neither quantity is determined solely by the end points of a thermodynamic process.



This device, called *Hero's engine*, was invented around 150 B.C. by Hero in Alexandria. When water is boiled in the flask, which is suspended by a cord, steam exits through two tubes at the sides (in opposite directions), creating a torque that rotates the flask.

20.5 THE FIRST LAW OF THERMODYNAMICS

 When we introduced the law of conservation of mechanical energy in Chapter 8, **10.6** we stated that the mechanical energy of a system is constant in the absence of non-conservative forces such as friction. That is, we did not include changes in the internal energy of the system in this mechanical model. The first law of thermodynamics is a generalization of the law of conservation of energy that encompasses changes in internal energy. It is a universally valid law that can be applied to many processes and provides a connection between the microscopic and macroscopic worlds.

We have discussed two ways in which energy can be transferred between a system and its surroundings. One is work done by the system, which requires that there be a macroscopic displacement of the point of application of a force (or pressure). The other is heat, which occurs through random collisions between the molecules of the system. Both mechanisms result in a change in the internal energy of the system and therefore usually result in measurable changes in the macroscopic variables of the system, such as the pressure, temperature, and volume of a gas.

To better understand these ideas on a quantitative basis, suppose that a system undergoes a change from an initial state to a final state. During this change, energy transfer by heat Q to the system occurs, and work W is done by the system. As an example, suppose that the system is a gas in which the pressure and volume change from P_i and V_i to P_f and V_f . If the quantity $Q - W$ is measured for various paths connecting the initial and final equilibrium states, we find that it is the same for all paths connecting the two states. We conclude that the quantity $Q - W$ is determined completely by the initial and final states of the system, and we call this quantity the **change in the internal energy** of the system. Although Q and W both depend on the path, **the quantity $Q - W$ is independent of the path**. If we use the symbol E_{int} to represent the internal energy, then the *change* in internal energy ΔE_{int} can be expressed as⁵

$$\Delta E_{\text{int}} = Q - W \quad (20.9)$$

$Q - W$ is the change in internal energy

First-law equation

⁵ It is an unfortunate accident of history that the traditional symbol for internal energy is U , which is also the traditional symbol for potential energy, as introduced in Chapter 8. To avoid confusion between potential energy and internal energy, we use the symbol E_{int} for internal energy in this book. If you take an advanced course in thermodynamics, however, be prepared to see U used as the symbol for internal energy.

where all quantities must have the same units of measure for energy.⁶ Equation 20.9 is known as the **first-law equation** and is a key concept in many applications. As a reminder, we use the convention that Q is positive when energy enters the system and negative when energy leaves the system, and that W is positive when the system does work on the surroundings and negative when work is done on the system.

When a system undergoes an infinitesimal change in state in which a small amount of energy dQ is transferred by heat and a small amount of work dW is done, the internal energy changes by a small amount dE_{int} . Thus, for infinitesimal processes we can express the first-law equation as⁷

$$dE_{\text{int}} = dQ - dW$$

The first-law equation is an energy conservation equation specifying that the only type of energy that changes in the system is the internal energy E_{int} . Let us look at some special cases in which this condition exists.

First, let us consider an *isolated system*—that is, one that does not interact with its surroundings. In this case, no energy transfer by heat takes place and the value of the work done by the system is zero; hence, the internal energy remains constant. That is, because $Q = W = 0$, it follows that $\Delta E_{\text{int}} = 0$, and thus $E_{\text{int},i} = E_{\text{int},f}$. We conclude that **the internal energy E_{int} of an isolated system remains constant**.

Next, we consider the case of a system (one not isolated from its surroundings) that is taken through a **cyclic process**—that is, a process that starts and ends at the same state. In this case, the change in the internal energy must again be zero, and therefore the energy Q added to the system must equal the work W done by the system during the cycle. That is, in a cyclic process,

$$\Delta E_{\text{int}} = 0 \quad \text{and} \quad Q = W$$

On a *PV* diagram, a cyclic process appears as a closed curve. (The processes described in Figure 20.5 are represented by open curves because the initial and final states differ.) It can be shown that **in a cyclic process, the net work done by the system per cycle equals the area enclosed by the path representing the process on a PV diagram**.

If the value of the work done by the system during some process is zero, then the change in internal energy ΔE_{int} equals the energy transfer Q into or out of the system:

$$\Delta E_{\text{int}} = Q$$

If energy enters the system, then Q is positive and the internal energy increases. For a gas, we can associate this increase in internal energy with an increase in the kinetic energy of the molecules. Conversely, if no energy transfer occurs during some process but work is done by the system, then the change in internal energy equals the negative value of the work done by the system:

$$\Delta E_{\text{int}} = -W$$

⁶ For the definition of work from our mechanics studies, the first law would be written as $\Delta E_{\text{int}} = Q + W$ because energy transfer into the system by either work or heat would increase the internal energy of the system. Because of the reversal of the definition of positive work discussed in Section 20.4, the first law appears as in Equation 20.9, with a minus sign.

⁷ Note that dQ and dW are not true differential quantities; however, dE_{int} is. Because dQ and dW are *inexact differentials*, they are often represented by the symbols dQ and dW . For further details on this point, see an advanced text on thermodynamics, such as R. P. Bauman, *Modern Thermodynamics and Statistical Mechanics*, New York, Macmillan Publishing Co., 1992.

