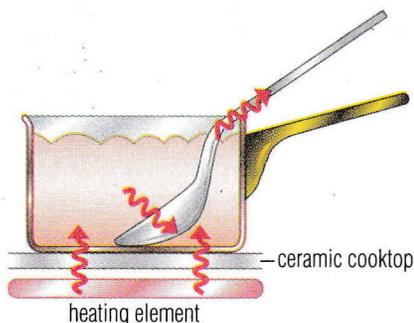
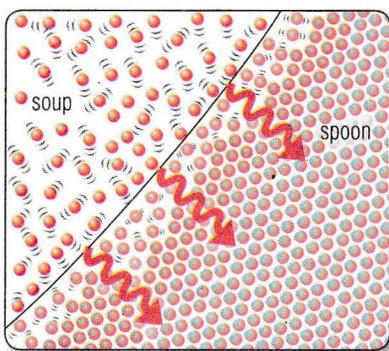


Using the relationship found in Question 10c, the nineteenth-century French physicist Pierre Louis Dulong and chemist Alexis Thérèse Petit discovered that the specific heats of most crystalline solids can be found from the equation  $c_{sp} = 3R/M$ . This relationship is called the *Dulong-Petit Law*.



15-7a Conduction



15-7b Thermal conduction takes place at the molecular level.

Substances that contain free electrons, such as metals, generally are good conductors of heat. Substances that do not contain free electrons, such as most solid ionic and molecular compounds, are generally poor thermal conductors (good insulators).

8. Compare the heat loss required to condense 1.0 g of steam to water at 100.0 °C and the heat lost to cool 1.0 g of water at 100.0 °C by 1.0 °C. The specific heat of water at 100.0 °C is 4.22 J/g·°C. Which, gram for gram, is more damaging to the unprotected skin—water at its boiling point or condensing steam?
- DM9. Construct a scatter plot of specific heat versus molar mass for the pure metals listed in Table 15-2 on page 344. Then construct a best-fit curve through the data points. What kind of relationship, if any, exists?
- DM10. a. Construct a scatter plot of the metals' specific heats versus the reciprocals of their molar masses. Construct a best-fit curve through the data points. If possible, force the  $y$ -intercept to pass through zero. Display the trendline's equation and the  $r^2$  value of the trendline fit. What relationship exists between the variables in this plot? Is this expected? Explain.
- b. What are the units associated with the slope of the trendline found in Part a? What property of metals does this combination of units describe?
- c. Divide the slope of the trendline and its units found in Part b by the universal gas constant  $R = 8.315 \text{ J/(K}\cdot\text{mol)}$  and round the result to 1 SD. The resulting number is called the *dimensionless heat capacity* ( $C^*$ ), which is a property of nearly all metals.

## 15C MECHANISMS FOR HEAT TRANSFER

There are three mechanisms for the transfer of thermal energy from one system to another: conduction, convection, and radiation.

### 15.13 Conduction

Hold a stainless steel spoon in a pot of boiling soup. You will begin to feel the spoon handle growing warm. Eventually, you will either have to drop the spoon or withdraw it from the soup to prevent being burned. This is an example of **conduction**. The hot soup particles accelerate the motion of the metal atoms in the bowl of the spoon. These rapidly vibrating molecules collide with the adjacent, slower-moving atoms within the metal, transmitting kinetic energy to the atoms farther up the handle. The rapid motion and associated kinetic energy is transmitted from atom to atom along the handle to your fingers.

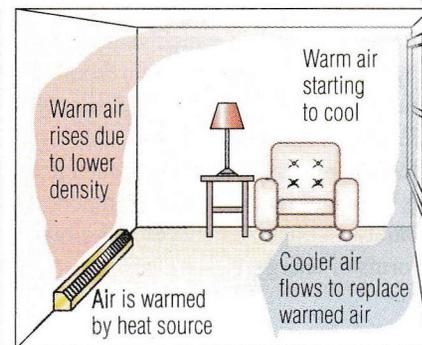
Some materials conduct thermal energy easily, while others act as thermal insulators. For example, if you had used a wooden spoon to stir the soup, you could have held onto the spoon indefinitely. To understand the difference, we must return to the atomic model. Recall that the major subatomic particles are protons, neutrons, and electrons. The protons and neutrons are in the nucleus, while the electrons surround the nucleus. Some substances hold their electrons firmly. Other substances, especially metals, hold some of their valence electrons so loosely that it takes little energy to remove them. In fact, some electrons are so independent of their nuclei that they are called *free electrons*. These free electrons readily transmit kinetic energy between atoms throughout a substance. Substances with free electrons are therefore good thermal conductors. Substances lacking free electrons do not conduct thermal energy well, so they are thermal insulators.

