

From the way the calorie and the British thermal unit were initially defined, the specific heat of water is

$$c = 1 \text{ cal/g} \cdot \text{C}^\circ = 1 \text{ Btu/lb} \cdot \text{F}^\circ = 4186.8 \text{ J/kg} \cdot \text{K}. \quad (18-15)$$

Table 18-3 shows the specific heats of some substances at room temperature. Note that the value for water is relatively high. The specific heat of any substance actually depends somewhat on temperature, but the values in Table 18-3 apply reasonably well in a range of temperatures near room temperature.



Checkpoint 3

A certain amount of heat Q will warm 1 g of material A by 3 C° and 1 g of material B by 4 C° . Which material has the greater specific heat?

Molar Specific Heat

In many instances the most convenient unit for specifying the amount of a substance is the mole (mol), where

$$1 \text{ mol} = 6.02 \times 10^{23} \text{ elementary units}$$

of any substance. Thus 1 mol of aluminum means 6.02×10^{23} atoms (the atom is the elementary unit), and 1 mol of aluminum oxide means 6.02×10^{23} molecules (the molecule is the elementary unit of the compound).

When quantities are expressed in moles, specific heats must also involve moles (rather than a mass unit); they are then called **molar specific heats**. Table 18-3 shows the values for some elemental solids (each consisting of a single element) at room temperature.

An Important Point

In determining and then using the specific heat of any substance, we need to know the conditions under which energy is transferred as heat. For solids and liquids, we usually assume that the sample is under constant pressure (usually atmospheric) during the transfer. It is also conceivable that the sample is held at constant volume while the heat is absorbed. This means that thermal expansion of the sample is prevented by applying external pressure. For solids and liquids, this is very hard to arrange experimentally, but the effect can be calculated, and it turns out that the specific heats under constant pressure and constant volume for any solid or liquid differ usually by no more than a few percent. Gases, as you will see, have quite different values for their specific heats under constant-pressure conditions and under constant-volume conditions.

Heats of Transformation

When energy is absorbed as heat by a solid or liquid, the temperature of the sample does not necessarily rise. Instead, the sample may change from one *phase*, or *state*, to another. Matter can exist in three common states: In the *solid state*, the molecules of a sample are locked into a fairly rigid structure by their mutual attraction. In the *liquid state*, the molecules have more energy and move about more. They may form brief clusters, but the sample does not have a rigid structure and can flow or settle into a container. In the *gas*, or *vapor*, *state*, the molecules have even more energy, are free of one another, and can fill up the full volume of a container.

Melting. To *melt* a solid means to change it from the solid state to the liquid state. The process requires energy because the molecules of the solid must be freed from their rigid structure. Melting an ice cube to form liquid water is a common example. To *freeze* a liquid to form a solid is the reverse of melting and requires that energy be removed from the liquid, so that the molecules can settle into a rigid structure.

Table 18-3 Some Specific Heats and Molar Specific Heats at Room Temperature

Substance	Specific Heat		Molar Specific Heat J/mol · K
	cal/g · K	J/kg · K	
<i>Elemental Solids</i>			
Lead	0.0305	128	26.5
Tungsten	0.0321	134	24.8
Silver	0.0564	236	25.5
Copper	0.0923	386	24.5
Aluminum	0.215	900	24.4
<i>Other Solids</i>			
Brass	0.092	380	
Granite	0.19	790	
Glass	0.20	840	
Ice (-10°C)	0.530	2220	
<i>Liquids</i>			
Mercury	0.033	140	
Ethyl alcohol	0.58	2430	
Seawater	0.93	3900	
Water	1.00	4187	

Table 18-4 Some Heats of Transformation

Substance	Melting		Boiling	
	Melting Point (K)	Heat of Fusion L_F (kJ/kg)	Boiling Point (K)	Heat of Vaporization L_V (kJ/kg)
Hydrogen	14.0	58.0	20.3	455
Oxygen	54.8	13.9	90.2	213
Mercury	234	11.4	630	296
Water	273	333	373	2256
Lead	601	23.2	2017	858
Silver	1235	105	2323	2336
Copper	1356	207	2868	4730

Vaporizing. To *vaporize* a liquid means to change it from the liquid state to the vapor (gas) state. This process, like melting, requires energy because the molecules must be freed from their clusters. Boiling liquid water to transfer it to water vapor (or steam—a gas of individual water molecules) is a common example. *Condensing* a gas to form a liquid is the reverse of vaporizing; it requires that energy be removed from the gas, so that the molecules can cluster instead of flying away from one another.