First-law equation for infinitesimal changes

Isolated system

Cyclic process

For example, if a gas is compressed by a moving piston in an insulated cylinder, no energy is transferred by heat and the work done by the gas is negative; thus, the internal energy increases because kinetic energy is transferred from the moving piston to the gas molecules.

On a microscopic scale, no distinction exists between the result of heat and that of work. Both heat and work can produce a change in the internal energy of a system. Although the macroscopic quantities Q and W are *not* properties of a system, they are related to the change of the internal energy of a system through the first-law equation. Once we define a process, or path, we can either calculate or measure Q and W , and we can find the change in the system's internal energy using the first-law equation.

One of the important consequences of the first law of thermodynamics is that there exists a quantity known as internal energy whose value is determined by the state of the system. The internal energy function is therefore called a *state function*.

20.6 SOME APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

Before we apply the first law of thermodynamics to specific systems, it is useful for us to first define some common thermodynamic processes. An **adiabatic process** is one during which no energy enters or leaves the system by heat—that is, $Q = 0$. An adiabatic process can be achieved either by thermally insulating the system from its surroundings (as shown in Fig. 20.6b) or by performing the process rapidly, so that there is little time for energy to transfer by heat. Applying the first law of thermodynamics to an adiabatic process, we see that

$$\Delta E_{\text{int}} = -W \quad (\text{adiabatic process}) \quad (20.10)$$

From this result, we see that if a gas expands adiabatically such that W is positive, then ΔE_{int} is negative and the temperature of the gas decreases. Conversely, the temperature of a gas increases when the gas is compressed adiabatically.

Adiabatic processes are very important in engineering practice. Some common examples are the expansion of hot gases in an internal combustion engine, the liquefaction of gases in a cooling system, and the compression stroke in a diesel engine.

The process described in Figure 20.6b, called an **adiabatic free expansion**, is unique. The process is adiabatic because it takes place in an insulated container. Because the gas expands into a vacuum, it does not apply a force on a piston as was depicted in Figure 20.6a, so no work is done on or by the gas. Thus, in this adiabatic process, both $Q = 0$ and $W = 0$. As a result, $\Delta E_{\text{int}} = 0$ for this process, as we can see from the first law. That is, **the initial and final internal energies of a gas are equal in an adiabatic free expansion**. As we shall see in the next chapter, the internal energy of an ideal gas depends only on its temperature. Thus, we expect no change in temperature during an adiabatic free expansion. This prediction is in accord with the results of experiments performed at low pressures. (Experiments performed at high pressures for real gases show a slight decrease or increase in temperature after the expansion. This change is due to intermolecular interactions, which represent a deviation from the model of an ideal gas.)

A process that occurs at constant pressure is called an **isobaric process**. In such a process, the values of the heat and the work are both usually nonzero. The

In an adiabatic process, $Q = 0$.

First-law equation for an adiabatic process

In an adiabatic free expansion, $\Delta E_{\text{int}} = 0$.

In an isobaric process, P remains constant.

work done by the gas is simply

$$W = P(V_f - V_i) \quad (\text{isobaric process}) \quad (20.11)$$

where P is the constant pressure.

A process that takes place at constant volume is called an **isovolumetric process**. In such a process, the value of the work done is clearly zero because the volume does not change. Hence, from the first law we see that in an isovolumetric process, because $W = 0$,

$$\Delta E_{\text{int}} = Q \quad (\text{isovolumetric process}) \quad (20.12)$$

This expression specifies that **if energy is added by heat to a system kept at constant volume, then all of the transferred energy remains in the system as an increase of the internal energy of the system**. For example, when a can of spray paint is thrown into a fire, energy enters the system (the gas in the can) by heat through the metal walls of the can. Consequently, the temperature, and thus the pressure, in the can increases until the can possibly explodes.

A process that occurs at constant temperature is called an **isothermal process**. A plot of P versus V at constant temperature for an ideal gas yields a hyperbolic curve called an *isotherm*. The internal energy of an ideal gas is a function of temperature only. Hence, in an isothermal process involving an ideal gas, $\Delta E_{\text{int}} = 0$. For an isothermal process, then, we conclude from the first law that the energy transfer Q must be equal to the work done by the gas—that is, $Q = W$. Any energy that enters the system by heat is transferred out of the system by work; as a result, no change of the internal energy of the system occurs.

First-law equation for a constant-volume process

In an isothermal process, T remains constant.

Quick Quiz 20.4

In the last three columns of the following table, fill in the boxes with $-$, $+$, or 0 . For each situation, the system to be considered is identified.

Situation	System	Q	W	ΔE_{int}
(a) Rapidly pumping up a bicycle tire	Air in the pump			
(b) Pan of room-temperature water sitting on a hot stove	Water in the pan			
(c) Air quickly leaking out of a balloon	Air originally in balloon			

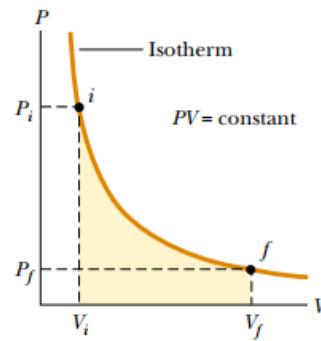


Figure 20.7 The PV diagram for an isothermal expansion of an ideal gas from an initial state to a final state. The curve is a hyperbola.