### 15.14 Convection

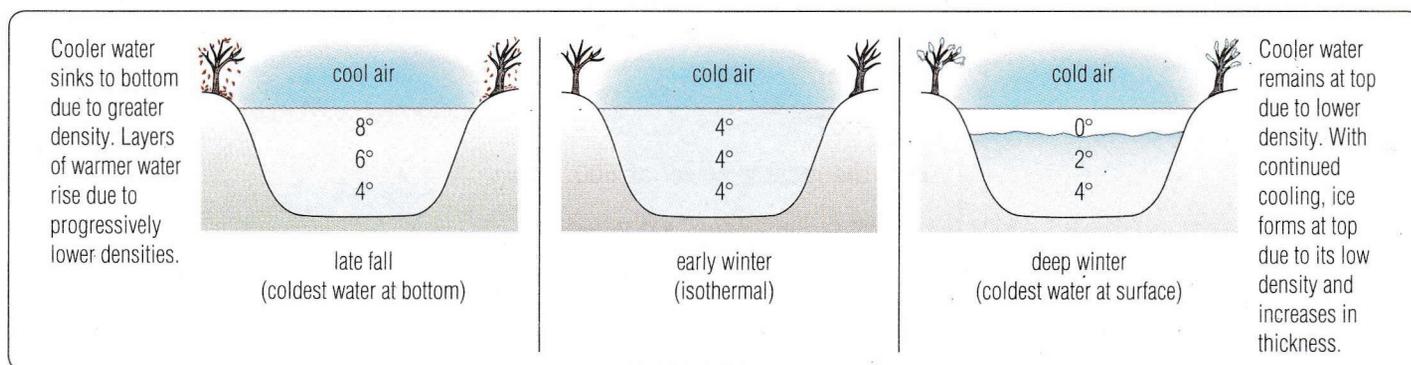
Air is a poor thermal conductor. However, a hot water radiator surrounded by air can heat an entire room. This is possible because air transports thermal energy by

convection. **Convection** moves thermal energy by physically moving material that has thermal energy. Gravity is the main force that causes this motion. The hot radiator transmits heat to the air mass directly around it through conduction and *radiation* (see Subsection 15.15). This warmer air expands, becoming less dense, and is displaced upward by the cooler, denser air around it. The cool air is soon heated and replaced with cooler air from the room. The cycle continues, setting up a convection current of rising and falling air in the room. Eventually, the warmed air cools, falls, and returns to the radiator to be heated again. In order to make most efficient use of this convection process, a well-designed house has its convective heat sources near the floor.

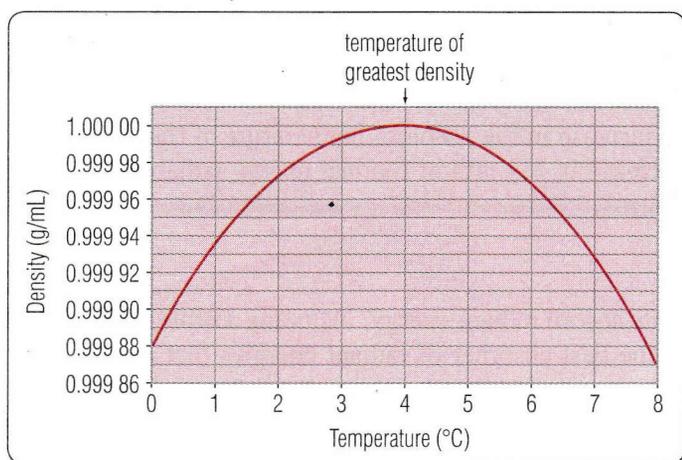
Water, as well as air, transmits thermal energy by convection. In bodies of water, the cooling process is especially interesting. Water is densest at 4 °C. A body of water—a lake, for example—cools from the top. When the top layer cools, it sinks and is replaced by warmer water from deeper in the lake. Since water at 4 °C is densest, no water can cool to below 4 °C until all the water in the lake has reached that temperature. When all the water is 4 °C, the surface layer cools to lower temperatures, and the lake freezes over from the top down. Since ice is less dense than liquid water at the same temperature, it floats. The net effect of this phenomenon is that freezing is delayed throughout the depth of the lake as long as possible. In deep lakes, even after the surface freezes, some unfrozen water exists under the ice all winter. This phenomenon, ordained by the Creator, preserves aquatic life through the winter months.



15-8 Convection



15-9a Surface-to-bottom temperature profile in a freshwater lake as it cools in winter



15-9b Density of water near its freezing point

Radiant energy, of which visible light is one form, is different from thermal energy, which can exist only in matter. Radiant energy is transformed into thermal energy when it is absorbed into matter. It is important to distinguish between these two forms of energy.

Josef Stefan (1835–93) was an Austrian physicist known for discovering the relationship between the radiant energy of an object and the fourth power of its absolute temperature (Stefan's law).

## 15.15 Radiation

The earth is warmed by thermal energy from the sun. However, since the density of the particles between the sun and the earth is so low, the sun's thermal energy cannot be transmitted by conduction or convection. The sun's electromagnetic energy reaches the earth by **radiation**, which is converted to thermal energy when it is absorbed by matter. The sun is not the only object that transfers thermal energy by radiation. Every object with a temperature greater than absolute zero transfers thermal energy in this way. "Cold" objects emit less radiation than "hot" objects. **Stefan's law** gives the correspondence between absolute temperature ( $T$ ) and the power of its radiant energy ( $S$ ),

$$S = \sigma T^4, \quad (15.5)$$

where  $\sigma$  is a proportionality constant, called the **Stefan-Boltzmann constant** ( $\sigma = 5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$ ), and  $T$  is the Kelvin temperature of the object's surface. Because  $S$  is proportional to temperature to the fourth power, an object radiates sixteen times as much energy at a given absolute temperature as it radiates at half that temperature.

### EXAMPLE 15-7

#### Thermal Energy and Radiation: Stefan's Law

What is the ratio of the radiant power of an iron bar at 600. K to its radiant power at 200. K?