The amount of energy per unit mass that must be transferred as heat when a sample completely undergoes a phase change is called the **heat of transformation** L . Thus, when a sample of mass m completely undergoes a phase change, the total energy transferred is

$$Q = Lm. \quad (18-16)$$

When the phase change is from liquid to gas (then the sample must absorb heat) or from gas to liquid (then the sample must release heat), the heat of transformation is called the **heat of vaporization** L_V . For water at its normal boiling or condensation temperature,

$$L_V = 539 \text{ cal/g} = 40.7 \text{ kJ/mol} = 2256 \text{ kJ/kg}. \quad (18-17)$$

When the phase change is from solid to liquid (then the sample must absorb heat) or from liquid to solid (then the sample must release heat), the heat of transformation is called the **heat of fusion** L_F . For water at its normal freezing or melting temperature,

$$L_F = 79.5 \text{ cal/g} = 6.01 \text{ kJ/mol} = 333 \text{ kJ/kg}. \quad (18-18)$$

Table 18-4 shows the heats of transformation for some substances.



Sample Problem 18.03 Hot slug in water, coming to equilibrium

A copper slug whose mass m_c is 75 g is heated in a laboratory oven to a temperature T of 312°C. The slug is then dropped into a glass beaker containing a mass $m_w = 220$ g of water. The heat capacity C_b of the beaker is 45 cal/K. The initial temperature T_i of the water and the beaker is 12°C. Assuming that the slug, beaker, and water are an isolated system and the water does not vaporize, find the final temperature T_f of the system at thermal equilibrium.

KEY IDEAS

- (1) Because the system is isolated, the system's total energy cannot change and only internal transfers of thermal energy

can occur. (2) Because nothing in the system undergoes a phase change, the thermal energy transfers can only change the temperatures.

Calculations: To relate the transfers to the temperature changes, we can use Eqs. 18-13 and 18-14 to write

$$\text{for the water: } Q_w = c_w m_w (T_f - T_i); \quad (18-19)$$

$$\text{for the beaker: } Q_b = C_b (T_f - T_i); \quad (18-20)$$

$$\text{for the copper: } Q_c = c_c m_c (T_f - T). \quad (18-21)$$

Because the total energy of the system cannot change, the sum of these three energy transfers is zero:

$$Q_w + Q_b + Q_c = 0. \quad (18-22)$$

Substituting Eqs. 18-19 through 18-21 into Eq. 18-22 yields

$$c_w m_w (T_f - T_i) + C_b (T_f - T_i) + c_c m_c (T_f - T) = 0. \quad (18-23)$$

Temperatures are contained in Eq. 18-23 only as differences. Thus, because the differences on the Celsius and Kelvin scales are identical, we can use either of those scales in this equation. Solving it for T_f , we obtain

$$T_f = \frac{c_c m_c T + C_b T_i + c_w m_w T_i}{c_w m_w + C_b + c_c m_c}.$$

Using Celsius temperatures and taking values for c_c and c_w from Table 18-3, we find the numerator to be

$$(0.0923 \text{ cal/g} \cdot \text{K})(75 \text{ g})(312^\circ\text{C}) + (45 \text{ cal/K})(12^\circ\text{C}) \\ + (1.00 \text{ cal/g} \cdot \text{K})(220 \text{ g})(12^\circ\text{C}) = 5339.8 \text{ cal},$$

and the denominator to be

$$(1.00 \text{ cal/g} \cdot \text{K})(220 \text{ g}) + 45 \text{ cal/K} \\ + (0.0923 \text{ cal/g} \cdot \text{K})(75 \text{ g}) = 271.9 \text{ cal/C}^\circ.$$

We then have

$$T_f = \frac{5339.8 \text{ cal}}{271.9 \text{ cal/C}^\circ} = 19.6^\circ\text{C} \approx 20^\circ\text{C}. \quad (\text{Answer})$$

From the given data you can show that

$$Q_w \approx 1670 \text{ cal}, \quad Q_b \approx 342 \text{ cal}, \quad Q_c \approx -2020 \text{ cal}.$$

Apart from rounding errors, the algebraic sum of these three heat transfers is indeed zero, as required by the conservation of energy (Eq. 18-22).

Sample Problem 18.04 Heat to change temperature and state

- (a) How much heat must be absorbed by ice of mass $m = 720 \text{ g}$ at -10°C to take it to the liquid state at 15°C ?