Isothermal Expansion of an Ideal Gas

Suppose that an ideal gas is allowed to expand quasi-statically at constant temperature, as described by the PV diagram shown in Figure 20.7. The curve is a hyperbola (see Appendix B, Eq. B.23), and the equation of state of an ideal gas with T constant indicates that the equation of this curve is $PV = \text{constant}$. The isothermal expansion of the gas can be achieved by placing the gas in thermal contact with an energy reservoir at the same temperature, as shown in Figure 20.6a.

Let us calculate the work done by the gas in the expansion from state i to state f . The work done by the gas is given by Equation 20.8. Because the gas is ideal and the process is quasi-static, we can use the expression $PV = nRT$ for each point on

the path. Therefore, we have

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

Because T is constant in this case, it can be removed from the integral along with n and R :

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln V \Big|_{V_i}^{V_f}$$

To evaluate the integral, we used $\int (dx/x) = \ln x$. Evaluating this at the initial and final volumes, we have

$$W = nRT \ln \left(\frac{V_f}{V_i} \right) \quad (20.13)$$

Work done by an ideal gas in an isothermal process

Numerically, this work W equals the shaded area under the PV curve shown in Figure 20.7. Because the gas expands, $V_f > V_i$, and the value for the work done by the gas is positive, as we expect. If the gas is compressed, then $V_f < V_i$, and the work done by the gas is negative.

Quick Quiz 20.5

Characterize the paths in Figure 20.8 as isobaric, isovolumetric, isothermal, or adiabatic. Note that $Q = 0$ for path B.

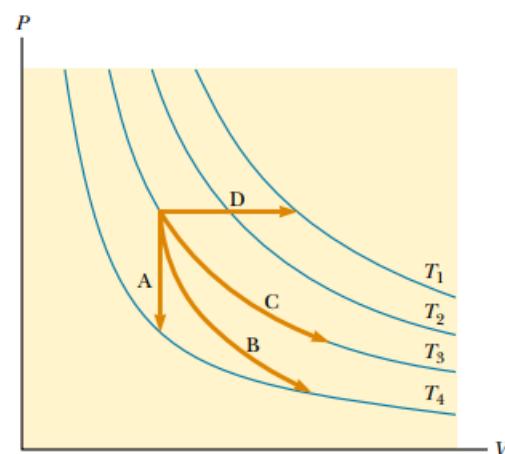


Figure 20.8 Identify the nature of paths A, B, C, and D.

EXAMPLE 20.6 An Isothermal Expansion

A 1.0-mol sample of an ideal gas is kept at 0.0°C during an expansion from 3.0 L to 10.0 L. (a) How much work is done by the gas during the expansion?

Solution Substituting the values into Equation 20.13, we have

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$W = (1.0 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(273 \text{ K}) \ln \left(\frac{10.0}{3.0} \right)$$

$$= 2.7 \times 10^3 \text{ J}$$

(b) How much energy transfer by heat occurs with the surroundings in this process?

Solution From the first law, we find that

$$\begin{aligned}\Delta E_{\text{int}} &= Q - W \\ 0 &= Q - W \\ Q &= W = 2.7 \times 10^3 \text{ J}\end{aligned}$$

(c) If the gas is returned to the original volume by means of an isobaric process, how much work is done by the gas?

Solution The work done in an isobaric process is given by Equation 20.11. We are not given the pressure, so we need to incorporate the ideal gas law:

$$\begin{aligned}W &= P(V_f - V_i) = \frac{nRT_i}{V_i} (V_f - V_i) \\ &= \frac{(1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{10.0 \times 10^{-3} \text{ m}^3} \\ &\quad \times (3.0 \times 10^{-3} \text{ m}^3 - 10.0 \times 10^{-3} \text{ m}^3) \\ &= -1.6 \times 10^3 \text{ J}\end{aligned}$$

Notice that we use the initial temperature and volume to determine the value of the constant pressure because we do not know the final temperature. The work done by the gas is negative because the gas is being compressed.

EXAMPLE 20.7 Boiling Water

Suppose 1.00 g of water vaporizes isobarically at atmospheric pressure ($1.013 \times 10^5 \text{ Pa}$). Its volume in the liquid state is $V_i = V_{\text{liquid}} = 1.00 \text{ cm}^3$, and its volume in the vapor state is $V_f = V_{\text{vapor}} = 1.671 \text{ cm}^3$. Find the work done in the expansion and the change in internal energy of the system. Ignore any mixing of the steam and the surrounding air—imagine that the steam simply pushes the surrounding air out of the way.