**Solution:**

$$S = \sigma T^4$$

Find the radiant power at 600. K.

$$S_{600 \text{ K}} = \sigma(600. \text{ K})^4 \text{ W}/\text{m}^2$$

Find the radiant power at 200. K.

$$S_{200 \text{ K}} = \sigma(200. \text{ K})^4 \text{ W}/\text{m}^2$$

Find the ratio of the radiant energies.

$$\frac{S_{600 \text{ K}}}{S_{200 \text{ K}}} = \frac{\sigma(600. \text{ K})^4}{\sigma(200. \text{ K})^4} = \frac{\alpha(3)^4 \cdot \cancel{(200. \text{ K})^4}}{\alpha \cancel{(200. \text{ K})^4}}$$

$$\frac{S_{600 \text{ K}}}{S_{200 \text{ K}}} = (3)^4 = 81$$

A threefold increase in the absolute temperature of the bar yields an eighty-one-fold increase in the rate of thermal energy radiated.

Black objects absorb radiant energy, including visible light. Therefore, a black object is also the best absorber of radiant energies that are the most easily converted to thermal energy. (That is why solar collectors on rooftops are painted black.) For similar reasons, a black object is the best radiator. Since lighter objects do not absorb energy as easily, there is less energy to re-radiate. A perfect (ideal) radiator and absorber is called a **blackbody**.

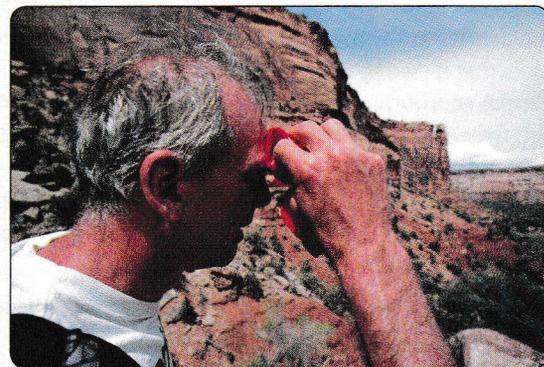
# Thermodynamic Laws

# 16

## DOMINION SCIENCE PROBLEM

### Miserable Heat

As the sun and the thermometer readings rise in the summer, we get more and more uncomfortable. But the hotter temperatures affect more than just our comfort. Hot air holds more humidity, and both of these factors can affect commerce and human health. Agriculture, meat processing, photography, restaurants, textiles, computers, manufacturing, libraries, and many industries rely on cooler temperatures and low humidity to function efficiently and to protect their customers and products. Diseases surface and spread faster in hot, humid weather. In recent decades, intense heat waves in the summertime have killed thousands of people in the United States. How can technology help us cope with this continuing problem?



16-1 Sometimes summer temperatures become miserably high.

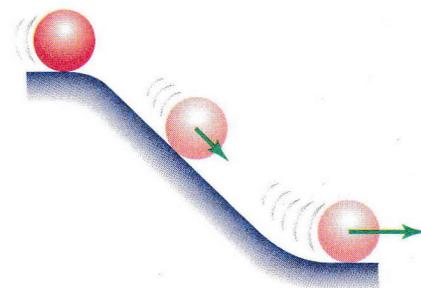
## 16A THE ZEROth AND FIRST LAWS

### 16.1 Introduction

So far you have studied two forms of energy—mechanical and thermal. Mechanical energy is a property of tangible objects. Two types of mechanical energy are potential energy and kinetic energy. Potential energy, one result of work, can be changed to kinetic energy—energy of motion. A motionless ball poised at the top of an inclined plane has potential energy. As the ball rolls down the inclined plane, it gains kinetic energy as it loses potential energy. When the ball reaches the bottom of the plane, the last of its gravitational potential energy disappears and it rolls along the flat surface with only kinetic energy. Total mechanical energy ( $E$ ) is the sum of the kinetic and potential energies due to the motion and position of physical objects.

Once the appropriate reference points for determining the system's motion and position are established, the system's total mechanical energy can be known. Subsequently, only the changes of the system's total mechanical energy ( $\Delta E$ ) are important from a physics perspective.

Thermal energy is due to the rapid, random motion of the molecular, atomic, and subatomic particles of matter. Like mechanical energy, thermal energy can be subdivided into potential energy and kinetic energy. The particles of a substance are constantly moving; therefore, they have kinetic energy. Their average kinetic energy is proportional to the temperature of the substance.



16-2 Mechanical potential energy can change to mechanical kinetic energy.

The innumerable particles of a substance also have potential energies, but it is extremely complicated to determine the reference points to establish these energies. The sum total of the particle kinetic and potential energies is called **internal energy ( $U$ )**. As with total mechanical energy, once the internal energy of a system is established or assumed for a given state of the system, only the change in internal energy becomes important. The changes of internal energy ( $\Delta U$ ) are usually much easier to calculate than the internal energy states at the beginning and end of a process.

## 16.2 The Zeroth Law of Thermodynamics

Some materials conduct heat well, while other materials are good insulators. An ideal insulating wall through which no thermal energy can pass is called an *adiabatic* boundary. An ideal conductor of thermal energy is called a **diathermic** material. Although no completely adiabatic or diathermic materials exist, the concepts are useful for simplifying discussions.

As you have probably noticed, when you place a hot object in contact with a cold object, the cold object becomes hotter, and the hot object becomes cooler. In time, the two objects reach the same temperature. That is, they reach a state of **thermal equilibrium**. Thermal energy has flowed from the hot object to the cold object. As you learned in Chapter 15, the flow of thermal energy is called *heat*.

Figure 16-3 depicts what is called the **zeroth law of thermodynamics**. This law states that two systems that are in thermal equilibrium with a third system must be in thermal equilibrium with each other. The law received its name because it is more basic than either the first or second law but was formulated after the other laws already had been named.