KEY IDEAS

The heating process is accomplished in three steps: (1) The ice cannot melt at a temperature below the freezing point—so initially, any energy transferred to the ice as heat can only increase the temperature of the ice, until 0°C is reached. (2) The temperature then cannot increase until all the ice melts—so any energy transferred to the ice as heat now can only change ice to liquid water, until all the ice melts. (3) Now the energy transferred to the liquid water as heat can only increase the temperature of the liquid water.

Warming the ice: The heat Q_1 needed to take the ice from the initial $T_i = -10^\circ\text{C}$ to the final $T_f = 0^\circ\text{C}$ (so that the ice can then melt) is given by Eq. 18-14 ($Q = cm \Delta T$). Using the specific heat of ice c_{ice} in Table 18-3 gives us

$$Q_1 = c_{\text{ice}} m (T_f - T_i) \\ = (2220 \text{ J/kg} \cdot \text{K})(0.720 \text{ kg})[0^\circ\text{C} - (-10^\circ\text{C})] \\ = 15\,984 \text{ J} \approx 15.98 \text{ kJ}.$$

Melting the ice: The heat Q_2 needed to melt all the ice is given by Eq. 18-16 ($Q = Lm$). Here L is the heat of fusion L_F , with the value given in Eq. 18-18 and Table 18-4. We find

$$Q_2 = L_F m = (333 \text{ kJ/kg})(0.720 \text{ kg}) \approx 239.8 \text{ kJ}.$$

Warming the liquid: The heat Q_3 needed to increase the temperature of the water from the initial value $T_i = 0^\circ\text{C}$ to the final value $T_f = 15^\circ\text{C}$ is given by Eq. 18-14 (with the specific heat of liquid water c_{liq}):

$$Q_3 = c_{\text{liq}} m (T_f - T_i) \\ = (4186.8 \text{ J/kg} \cdot \text{K})(0.720 \text{ kg})(15^\circ\text{C} - 0^\circ\text{C}) \\ = 45\,217 \text{ J} \approx 45.22 \text{ kJ}.$$

Total: The total required heat Q_{tot} is the sum of the amounts required in the three steps:

$$Q_{\text{tot}} = Q_1 + Q_2 + Q_3 \\ = 15.98 \text{ kJ} + 239.8 \text{ kJ} + 45.22 \text{ kJ} \\ \approx 300 \text{ kJ}. \quad (\text{Answer})$$

Note that most of the energy goes into melting the ice rather than raising the temperature.

- (b) If we supply the ice with a total energy of only 210 kJ (as heat), what are the final state and temperature of the water?

KEY IDEA

From step 1, we know that 15.98 kJ is needed to raise the temperature of the ice to the melting point. The remaining heat Q_{rem} is then $210 \text{ kJ} - 15.98 \text{ kJ}$, or about 194 kJ. From step 2, we can see that this amount of heat is insufficient to melt all the ice. Because the melting of the ice is incomplete, we must end up with a mixture of ice and liquid; the temperature of the mixture must be the freezing point, 0°C .

Calculations: We can find the mass m of ice that is melted by the available energy Q_{rem} by using Eq. 18-16 with L_F :

$$m = \frac{Q_{\text{rem}}}{L_F} = \frac{194 \text{ kJ}}{333 \text{ kJ/kg}} = 0.583 \text{ kg} \approx 580 \text{ g}.$$

Thus, the mass of the ice that remains is $720 \text{ g} - 580 \text{ g}$, or 140 g, and we have

$$580 \text{ g water} \quad \text{and} \quad 140 \text{ g ice, at } 0^\circ\text{C}. \quad (\text{Answer})$$



Additional examples, video, and practice available at WileyPLUS



18-5 THE FIRST LAW OF THERMODYNAMICS

Learning Objectives

After reading this module, you should be able to . . .

- 18.20** If an enclosed gas expands or contracts, calculate the work W done by the gas by integrating the gas pressure with respect to the volume of the enclosure.
- 18.21** Identify the algebraic sign of work W associated with expansion and contraction of a gas.
- 18.22** Given a p - V graph of pressure versus volume for a process, identify the starting point (the initial state) and the final point (the final state) and calculate the work by using graphical integration.
- 18.23** On a p - V graph of pressure versus volume for a gas, identify the algebraic sign of the work associated with a right-going process and a left-going process.
- 18.24** Apply the first law of thermodynamics to relate the change in the internal energy ΔE_{int} of a gas, the energy Q transferred as heat to or from the gas, and the work W done on or by the gas.