Solution Because the expansion takes place at constant pressure, the work done by the system in pushing away the surrounding air is, from Equation 20.11,

$$\begin{aligned}W &= P(V_f - V_i) \\ &= (1.013 \times 10^5 \text{ Pa})(1.671 \times 10^{-6} \text{ m}^3 - 1.00 \times 10^{-6} \text{ m}^3) \\ &= 169 \text{ J}\end{aligned}$$

To determine the change in internal energy, we must know the energy transfer Q needed to vaporize the water. Using Equation 20.6 and the latent heat of vaporization for water, we have

$$Q = mL_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2260 \text{ J}$$

Hence, from the first law, the change in internal energy is

$$\Delta E_{\text{int}} = Q - W = 2260 \text{ J} - 169 \text{ J} = 2090 \text{ J} = 2.09 \text{ kJ}$$

The positive value for ΔE_{int} indicates that the internal energy of the system increases. We see that most ($2090 \text{ J}/2260 \text{ J} = 93\%$) of the energy transferred to the liquid goes into increasing the internal energy of the system. Only $169 \text{ J}/2260 \text{ J} = 7\%$ leaves the system by work done by the steam on the surrounding atmosphere.

EXAMPLE 20.8 Heating a Solid

A 1.0-kg bar of copper is heated at atmospheric pressure. If its temperature increases from 20°C to 50°C , (a) what is the work done by the copper on the surrounding atmosphere?

Solution Because the process is isobaric, we can find the work done by the copper using Equation 20.11, $W = P(V_f - V_i)$. We can calculate the change in volume of the copper using Equation 19.6. Using the average linear expansion coefficient for copper given in Table 19.2, and remembering that $\beta = 3\alpha$, we obtain

$$\begin{aligned}\Delta V &= \beta V_i \Delta T \\ &= [5.1 \times 10^{-5} (\text{ }^\circ\text{C})^{-1}] (50^\circ\text{C} - 20^\circ\text{C}) V_i = 1.5 \times 10^{-3} V_i\end{aligned}$$

The volume V_i is equal to m/ρ , and Table 15.1 indicates that the density of copper is $8.92 \times 10^3 \text{ kg/m}^3$. Hence,

$$\Delta V = (1.5 \times 10^{-3}) \left(\frac{1.0 \text{ kg}}{8.92 \times 10^3 \text{ kg/m}^3} \right) = 1.7 \times 10^{-7} \text{ m}^3$$

The work done is

$$\begin{aligned}W &= P\Delta V = (1.013 \times 10^5 \text{ N/m}^2)(1.7 \times 10^{-7} \text{ m}^3) \\ &= 1.7 \times 10^{-2} \text{ J}\end{aligned}$$

(b) What quantity of energy is transferred to the copper by heat?

Solution Taking the specific heat of copper from Table 20.1 and using Equation 20.4, we find that the energy transferred by heat is

$$Q = mc\Delta T = (1.0 \text{ kg})(387 \text{ J/kg} \cdot ^\circ\text{C})(30^\circ\text{C}) = 1.2 \times 10^4 \text{ J}$$

(c) What is the increase in internal energy of the copper?

Solution From the first law of thermodynamics, we have

$$\Delta E_{\text{int}} = Q - W = 1.2 \times 10^4 \text{ J} - 1.7 \times 10^{-2} \text{ J} = 1.2 \times 10^4 \text{ J}$$

Note that almost all of the energy transferred into the system by heat goes into increasing the internal energy. The fraction of energy used to do work on the surrounding atmosphere is only about 10^{-6} ! Hence, when analyzing the thermal expansion of a solid or a liquid, the small amount of work done by the system is usually ignored.

20.7 ENERGY TRANSFER MECHANISMS

It is important to understand the rate at which energy is transferred between a system and its surroundings and the mechanisms responsible for the transfer. Therefore, let us now look at three common energy transfer mechanisms that can result in a change in internal energy of a system.

Thermal Conduction

The energy transfer process that is most clearly associated with a temperature difference is **thermal conduction**. In this process, the transfer can be represented on an atomic scale as an exchange of kinetic energy between microscopic particles—molecules, atoms, and electrons—in which less energetic particles gain energy in collisions with more energetic particles. For example, if you hold one end of a long metal bar and insert the other end into a flame, you will find that the temperature of the metal in your hand soon increases. The energy reaches your hand by means of conduction. We can understand the process of conduction by examining what is happening to the microscopic particles in the metal. Initially, before the rod is inserted into the flame, the microscopic particles are vibrating about their equilibrium positions. As the flame heats the rod, those particles near the flame begin to vibrate with greater and greater amplitudes. These particles, in turn, collide with their neighbors and transfer some of their energy in the collisions. Slowly, the amplitudes of vibration of metal atoms and electrons farther and farther from the flame increase until, eventually, those in the metal near your hand are affected. This increased vibration represents an increase in the temperature of the metal and of your potentially burned hand.

The rate of thermal conduction depends on the properties of the substance being heated. For example, it is possible to hold a piece of asbestos in a flame indefinitely. This implies that very little energy is conducted through the asbestos. In general, metals are good thermal conductors, and materials such as asbestos, cork, paper, and fiberglass are poor conductors. Gases also are poor conductors because the separation distance between the particles is so great. Metals are good thermal conductors because they contain large numbers of electrons that are relatively free to move through the metal and so can transport energy over large distances. Thus, in a good conductor, such as copper, conduction takes place both by means of the vibration of atoms and by means of the motion of free electrons.