In (a), system A is separated from system B by an adiabatic barrier, and both are linked to system C by diathermic barriers. Although A and B cannot exchange thermal energy with each other, both can exchange thermal energy with C. In (b) the barriers have been switched so that A and B can exchange thermal energy with each other, but C is thermally insulated from both A and B. According to the zeroth law, if no net energy exchange occurs in (a), then none will occur in (b).

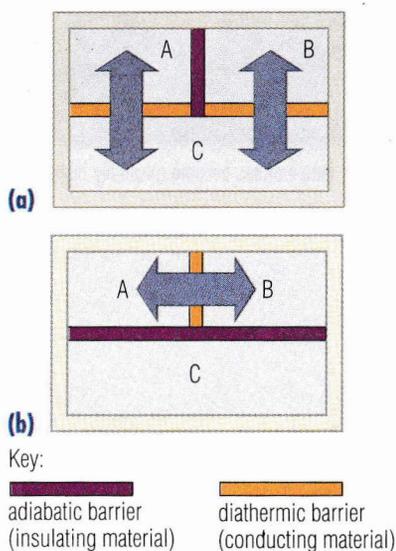
The principle becomes still more understandable when you view it in terms of temperature. In (a), systems A and B are at the same temperature as C. (You must, of course, assume that each system is itself at a uniform temperature.) System A must therefore be at the same temperature as system B. When the adiabatic barrier between them is replaced with a diathermic barrier, neither system will warm (that is, transfer thermal energy to) the other. Moreover, since all three systems are at the same temperature, no thermal energy can flow in any direction, regardless of how the barriers are placed.

## 16.3 The General Law of Conservation of Energy— The First Law

Before progressing further, we need to gather together what we know about energy transfers in order to establish a fundamental or general energy conservation principle. Energy can be added to a system by either of two processes: (a) mechanical work ( $W_{ncf}$ ) through the application of external nonconservative forces or (b) heat transfer ( $Q$ ) through temperature differences with the system's surroundings. The energy transferred to the system by these means is seen as a change of the internal energy of the system ( $\Delta U$ ) or as a change in the system's total mechanical energy ( $\Delta E$ ) or both. The *general energy conservation law* can be written

$$Q + W_{ncf} = \Delta U + \Delta E \quad (16.1)$$

The **zeroth law of thermodynamics** states that if two systems are in thermal equilibrium with a third, then they are in thermal equilibrium with each other.



**16-3** Three systems in thermal equilibrium demonstrating the zeroth law of thermodynamics. (a) If systems A and B are individually in thermal equilibrium with system C, then (b) they must be in thermal equilibrium with each other.

The symbol  $W_{ncf}$  represents the mechanical work done on a thermodynamic system by external nonconservative forces. This symbol is different from that used in earlier chapters because in studying thermodynamics, it is usually more important to analyze the work a system does on its surroundings ( $W$ ).

When we discussed basic mechanics, we assumed that no heat transfers took place and no changes of internal energy occurred ( $\Delta U = 0$  J). When discussing basic thermodynamics principles, we will make the assumption that the total mechanical energy of the system is constant ( $\Delta E = 0$  J). Therefore, the only forces doing work on the system are nonconservative forces. Equation 16.1 can then be rewritten as

$$Q + W_{\text{ncf}} = \Delta U. \quad (16.2)$$

Rather than being concerned about the work done on a system, as we were in our study of mechanics, it is more useful in thermodynamics to evaluate the effects of a system on its **surroundings**; therefore the work notation in Equation 16.2 needs to be modified slightly. Recall from our study of Newton's laws that every force on a system is paired with an opposite force acting on another system. It follows that if a system's surroundings do mechanical work on it through the application of a nonconservative force, then the system must also do work on its surroundings via the reaction force. The work by the system on its surroundings is therefore the negative of the work on the system ( $W_{\text{ncf}} = -W$ ). Equation 16.2 then becomes

$$Q - W = \Delta U, \text{ or}$$

$$Q = \Delta U + W. \quad (16.3)$$

Equation 16.3 is the mathematical statement of the **first law of thermodynamics**. The first law extends the principle of the conservation of total mechanical energy to internal energy as well. We will investigate the applications and limitations of the first law in the following discussion of thermodynamic processes.

## 16.4 Heat Engines

Thermal energy can be changed into mechanical energy. An engine called a **heat engine** can do mechanical work by absorbing and discharging heat. The simplest "machine" that converts thermal energy to work is an expanding gas. For a gas to expand usefully, it must be confined in an expandable container. One such container is a cylinder fitted with a gas-tight piston. Assuming that the piston is massless and frictionless simplifies calculations. As the gas expands, it is no longer in thermal equilibrium. It heats or cools unevenly. To avoid this problem, we allow the gas to expand in extremely minute steps, letting it return to thermal equilibrium between steps. Consequently, the gas expands without ever being far from thermal equilibrium. A process that proceeds in this way is called a *quasi-static process*.

For quasi-static processes, the gas pressure inside the cylinder is at all times in equilibrium with the external pressure. When the gas is compressed from a volume  $V_1$  to a volume  $V_2$  by an external pressure  $P$ , work is done on the gas. (You can verify that energy is added to the gas because it warms when it is compressed.)