Key Ideas

- A gas may exchange energy with its surroundings through work. The amount of work W done by a gas as it expands or contracts from an initial volume V_i to a final volume V_f is given by

$$W = \int dW = \int_{V_i}^{V_f} p \, dV.$$

The integration is necessary because the pressure p may vary during the volume change.

- The principle of conservation of energy for a thermodynamic process is expressed in the first law of thermodynamics, which may assume either of the forms

$$\Delta E_{\text{int}} = E_{\text{int},f} - E_{\text{int},i} = Q - W \quad (\text{first law})$$

or $dE_{\text{int}} = dQ - dW \quad (\text{first law}).$

E_{int} represents the internal energy of the material, which depends only on the material's state (temperature,

18.25 Identify the algebraic sign of a heat transfer Q that is associated with a transfer to a gas and a transfer from the gas.

18.26 Identify that the internal energy ΔE_{int} of a gas tends to increase if the heat transfer is *to* the gas, and it tends to decrease if the gas does work on its environment.

18.27 Identify that in an adiabatic process with a gas, there is no heat transfer Q with the environment.

18.28 Identify that in a constant-volume process with a gas, there is no work W done by the gas.

18.29 Identify that in a cyclical process with a gas, there is no net change in the internal energy ΔE_{int} .

18.30 Identify that in a free expansion with a gas, the heat transfer Q , work done W , and change in internal energy ΔE_{int} are each zero.

pressure, and volume). Q represents the energy exchanged as heat between the system and its surroundings; Q is positive if the system absorbs heat and negative if the system loses heat. W is the work done *by* the system; W is positive if the system expands against an external force from the surroundings and negative if the system contracts because of an external force.

- Q and W are path dependent; ΔE_{int} is path independent.
- The first law of thermodynamics finds application in several special cases:

adiabatic processes: $Q = 0, \Delta E_{\text{int}} = -W$

constant-volume processes: $W = 0, \Delta E_{\text{int}} = Q$

cyclical processes: $\Delta E_{\text{int}} = 0, Q = W$

free expansions: $Q = W = \Delta E_{\text{int}} = 0$

A Closer Look at Heat and Work

Here we look in some detail at how energy can be transferred as heat and work between a system and its environment. Let us take as our system a gas confined to a cylinder with a movable piston, as in Fig. 18-13. The upward force on the piston due to the pressure of the confined gas is equal to the weight of lead shot loaded onto the top of the piston. The walls of the cylinder are made of insulating material that does not allow any transfer of energy as heat. The bottom of the cylinder rests on a reservoir for thermal energy, a *thermal reservoir* (perhaps a hot plate) whose temperature T you can control by turning a knob.

The system (the gas) starts from an *initial state* i , described by a pressure p_i , a volume V_i , and a temperature T_i . You want to change the system to a *final state* f , described by a pressure p_f , a volume V_f , and a temperature T_f . The procedure by which you change the system from its initial state to its final state is called a *thermodynamic process*. During such a process, energy may be trans-

fected into the system from the thermal reservoir (positive heat) or vice versa (negative heat). Also, work can be done by the system to raise the loaded piston (positive work) or lower it (negative work). We assume that all such changes occur slowly, with the result that the system is always in (approximate) thermal equilibrium (every part is always in thermal equilibrium).

Suppose that you remove a few lead shot from the piston of Fig. 18-13, allowing the gas to push the piston and remaining shot upward through a differential displacement $d\vec{s}$ with an upward force \vec{F} . Since the displacement is tiny, we can assume that \vec{F} is constant during the displacement. Then \vec{F} has a magnitude that is equal to pA , where p is the pressure of the gas and A is the face area of the piston. The differential work dW done by the gas during the displacement is