Conduction occurs only if there is a difference in temperature between two parts of the conducting medium. Consider a slab of material of thickness Δx and cross-sectional area A . One face of the slab is at a temperature T_1 , and the other face is at a temperature $T_2 > T_1$ (Fig. 20.9). Experimentally, it is found that the



Melted snow pattern on a parking lot surface indicates the presence of underground hot water pipes used to aid snow removal. Energy from the water is conducted from the pipes to the pavement, where it causes the snow to melt.

energy Q transferred in a time Δt flows from the hotter face to the colder one. The rate $Q/\Delta t$ at which this energy flows is found to be proportional to the cross-sectional area and the temperature difference $\Delta T = T_2 - T_1$, and inversely proportional to the thickness:

$$\frac{Q}{\Delta t} \propto A \frac{\Delta T}{\Delta x}$$

It is convenient to use the symbol for power \mathcal{P} to represent the **rate of energy transfer**: $\mathcal{P} = Q/\Delta t$. Note that \mathcal{P} has units of watts when Q is in joules and Δt is in seconds. For a slab of infinitesimal thickness dx and temperature difference dT , we can write the **law of thermal conduction** as

Law of thermal conduction

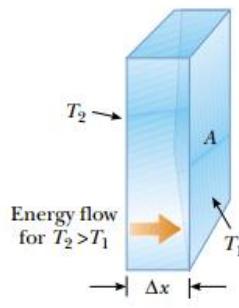


Figure 20.9 Energy transfer through a conducting slab with a cross-sectional area A and a thickness Δx . The opposite faces are at different temperatures T_1 and T_2 .

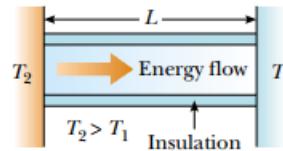


Figure 20.10 Conduction of energy through a uniform, insulated rod of length L . The opposite ends are in thermal contact with energy reservoirs at different temperatures.

where the proportionality constant k is the **thermal conductivity** of the material and $|dT/dx|$ is the **temperature gradient** (the variation of temperature with position).

Suppose that a long, uniform rod of length L is thermally insulated so that energy cannot escape by heat from its surface except at the ends, as shown in Figure 20.10. One end is in thermal contact with an energy reservoir at temperature T_1 , and the other end is in thermal contact with a reservoir at temperature $T_2 > T_1$. When a steady state has been reached, the temperature at each point along the rod is constant in time. In this case if we assume that k is not a function of temperature, the temperature gradient is the same everywhere along the rod and is

$$\left| \frac{dT}{dx} \right| = \frac{T_2 - T_1}{L}$$

Thus the rate of energy transfer by conduction through the rod is

$$\mathcal{P} = kA \frac{(T_2 - T_1)}{L} \quad (20.15)$$

Substances that are good thermal conductors have large thermal conductivity values, whereas good thermal insulators have low thermal conductivity values. Table 20.3 lists thermal conductivities for various substances. Note that metals are generally better thermal conductors than nonmetals are.

Quick Quiz 20.6

Will an ice cube wrapped in a wool blanket remain frozen for (a) a shorter length of time, (b) the same length of time, or (c) a longer length of time than an identical ice cube exposed to air at room temperature?

For a compound slab containing several materials of thicknesses L_1, L_2, \dots and thermal conductivities k_1, k_2, \dots , the rate of energy transfer through the slab at steady state is

$$\mathcal{P} = \frac{A(T_2 - T_1)}{\sum_i (L_i/k_i)} \quad (20.16)$$

TABLE 20.3 Thermal Conductivities

Substance	Thermal Conductivity (W/m·°C)
Metals (at 25°C)	
Aluminum	238
Copper	397
Gold	314
Iron	79.5
Lead	34.7
Silver	427
Nonmetals (approximate values)	
Asbestos	0.08
Concrete	0.8
Diamond	2 300
Glass	0.8
Ice	2
Rubber	0.2
Water	0.6
Wood	0.08
Gases (at 20°C)	
Air	0.023 4
Helium	0.138
Hydrogen	0.172
Nitrogen	0.023 4
Oxygen	0.023 8

where T_1 and T_2 are the temperatures of the outer surfaces (which are held constant) and the summation is over all slabs. The following example shows how this equation results from a consideration of two thicknesses of materials.

EXAMPLE 20.9 Energy Transfer Through Two Slabs

Two slabs of thickness L_1 and L_2 and thermal conductivities k_1 and k_2 are in thermal contact with each other, as shown in Figure 20.11. The temperatures of their outer surfaces are T_1 and T_2 , respectively, and $T_2 > T_1$. Determine the temperature at the interface and the rate of energy transfer by conduction through the slabs in the steady-state condition.