The simplified formula for work is

$$W = Fd. \quad (16.4)$$

Pressure is force per unit area, so force exerted by the gas equals pressure times the cross-sectional area of the piston:

$$F = P_{\text{gas}}A$$

Substituting for force in Equation 16.4,

$$W = (P_{\text{gas}}A)d.$$

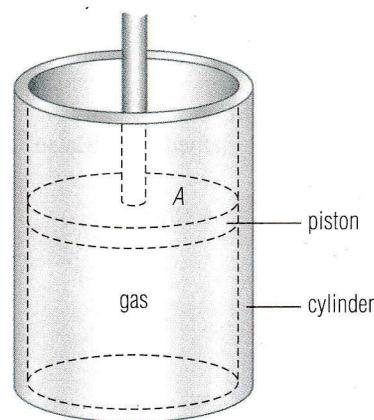
The **surroundings** of a system are everything in the universe that is outside the system's boundaries.

The work done on a thermodynamic system is the negative of the work done on the system's surroundings. This is a direct consequence of Newton's third law of motion: every force is balanced by an equal but opposite force on a different system.

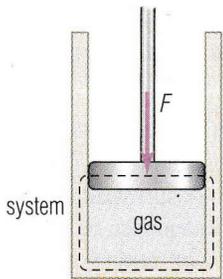
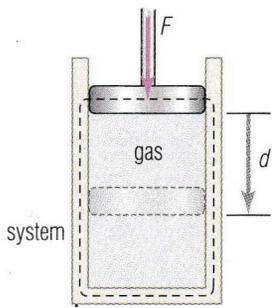
$$W = -W_{\text{ncf}}$$

The **first law of thermodynamics** states that the heat transferred to or from a system is equal to the sum of the change of the system's internal energy and the work the system does on its surroundings.

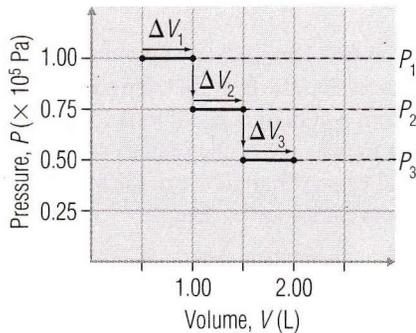
$$Q = \Delta U + W$$



16-4 A simple heat engine



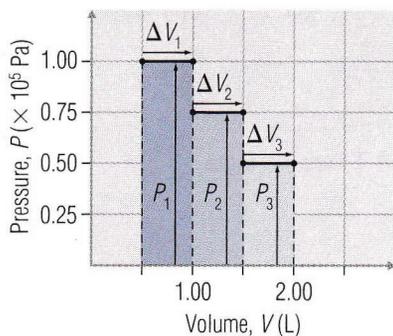
16-5 A gas is compressed by a pressure,  $P$ .



16-6 A  $P$ - $V$  diagram of an expanding gas in a quasi-static process

Recall that the SI pressure unit is the **pascal (Pa)**, named after Blaise Pascal

$$1 \text{ Pa} = 1 \text{ N/m}^2$$



16-7 An area under a curve on a  $P$ - $V$  diagram indicates the work done by a process between the two states represented by the endpoints of the curve.

But the cross-sectional area of the cylinder times the displacement distance of the piston is just the volume change ( $\Delta V$ ) of the gas in the cylinder, so the work done by the gas as it is compressed by a constant external pressure is

$$W = P_{\text{gas}} \Delta V.$$

The change of volume when a gas is compressed is negative. Therefore, the work done by the gas *on its surroundings* (see Subsection 16.3) is negative when it is compressed. This result makes sense, since the surroundings are losing energy and the gas is gaining energy.

When the gas expands against the applied pressure, the gas does *positive* work on its surroundings. (A gas that does work by expanding loses thermal energy, so it cools.) In general, for expansion or contraction against a constant pressure, the work done *by* the gas is

$$W = P(V_2 - V_1).$$

The pressure against the gas is not always constant. When the pressure varies during an expansion or a contraction, the work is the sum of the work done in each step. In a quasi-static process, you can assume that for a small volume change the pressure is constant, so

$$W_{\text{total}} = (P\Delta V)_1 + (P\Delta V)_2 + (P\Delta V)_3 + \dots + (P\Delta V)_n. \quad (16.5)$$

## 16.5 $P$ - $V$ Diagrams

Equation 16.5 becomes easier to solve if you plot the pressure versus the volume on a graph called a  **$P$ - $V$  diagram**. For instance, in Figure 16-6 the gas is originally at 0.50 L and  $1.00 \times 10^5$  Pa. It expands to 1.00 L ( $\Delta V = 0.50$  L) at  $1.00 \times 10^5$  Pa. Then, while the volume remains constant, the pressure changes to  $0.75 \times 10^5$  Pa. The gas expands to 1.50 L at  $0.75 \times 10^5$  Pa. The pressure is again lowered to  $0.50 \times 10^5$  Pa. Finally, the gas expands to 2.00 L. The total work done by the gas is as follows:

$$W_{\text{total}} = (P\Delta V)_1 + (P\Delta V)_2 + (P\Delta V)_3$$

$$W_{\text{total}} = (1.00 \times 10^5 \text{ Pa})(+0.50 \text{ L}) + (0.75 \times 10^5 \text{ Pa})(+0.50 \text{ L}) + (0.50 \times 10^5 \text{ Pa})(+0.50 \text{ L})$$

$$W_{\text{total}} = 0.50 \times 10^5 \text{ Pa}\cdot\text{L} + 0.375 \times 10^5 \text{ Pa}\cdot\text{L} + 0.25 \times 10^5 \text{ Pa}\cdot\text{L}$$

$$W_{\text{total}} = 1.125 \times 10^5 \text{ Pa}\cdot\text{L}$$

$$W_{\text{total}} \cong 1.13 \times 10^5 \text{ Pa}\cdot\text{L}$$

Since  $1 \text{ Pa} = 1 \text{ N/m}^2$ , and  $1 \text{ L} = 0.001 \text{ m}^3$ ,

$$\frac{1.13 \times 10^5 \text{ N/m}^2 \times 0.001 \text{ m}^3}{1 \text{ N}} = 113 \text{ N}\cdot\text{m} = 113 \text{ J}.$$