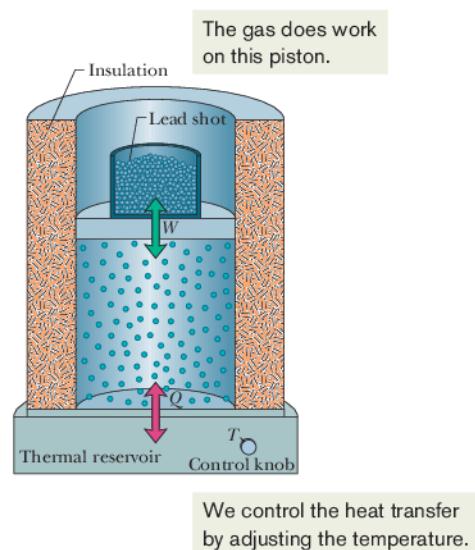
$$\begin{aligned} dW &= \vec{F} \cdot d\vec{s} = (pA)(ds) = p(A ds) \\ &= p dV, \end{aligned} \quad (18-24)$$

in which dV is the differential change in the volume of the gas due to the movement of the piston. When you have removed enough shot to allow the gas to change its volume from V_i to V_f , the total work done by the gas is

$$W = \int dW = \int_{V_i}^{V_f} p dV. \quad (18-25)$$

During the volume change, the pressure and temperature may also change. To evaluate Eq. 18-25 directly, we would need to know how pressure varies with volume for the actual process by which the system changes from state i to state f .

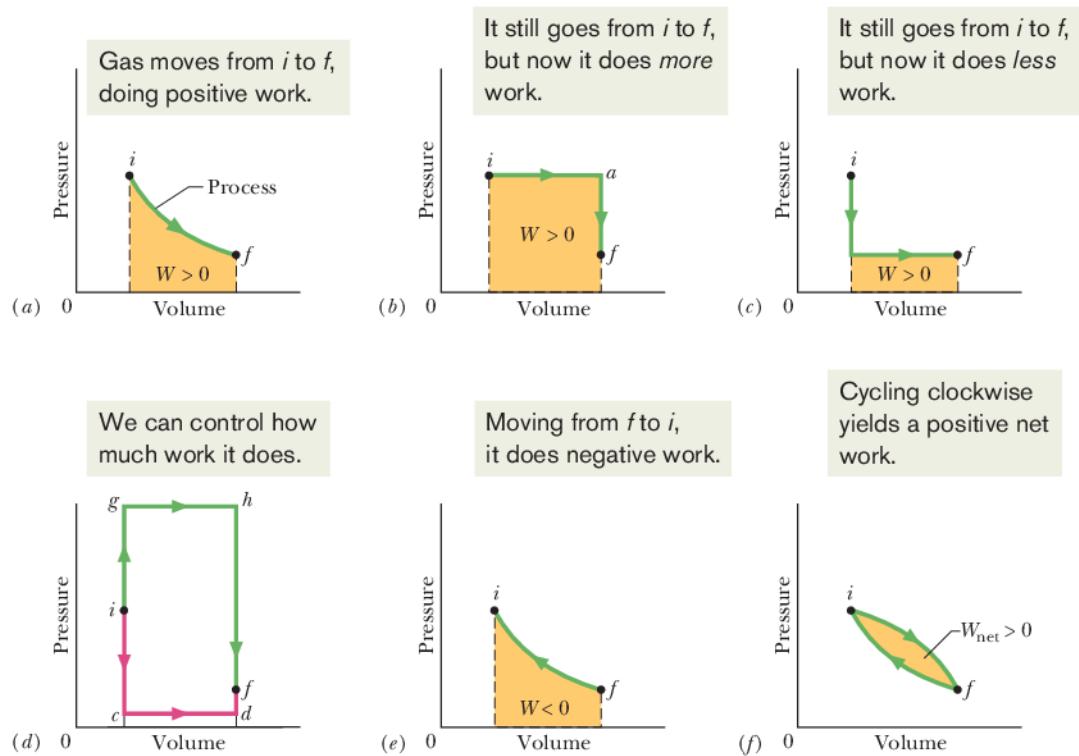
One Path. There are actually many ways to take the gas from state i to state f . One way is shown in Fig. 18-14a, which is a plot of the pressure of the gas versus its volume and which is called a *p-V* diagram. In Fig. 18-14a, the curve indicates that the



We control the heat transfer by adjusting the temperature.

Figure 18-13 A gas is confined to a cylinder with a movable piston. Heat Q can be added to or withdrawn from the gas by regulating the temperature T of the adjustable thermal reservoir. Work W can be done by the gas by raising or lowering the piston.