Solution If T is the temperature at the interface, then the rate at which energy is transferred through slab 1 is

$$(1) \quad \mathcal{P}_1 = \frac{k_1 A(T - T_1)}{L_1}$$

The rate at which energy is transferred through slab 2 is

$$(2) \quad \mathcal{P}_2 = \frac{k_2 A(T_2 - T)}{L_2}$$

When a steady state is reached, these two rates must be equal; hence,

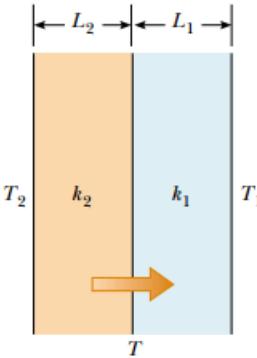


Figure 20.11 Energy transfer by conduction through two slabs in thermal contact with each other. At steady state, the rate of energy transfer through slab 1 equals the rate of energy transfer through slab 2.

$$\frac{k_1 A(T - T_1)}{L_1} = \frac{k_2 A(T_2 - T)}{L_2}$$

Solving for T gives

$$(3) \quad T = \frac{k_1 L_2 T_1 + k_2 L_1 T_2}{k_1 L_2 + k_2 L_1}$$

Substituting (3) into either (1) or (2), we obtain

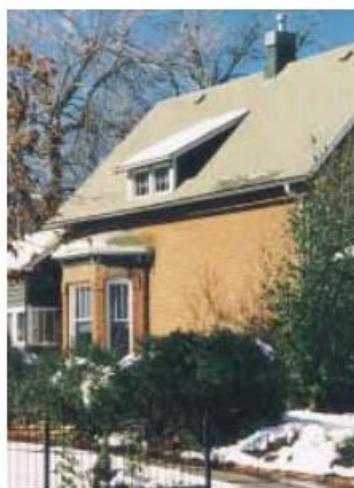
$$\mathcal{P} = \frac{A(T_2 - T_1)}{(L_1/k_1) + (L_2/k_2)}$$

Extension of this model to several slabs of materials leads to Equation 20.16.

Home Insulation

In engineering practice, the term L/k for a particular substance is referred to as the **R value** of the material. Thus, Equation 20.16 reduces to

$$\mathcal{P} = \frac{A(T_2 - T_1)}{\sum_i R_i} \quad (20.17)$$



Energy is conducted from the inside to the exterior more rapidly on the part of the roof where the snow has melted. The dormer appears to have been added and insulated. The main roof does not appear to be well insulated.

where $R_i = L_i/k_i$. The R values for a few common building materials are given in Table 20.4. In the United States, the insulating properties of materials used in buildings are usually expressed in engineering units, not SI units. Thus, in Table 20.4, measurements of R values are given as a combination of British thermal units, feet, hours, and degrees Fahrenheit.

At any vertical surface open to the air, a very thin stagnant layer of air adheres to the surface. One must consider this layer when determining the R value for a wall. The thickness of this stagnant layer on an outside wall depends on the speed of the wind. Energy loss from a house on a windy day is greater than the loss on a day when the air is calm. A representative R value for this stagnant layer of air is given in Table 20.4.

TABLE 20.4 *R* Values for Some Common Building Materials

Material	<i>R</i> value ($\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$)
Hardwood siding (1 in. thick)	0.91
Wood shingles (lapped)	0.87
Brick (4 in. thick)	4.00
Concrete block (filled cores)	1.93
Fiberglass batting (3.5 in. thick)	10.90
Fiberglass batting (6 in. thick)	18.80
Fiberglass board (1 in. thick)	4.35
Cellulose fiber (1 in. thick)	3.70
Flat glass (0.125 in. thick)	0.89
Insulating glass (0.25-in. space)	1.54
Air space (3.5 in. thick)	1.01
Stagnant air layer	0.17
Drywall (0.5 in. thick)	0.45
Sheathing (0.5 in. thick)	1.32



This thermogram of a home, made during cold weather, shows colors ranging from white and orange (areas of greatest energy loss) to blue and purple (areas of least energy loss).

EXAMPLE 20.10 The R Value of a Typical Wall

Calculate the total R value for a wall constructed as shown in Figure 20.12a. Starting outside the house (toward the front in the figure) and moving inward, the wall consists of 4-in. brick, 0.5-in. sheathing, an air space 3.5 in. thick, and 0.5-in. drywall. Do not forget the stagnant air layers inside and outside the house.

Solution Referring to Table 20.4, we find that

R_1 (outside stagnant air layer)	= 0.17 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_2 (brick)	= 4.00 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_3 (sheathing)	= 1.32 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_4 (air space)	= 1.01 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_5 (drywall)	= 0.45 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_6 (inside stagnant air layer)	= 0.17 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$
R_{total}	= 7.12 $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$

Exercise If a layer of fiberglass insulation 3.5 in. thick is placed inside the wall to replace the air space, as shown in Figure 20.12b, what is the new total R value? By what factor is the energy loss reduced?

Answer $R = 17 \text{ ft}^2 \cdot ^\circ\text{F} \cdot \text{h/Btu}$; 2.4.

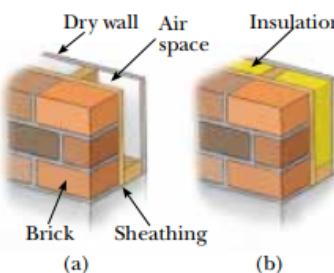


Figure 20.12 An exterior house wall containing (a) an air space and (b) insulation.

Convection

At one time or another, you probably have warmed your hands by holding them over an open flame. In this situation, the air directly above the flame is heated and expands. As a result, the density of this air decreases and the air rises. This warmed mass of air heats your hands as it flows by. **Energy transferred by the movement of a heated substance is said to have been transferred by convection.** When the movement results from differences in density, as with air around a fire, it is referred to as *natural convection*. Air flow at a beach is an example of natural convection, as is the mixing that occurs as surface water in a lake cools and sinks (see



Figure 20.13 Convection currents are set up in a room heated by a radiator.