Notice that each term in the work equation is equal to the block of the area under the corresponding step of the graph of the quasi-static process on the  $P$ - $V$  diagram (Figure 16-7). That is, the area under the curve representing the process on a  $P$ - $V$  diagram is equal to the absolute value of the work done by the gas during the process. This result is true for any confined gas process (expansion or contraction). The sign of the work depends on whether the gas gains or loses

energy. If the gas expands, it does work on its surroundings, so the sign is positive. If the gas contracts or is compressed, the surroundings do work on it, so the sign is negative.

### EXAMPLE 16-1

#### Work of an Expanding Gas

A gas originally at  $1.00 \times 10^5$  Pa and 1.00 L expands until its volume is 2.00 L and its pressure is  $0.50 \times 10^5$  Pa. How much work is done by the gas?

#### Solution:

The gas in the cylinder is the system. Work is determined relative to the system's surroundings.

The work by the gas is related to the numerical value of the entire shaded area of Figure 16-8. The easiest way to find the area is to calculate the area of the triangle above the dotted line and add it to the area of the rectangle below the dotted line.

The area of the triangle is

$$A_{\Delta} = \frac{1}{2}bh, \text{ where } b = |\Delta V| = +1.00 \text{ L and } h = |\Delta P| = +0.50 \times 10^5 \text{ Pa}$$

$$A_{\Delta} = \frac{1}{2}(1.00 \text{ L})(0.50 \times 10^5 \text{ Pa})$$

$$A_{\Delta} = 0.25 \times 10^5 \text{ Pa}\cdot\text{L} = 25 \text{ N}\cdot\text{m}$$

$$A_{\Delta} = 25 \text{ J.}$$

The rectangle's area is

$$A_{\square} = bh, \text{ where } b = |\Delta V| = +1.00 \text{ L and } h = P_2 = 0.50 \times 10^5 \text{ Pa}$$

$$A_{\square} = (1.00 \text{ L})(0.50 \times 10^5 \text{ Pa})$$

$$A_{\square} = 0.50 \times 10^5 \text{ Pa}\cdot\text{L} = 50. \text{ N}\cdot\text{m}$$

$$A_{\square} = 50. \text{ J.}$$

The total area is then

$$A_{\text{total}} = A_{\Delta} + A_{\square}$$

$$A_{\text{total}} = 25 \text{ J} + 50. \text{ J}$$

$$A_{\text{total}} = 75 \text{ J.}$$

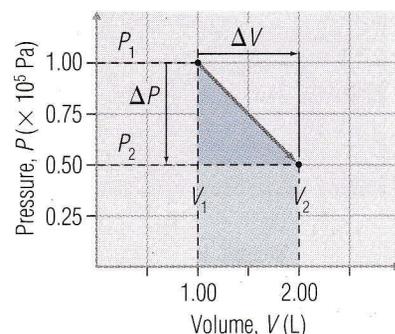
The total area under the curve equals the absolute value of the work done, so

$$|W| = 75 \text{ J.}$$

Since the gas expanded, the work done by the gas is positive.

$$W = +75 \text{ J}$$

The gas does about 75 J of work on its surroundings as it expands.

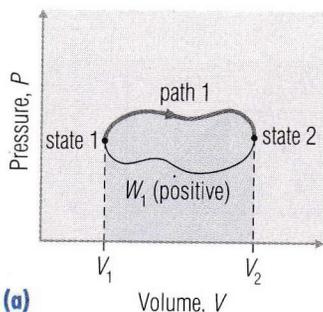


**16-8** A graph showing the work done by an expanding gas for Example 16-1

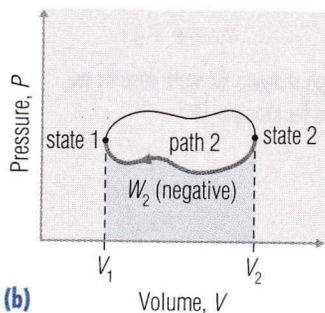
The mathematical technique we use in Example 16-1 illustrates the great importance of *integral calculus* in physics. Since the pressure and volume shown in Figure 16-8 change in a linear (straight-line) fashion, ordinary algebra lets us calculate the area of the shaded space. However, many real-world processes aren't perfectly linear (see Figure 16-10). In order to find the area under nonlinear curves, we must either be satisfied with algebraic approximations or use the techniques of integral calculus. The development of calculus is what made classical physics possible.

### Problem-Solving Strategy 16.1

If a cycle proceeds clockwise on a  $P$ - $V$  diagram, then the system is a heat engine doing positive work. If the cycle proceeds counterclockwise, then work is being done on the system (as in a refrigerator).