Figure 18-14 (a) The shaded area represents the work W done by a system as it goes from an initial state i to a final state f . Work W is positive because the system's volume increases. (b) W is still positive, but now greater. (c) W is still positive, but now smaller. (d) W can be even smaller (path $icdf$) or larger (path $ighf$). (e) Here the system goes from state f to state i as the gas is compressed to less volume by an external force. The work W done by the system is now negative. (f) The net work W_{net} done by the system during a complete cycle is represented by the shaded area.



pressure decreases as the volume increases. The integral in Eq. 18-25 (and thus the work W done by the gas) is represented by the shaded area under the curve between points i and f . Regardless of what exactly we do to take the gas along the curve, that work is positive, due to the fact that the gas increases its volume by forcing the piston upward.

Another Path. Another way to get from state i to state f is shown in Fig. 18-14b. There the change takes place in two steps—the first from state i to state a , and the second from state a to state f .

Step ia of this process is carried out at constant pressure, which means that you leave undisturbed the lead shot that ride on top of the piston in Fig. 18-13. You cause the volume to increase (from V_i to V_f) by slowly turning up the temperature control knob, raising the temperature of the gas to some higher value T_a . (Increasing the temperature increases the force from the gas on the piston, moving it upward.) During this step, positive work is done by the expanding gas (to lift the loaded piston) and heat is absorbed by the system from the thermal reservoir (in response to the arbitrarily small temperature differences that you create as you turn up the temperature). This heat is positive because it is added to the system.

Step af of the process of Fig. 18-14b is carried out at constant volume, so you must wedge the piston, preventing it from moving. Then as you use the control knob to decrease the temperature, you find that the pressure drops from p_a to its final value p_f . During this step, heat is lost by the system to the thermal reservoir.

For the overall process iaf , the work W , which is positive and is carried out only during step ia , is represented by the shaded area under the curve. Energy is transferred as heat during both steps ia and af , with a net energy transfer Q .

Reversed Steps. Figure 18-14c shows a process in which the previous two steps are carried out in reverse order. The work W in this case is smaller than for Fig. 18-14b, as is the net heat absorbed. Figure 18-14d suggests that you can make the work done by the gas as small as you want (by following a path like $icdf$) or as large as you want (by following a path like $ighf$).

To sum up: A system can be taken from a given initial state to a given final state by an infinite number of processes. Heat may or may not be involved, and in general, the work W and the heat Q will have different values for different processes. We say that heat and work are *path-dependent* quantities.

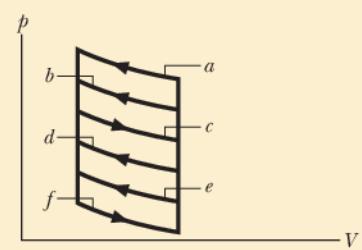
Negative Work. Figure 18-14e shows an example in which negative work is done by a system as some external force compresses the system, reducing its volume. The absolute value of the work done is still equal to the area beneath the curve, but because the gas is *compressed*, the work done by the gas is negative.

Cycle. Figure 18-14f shows a *thermodynamic cycle* in which the system is taken from some initial state i to some other state f and then back to i . The net work done by the system during the cycle is the sum of the *positive* work done during the expansion and the *negative* work done during the compression. In Fig. 18-14f, the net work is positive because the area under the expansion curve (i to f) is greater than the area under the compression curve (f to i).



Checkpoint 4

The p - V diagram here shows six curved paths (connected by vertical paths) that can be followed by a gas. Which two of the curved paths should be part of a closed cycle (those curved paths plus connecting vertical paths) if the net work done by the gas during the cycle is to be at its maximum positive value?



The First Law of Thermodynamics

You have just seen that when a system changes from a given initial state to a given final state, both the work W and the heat Q depend on the nature of the process. Experimentally, however, we find a surprising thing. *The quantity $Q - W$ is the same for all processes.* It depends only on the initial and final states and does not depend at all on how the system gets from one to the other. All other combinations of Q and W , including Q alone, W alone, $Q + W$, and $Q - 2W$, are *path dependent*; only the quantity $Q - W$ is not.

The quantity $Q - W$ must represent a change in some intrinsic property of the system. We call this property the *internal energy* E_{int} and we write

$$\Delta E_{\text{int}} = E_{\text{int},f} - E_{\text{int},i} = Q - W \quad (\text{first law}). \quad (18-26)$$

Equation 18-26 is the **first law of thermodynamics**. If the thermodynamic system undergoes only a differential change, we can write the first law as*

$$dE_{\text{int}} = dQ - dW \quad (\text{first law}). \quad (18-27)$$



The internal energy E_{int} of a system tends to increase if energy is added as heat Q and tends to decrease if energy is lost as work W done by the system.