Stefan's law

Chapter 19). When the heated substance is forced to move by a fan or pump, as in some hot-air and hot-water heating systems, the process is called *forced convection*.

If it were not for convection currents, it would be very difficult to boil water. As water is heated in a teakettle, the lower layers are warmed first. The heated water expands and rises to the top because its density is lowered. At the same time, the denser, cool water at the surface sinks to the bottom of the kettle and is heated.

The same process occurs when a room is heated by a radiator. The hot radiator warms the air in the lower regions of the room. The warm air expands and rises to the ceiling because of its lower density. The denser, cooler air from above sinks, and the continuous air current pattern shown in Figure 20.13 is established.

Radiation

The third means of energy transfer that we shall discuss is **radiation**. All objects radiate energy continuously in the form of electromagnetic waves (see Chapter 34) produced by thermal vibrations of the molecules. You are likely familiar with electromagnetic radiation in the form of the orange glow from an electric stove burner, an electric space heater, or the coils of a toaster.

The rate at which an object radiates energy is proportional to the fourth power of its absolute temperature. This is known as **Stefan's law** and is expressed in equation form as

$$\mathcal{P} = \sigma A e T^4 \quad (20.18)$$

where \mathcal{P} is the power in watts radiated by the object, σ is a constant equal to $5.6696 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$, A is the surface area of the object in square meters, e is the **emissivity** constant, and T is the surface temperature in kelvins. The value of e can vary between zero and unity, depending on the properties of the surface of the object. The emissivity is equal to the fraction of the incoming radiation that the surface absorbs.

Approximately 1 340 J of electromagnetic radiation from the Sun passes perpendicularly through each 1 m^2 at the top of the Earth's atmosphere every second. This radiation is primarily visible and infrared light accompanied by a significant amount of ultraviolet radiation. We shall study these types of radiation in detail in Chapter 34. Some of this energy is reflected back into space, and some is absorbed by the atmosphere. However, enough energy arrives at the surface of the Earth each day to supply all our energy needs on this planet hundreds of times over—if only it could be captured and used efficiently. The growth in the number of solar energy-powered houses built in this country reflects the increasing efforts being made to use this abundant energy. Radiant energy from the Sun affects our day-to-day existence in a number of ways. For example, it influences the Earth's average temperature, ocean currents, agriculture, and rain patterns.

What happens to the atmospheric temperature at night is another example of the effects of energy transfer by radiation. If there is a cloud cover above the Earth, the water vapor in the clouds absorbs part of the infrared radiation emitted by the Earth and re-emits it back to the surface. Consequently, temperature levels at the surface remain moderate. In the absence of this cloud cover, there is nothing to prevent this radiation from escaping into space; thus the temperature decreases more on a clear night than on a cloudy one.

As an object radiates energy at a rate given by Equation 20.18, it also absorbs electromagnetic radiation. If the latter process did not occur, an object would eventually radiate all its energy, and its temperature would reach absolute zero. The energy an object absorbs comes from its surroundings, which consist of other objects that radiate energy. If an object is at a temperature T and its surroundings

are at a temperature T_0 , then the net energy gained or lost each second by the object as a result of radiation is

$$\mathcal{P}_{\text{net}} = \sigma A e (T^4 - T_0^4) \quad (20.19)$$

When an object is in equilibrium with its surroundings, it radiates and absorbs energy at the same rate, and so its temperature remains constant. When an object is hotter than its surroundings, it radiates more energy than it absorbs, and its temperature decreases. An **ideal absorber** is defined as an object that absorbs all the energy incident on it, and for such a body, $e = 1$. Such an object is often referred to as a **black body**. An ideal absorber is also an ideal radiator of energy. In contrast, an object for which $e = 0$ absorbs none of the energy incident on it. Such an object reflects all the incident energy, and thus is an **ideal reflector**.

The Dewar Flask

The *Dewar flask*⁸ is a container designed to minimize energy losses by conduction, convection, and radiation. Such a container is used to store either cold or hot liquids for long periods of time. (A Thermos bottle is a common household equivalent of a Dewar flask.) The standard construction (Fig. 20.14) consists of a double-walled Pyrex glass vessel with silvered walls. The space between the walls is evacuated to minimize energy transfer by conduction and convection. The silvered surfaces minimize energy transfer by radiation because silver is a very good reflector and has very low emissivity. A further reduction in energy loss is obtained by reducing the size of the neck. Dewar flasks are commonly used to store liquid nitrogen (boiling point: 77 K) and liquid oxygen (boiling point: 90 K).

To confine liquid helium (boiling point: 4.2 K), which has a very low heat of vaporization, it is often necessary to use a double Dewar system in which the Dewar flask containing the liquid is surrounded by a second Dewar flask. The space between the two flasks is filled with liquid nitrogen.

Newer designs of storage containers use “super insulation” that consists of many layers of reflecting material separated by fiberglass. All of this is in a vacuum, and no liquid nitrogen is needed with this design.