(a)



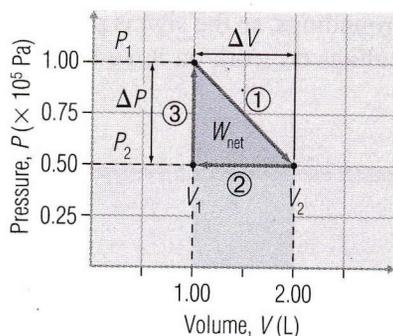
(b)

**16-10** (a) The expanding gas does positive work while expanding from  $V_1$  to  $V_2$ . (b) The gas does negative work as it is compressed from  $V_2$  to  $V_1$ .

### Problem-Solving Strategy 16.2

If a process moves from left to right along any path on a  $P$ - $V$  diagram, then the system is doing work. If the process moves from right to left along any path, then work is being done on the system.

One state variable that you are familiar with is the balance of your bank account. It doesn't really matter to you what form of money (coins, bills, checks, ATM transfers, etc.) adds value to the account balance, as long as your balance increases. The state of your account is the cash balance that it has at any given moment.



**16-9** Work done by a gas that expands in a cycle

$$W_1 = 7.5 \times 10^4 \text{ Pa}\cdot\text{L} = +75 \text{ J}$$

For the second step, where the volume is reduced at constant pressure, the area under curve ② is

$$A_2 = (1.00 \text{ L})(5.0 \times 10^4 \text{ Pa})$$

$$A_2 = 5.0 \times 10^4 \text{ Pa}\cdot\text{L}$$

$$A_2 = 50. \text{ J.}$$

Since the gas is compressed (contracts), the work by the gas is negative.

$$W_2 = -50. \text{ J}$$

For the third step, ③, the volume is constant; therefore, no work is done.

$$W_3 = 0 \text{ J}$$

The total work for the cycle is

$$W_{\text{total}} = W_1 + W_2 + W_3$$

$$W_{\text{total}} = (+75 \text{ J}) + (-50 \text{ J}) + 0 \text{ J}$$

$$W_{\text{total}} = +25 \text{ J.}$$

Notice that the net work by the gas is the same as the area enclosed by the path of the cycle (the triangular area in Example 16-1). This is a general principle: *For a cycle, the absolute value of the total work done is equal to the area enclosed by the path of the cycle on a  $P$ - $V$  diagram.* A cycle that has a clockwise path on the diagram does positive work. Such a system is a heat engine. A cycle that has a counterclockwise path on the diagram does negative work. An example of a system that follows such a path is a refrigerator.

The work done by a gas, unlike work done against gravity, *depends on the path of the process on a  $P$ - $V$  diagram.* The thermal energy added to the gas also depends on the expansion path. Experiments show, however, that for systems whose total mechanical energy is constant, the quantity  $(Q - W)$  is the same regardless of the thermodynamic path between two states. This quantity is the change in the internal energy of the gas,  $\Delta U$ , according to the first law of thermodynamics. Since the change of internal energy does not depend on the way the energy is added (the path between two thermodynamic states), the internal energy is called path-independent. Path-independent quantities are called **state variables** since they depend only on the thermodynamic state of the gas at a given time and not on how it got there. Internal energy, temperature, pressure, and volume are some state variables. They define the state of a gas.

## 16.6 Expansion Cycles

If a gas is to be useful as a machine, it must be able to expand repeatedly, following a cycle. When the gas from the previous example returns to its original state, as Figure 16-9 shows, it is ready to expand again. For the first step in the cycle, ①, the gas expands as it did in the example, and the same amount of work is done by the gas on its surroundings:

## 16.7 Thermodynamic Systems

We have mentioned in our discussion an entity called a **thermodynamic system**. As you know, a system is a piece of the universe isolated, at least mentally, for study. Other examples of possible thermodynamic systems are a calorimeter containing hot water, an ice cube, and an internal combustion engine. The boundaries of the system are set by the person studying the system. For an expanding gas, the cylinder walls and the piston are the boundaries of the system. Anything that is not a part of a system is a part of its surroundings.

Systems are classified into three categories. An **open system**, such as an ice cube resting on a kitchen counter, can exchange both energy and matter with its surroundings. A **closed system** can exchange energy but not matter with its surroundings. An expanding gas in a thermally conducting cylinder with a gas-tight piston is a closed system. An **isolated system**, such as a liquid in a perfectly insulated vacuum flask, cannot exchange either matter or energy with its surroundings. In practice, there are no truly isolated systems except for the universe itself.

In an isolated system, energy is conserved. That is, the amount of energy in an isolated system is constant. Energy may be converted from one form to another, but no energy enters or leaves the system, nor does it appear or disappear: Since the universe is an isolated system, its total amount of energy is constant. When energy is exchanged between an open or closed system and its surroundings, all the energy lost by one must be gained by the other, since the system and its surroundings ultimately include the entire universe. This fact is the reason for the following equation in Chapter 15:

$$Q_{\text{system}} + Q_{\text{surroundings}} = 0 \text{ J}$$

Although no practical system is isolated, a system enclosed in a calorimeter or other vacuum-insulated container approximates an isolated system for short periods of time. The first law of thermodynamics is one of the great conservation laws of science. It states that in a isolated system, the total quantity of energy (in the forms of thermal energy and mechanical work) is constant, neither being created nor destroyed. This law is consistent with numerous biblical references proclaiming the finished work of God at the end of the Creation week.

## 16.8 Thermodynamic Processes

A *thermodynamic process* is a change in the thermodynamic state of a system. Although it is possible for all state variables to change at the same time, analysis and calculations are easier if at least one variable is held constant throughout the process. Processes are named to indicate which variables are held constant.