In Chapter 8, we discussed the principle of energy conservation as it applies to isolated systems—that is, to systems in which no energy enters or leaves the system. The first law of thermodynamics is an extension of that principle to systems that are *not* isolated. In such cases, energy may be transferred into or out of the system as either work W or heat Q . In our statement of the first law of thermodynamics above, we assume that there are no changes in the kinetic energy or the potential energy of the system as a whole; that is, $\Delta K = \Delta U = 0$.

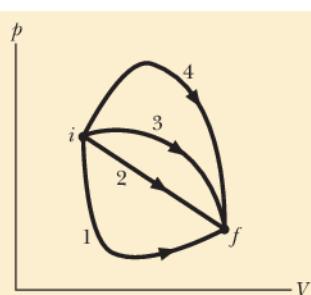
Rules. Before this chapter, the term *work* and the symbol W always meant the work done *on* a system. However, starting with Eq. 18-24 and continuing through the next two chapters about thermodynamics, we focus on the work done *by* a system, such as the gas in Fig. 18-13.

The work done *on* a system is always the negative of the work done *by* the system, so if we rewrite Eq. 18-26 in terms of the work W_{on} done *on* the system, we have $\Delta E_{\text{int}} = Q + W_{\text{on}}$. This tells us the following: The internal energy of a system tends to increase if heat is absorbed by the system or if positive work is done *on* the system. Conversely, the internal energy tends to decrease if heat is lost by the system or if negative work is done *on* the system.



Checkpoint 5

The figure here shows four paths on a p - V diagram along which a gas can be taken from state i to state f . Rank the paths according to (a) the change ΔE_{int} in the internal energy of the gas, (b) the work W done by the gas, and (c) the magnitude of the energy transferred as heat Q between the gas and its environment, greatest first.



*Here dQ and dW , unlike dE_{int} , are not true differentials; that is, there are no such functions as $Q(p, V)$ and $W(p, V)$ that depend only on the state of the system. The quantities dQ and dW are called *inexact differentials* and are usually represented by the symbols dQ and dW . For our purposes, we can treat them simply as infinitesimally small energy transfers.

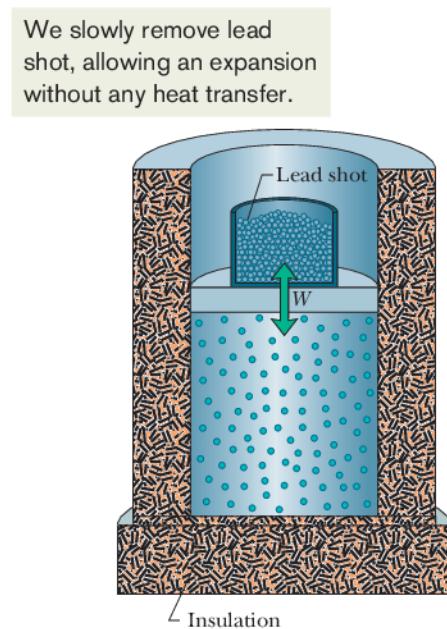


Figure 18-15 An adiabatic expansion can be carried out by slowly removing lead shot from the top of the piston. Adding lead shot reverses the process at any stage.

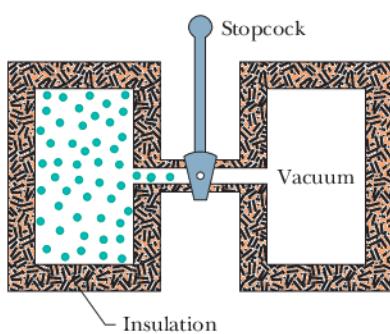


Figure 18-16 The initial stage of a free-expansion process. After the stopcock is opened, the gas fills both chambers and eventually reaches an equilibrium state.

Some Special Cases of the First Law of Thermodynamics

Here are four thermodynamic processes as summarized in Table 18-5.

- 1. Adiabatic processes.** An adiabatic process is one that occurs so rapidly or occurs in a system that is so well insulated that *no transfer of energy as heat* occurs between the system and its environment. Putting $Q = 0$ in the first law (Eq. 18-26) yields

$$\Delta E_{\text{int}} = -W \quad (\text{adiabatic process}). \quad (18-28)$$

This tells us that if work is done *by* the system (that is, if W is positive), the internal energy of the system decreases by the amount of work. Conversely, if work is done *on* the system (that is, if W is negative), the internal energy of the system increases by that amount.