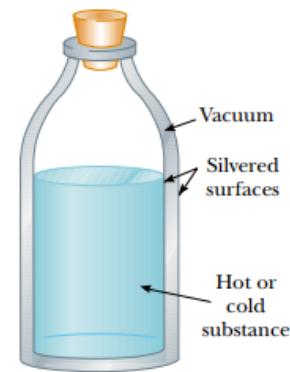


Figure 20.14 A cross-sectional view of a Dewar flask, which is used to store hot or cold substances.

EXAMPLE 20.11 Who Turned Down the Thermostat?

A student is trying to decide what to wear. The surroundings (his bedroom) are at 20.0°C. If the skin temperature of the unclothed student is 35°C, what is the net energy loss from his body in 10.0 min by radiation? Assume that the emissivity of skin is 0.900 and that the surface area of the student is 1.50 m².

Solution Using Equation 20.19, we find that the net rate of energy loss from the skin is

$$\begin{aligned} \mathcal{P}_{\text{net}} &= \sigma A e (T^4 - T_0^4) \\ &= (5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4) (1.50 \text{ m}^2) \\ &\times (0.900) [(308 \text{ K})^4 - (293 \text{ K})^4] = 125 \text{ W} \end{aligned}$$

(Why is the temperature given in kelvins?) At this rate, the total energy lost by the skin in 10 min is

$$Q = \mathcal{P}_{\text{net}} \times \Delta t = (125 \text{ W})(600 \text{ s}) = 7.5 \times 10^4 \text{ J}$$

Note that the energy radiated by the student is roughly equivalent to that produced by two 60-W light bulbs!

⁸ Invented by Sir James Dewar (1842–1923).

SUMMARY

Internal energy is all of a system's energy that is associated with the system's microscopic components. Internal energy includes kinetic energy of translation, rotation, and vibration of molecules, potential energy within molecules, and potential energy between molecules.

Heat is the transfer of energy across the boundary of a system resulting from a temperature difference between the system and its surroundings. We use the symbol Q for the amount of energy transferred by this process.

The **calorie** is the amount of energy necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C. The **mechanical equivalent of heat** is 1 cal = 4.186 J.

The **heat capacity** C of any sample is the amount of energy needed to raise the temperature of the sample by 1°C. The energy Q required to change the temperature of a mass m of a substance by an amount ΔT is

$$Q = mc\Delta T \quad (20.4)$$

where c is the **specific heat** of the substance.

The energy required to change the phase of a pure substance of mass m is

$$Q = mL \quad (20.6)$$

where L is the **latent heat** of the substance and depends on the nature of the phase change and the properties of the substance.

The **work done** by a gas as its volume changes from some initial value V_i to some final value V_f is

$$W = \int_{V_i}^{V_f} P dV \quad (20.8)$$

where P is the pressure, which may vary during the process. In order to evaluate W , the process must be fully specified—that is, P and V must be known during each step. In other words, the work done depends on the path taken between the initial and final states.

The **first law of thermodynamics** states that when a system undergoes a change from one state to another, the change in its internal energy is

$$\Delta E_{\text{int}} = Q - W \quad (20.9)$$

where Q is the energy transferred into the system by heat and W is the work done by the system. Although Q and W both depend on the path taken from the initial state to the final state, the quantity ΔE_{int} is path-independent. This central equation is a statement of conservation of energy that includes changes in internal energy.

In a **cyclic process** (one that originates and terminates at the same state), $\Delta E_{\text{int}} = 0$ and, therefore, $Q = W$. That is, the energy transferred into the system by heat equals the work done by the system during the process.

In an **adiabatic process**, no energy is transferred by heat between the system and its surroundings ($Q = 0$). In this case, the first law gives $\Delta E_{\text{int}} = -W$. That is, the internal energy changes as a consequence of work being done by the system. In the **adiabatic free expansion** of a gas, $Q = 0$ and $W = 0$; thus, $\Delta E_{\text{int}} = 0$. That is, the internal energy of the gas does not change in such a process.

An **isobaric process** is one that occurs at constant pressure. The work done in such a process is $W = P(V_f - V_i)$.

An **isovolumetric process** is one that occurs at constant volume. No work is done in such a process, so $\Delta E_{\text{int}} = Q$.

An **isothermal process** is one that occurs at constant temperature. The work done by an ideal gas during an isothermal process is

$$W = nRT \ln\left(\frac{V_f}{V_i}\right) \quad (20.13)$$

Energy may be transferred by work, which we addressed in Chapter 7, and by conduction, convection, or radiation. **Conduction** can be viewed as an exchange of kinetic energy between colliding molecules or electrons. The rate at which energy flows by conduction through a slab of area A is

$$\mathcal{P} = kA \left| \frac{dT}{dx} \right| \quad (20.14)$$

where k is the **thermal conductivity** of the material from which the slab is made and $|dT/dx|$ is the **temperature gradient**. This equation can be used in many situations in which the rate of transfer of energy through materials is important.

In **convection**, a heated substance moves from one place to another.

All bodies emit **radiation** in the form of electromagnetic waves at the rate

$$\mathcal{P} = \sigma A e T^4 \quad (20.18)$$

A body that is hotter than its surroundings radiates more energy than it absorbs, whereas a body that is cooler than its surroundings absorbs more energy than it radiates.