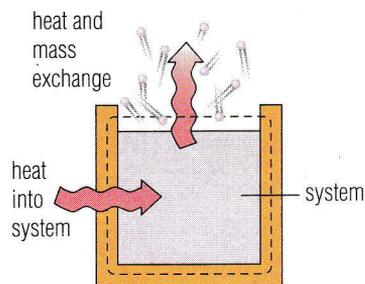
An *adiabatic process* exchanges no thermal energy between the system and its surroundings. For adiabatic processes,  $Q$  is zero; therefore, the first law becomes

$$0 \text{ J} = \Delta U + W, \text{ or} \\ \Delta U = -W.$$

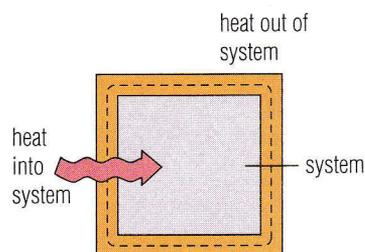
Since internal energy of a gas is directly proportional to temperature, a change in internal energy is indicated by a change in temperature. If the gas expands, doing positive work, then internal energy decreases, and the gas temperature drops; if the gas is compressed so that it does negative work, temperature and internal energy increase.

For an **isothermal** process, the temperature of the system is constant. If you assume that the system is not in the process of melting, freezing, boiling, or

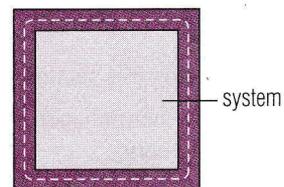
Thermodynamically, neither the piston nor the cylinder walls are parts of the gas system.



16-11a An open system



16-11b A closed system



16-11c An isolated system

The first law of thermodynamics is one of the most thoroughly tested and confirmed laws in physical science. If a scientist claims that energy or mass (a different form of energy) spontaneously has appeared in the universe, you know that his idea violates this law of science.

In *adiabatic* processes, thermal energy is constant ( $Q = 0 \text{ J}$ ).

Recall that  $W$  is work *on the surroundings* by the system and is the negative of the work *on the system* ( $W = -W_{\text{ncf}}$ ).

In **isothermal** processes, temperature is constant ( $\Delta U = 0 \text{ J}$ ).

This statement is not a violation of the second law of thermodynamics because it represents only a step in a cycle and not the entire cycle (see Section 16B).

In an **isochoric** (EYE so KOR ik) process, volume is constant ( $W = 0 \text{ J}$ ).

In an **isobaric** process, pressure is constant, and work done is a function of volume alone.

### 16A Objectives

After completing this section, I can

- ✓ differentiate internal energy from mechanical energy.
- ✓ explain why the zeroth law of thermodynamics defines thermal equilibrium.
- ✓ state the first law of thermodynamics and discuss how it pertains to the principle of conservation.
- ✓ describe the general characteristics of a heat engine.
- ✓ explain why the concept of quasi-static processes is useful for describing the operation of a heat engine.
- ✓ graph and interpret  $P$ - $V$  diagrams.
- ✓ explain the significance of the expansion cycle of a heat engine in doing useful work.
- ✓ describe the properties of the three thermodynamic systems and give an example of each.
- ✓ differentiate among the five thermodynamic processes discussed in the text.

condensing (phase changes involving the exchange of latent heats at constant temperatures), the internal energy is also constant ( $\Delta U = 0 \text{ J}$ ). The first law becomes

$$Q = 0 \text{ J} + W, \text{ or} \\ Q = W.$$

This means that all of the heat transferred is converted to work.

During an **isochoric** process, the volume is constant. Remember, work is done on or by a gas only when its volume changes. Therefore,

$$Q = \Delta U + 0 \text{ J}, \text{ or} \\ Q = \Delta U.$$

All the thermal energy added to the system increases the internal energy of the system.

An **isobaric** process is a process for which the pressure is constant. Isobaric processes give the simplest equation for work,

$$W = P\Delta V.$$

The first law of thermodynamics for this process is

$$Q = \Delta U + P\Delta V.$$

The calculations for work and energy are much simpler when it is possible to use the ideal gas relationships in the general gas law. At low pressures, real gases behave much like ideal gases, and the approximation is valid. A process that allows the use of ideal gas relationships is known as an **ideal gas process**.

## 16A Section Review

1. What is a barrier that conducts no thermal energy called?
2. On a cold winter morning, if the air outside a car is in thermal equilibrium with the glass in the car's window and the window glass is in thermal equilibrium with the air inside the car, what can be said about the temperatures of the inside and outside air? What is your authority for your answer?
3. How is the work done by the surroundings on a thermodynamic system related to the work the system does on its surroundings? What principle of mechanics allows you to answer this question?
4. To what is the area under a  $P$ - $V$  curve equivalent?
5. What kind of thermodynamic engine follows a counterclockwise path on a  $P$ - $V$  diagram?
6. What kind of thermodynamic system is a sealed plastic container full of steaming hot soup in a refrigerator?
7. For a closed gas thermodynamic system, what kind of process exchanges thermal energy for change in internal energy?
- ★8. A gas cylinder system similar to that described in this section originally has a volume of  $1.80 \times 10^{-3} \text{ m}^3$  at  $1.01 \times 10^5 \text{ Pa}$ . If the volume and pressure of the gas change along a linear path on the  $P$ - $V$  diagram to  $1.22 \times 10^{-3} \text{ m}^3$  and  $2.02 \times 10^5 \text{ Pa}$ , what is the work done by the gas in joules?