Figure 18-15 shows an idealized adiabatic process. Heat cannot enter or leave the system because of the insulation. Thus, the only way energy can be transferred between the system and its environment is by work. If we remove shot from the piston and allow the gas to expand, the work done by the system (the gas) is positive and the internal energy of the gas decreases. If, instead, we add shot and compress the gas, the work done by the system is negative and the internal energy of the gas increases.

- 2. Constant-volume processes.** If the volume of a system (such as a gas) is held constant, that system can do no work. Putting $W = 0$ in the first law (Eq. 18-26) yields

$$\Delta E_{\text{int}} = Q \quad (\text{constant-volume process}). \quad (18-29)$$

Thus, if heat is absorbed by a system (that is, if Q is positive), the internal energy of the system increases. Conversely, if heat is lost during the process (that is, if Q is negative), the internal energy of the system must decrease.

- 3. Cyclical processes.** There are processes in which, after certain interchanges of heat and work, the system is restored to its initial state. In that case, no intrinsic property of the system—including its internal energy—can possibly change. Putting $\Delta E_{\text{int}} = 0$ in the first law (Eq. 18-26) yields

$$Q = W \quad (\text{cyclical process}). \quad (18-30)$$

Thus, the net work done during the process must exactly equal the net amount of energy transferred as heat; the store of internal energy of the system remains unchanged. Cyclical processes form a closed loop on a p - V plot, as shown in Fig. 18-14f. We discuss such processes in detail in Chapter 20.

- 4. Free expansions.** These are adiabatic processes in which no transfer of heat occurs between the system and its environment and no work is done on or by the system. Thus, $Q = W = 0$, and the first law requires that

$$\Delta E_{\text{int}} = 0 \quad (\text{free expansion}). \quad (18-31)$$

Figure 18-16 shows how such an expansion can be carried out. A gas, which is in thermal equilibrium within itself, is initially confined by a closed stopcock to one half of an insulated double chamber; the other half is evacuated. The stopcock is opened, and the gas expands freely to fill both halves of the chamber. No heat is

Table 18-5 The First Law of Thermodynamics: Four Special Cases

The Law: $\Delta E_{\text{int}} = Q - W$ (Eq. 18-26)		
Process	Restriction	Consequence
Adiabatic	$Q = 0$	$\Delta E_{\text{int}} = -W$
Constant volume	$W = 0$	$\Delta E_{\text{int}} = Q$
Closed cycle	$\Delta E_{\text{int}} = 0$	$Q = W$
Free expansion	$Q = W = 0$	$\Delta E_{\text{int}} = 0$

transferred to or from the gas because of the insulation. No work is done by the gas because it rushes into a vacuum and thus does not meet any pressure.

A free expansion differs from all other processes we have considered because it cannot be done slowly and in a controlled way. As a result, at any given instant during the sudden expansion, the gas is not in thermal equilibrium and its pressure is not uniform. Thus, although we can plot the initial and final states on a p - V diagram, we cannot plot the expansion itself.



Checkpoint 6

For one complete cycle as shown in the p - V diagram here, are (a) ΔE_{int} for the gas and (b) the net energy transferred as heat Q positive, negative, or zero?



Sample Problem 18.05 First law of thermodynamics: work, heat, internal energy change

Let 1.00 kg of liquid water at 100°C be converted to steam at 100°C by boiling at standard atmospheric pressure (which is 1.00 atm or 1.01×10^5 Pa) in the arrangement of Fig. 18-17. The volume of that water changes from an initial value of 1.00×10^{-3} m³ as a liquid to 1.671 m³ as steam.

(a) How much work is done by the system during this process?

KEY IDEAS

(1) The system must do positive work because the volume increases. (2) We calculate the work W done by integrating the pressure with respect to the volume (Eq. 18-25).

Calculation: Because here the pressure is constant at 1.01×10^5 Pa, we can take p outside the integral. Thus,

$$\begin{aligned} W &= \int_{V_i}^{V_f} p \, dV = p \int_{V_i}^{V_f} dV = p(V_f - V_i) \\ &= (1.01 \times 10^5 \text{ Pa})(1.671 \text{ m}^3 - 1.00 \times 10^{-3} \text{ m}^3) \\ &= 1.69 \times 10^5 \text{ J} = 169 \text{ kJ.} \end{aligned} \quad (\text{Answer})$$

(b) How much energy is transferred as heat during the process?

KEY IDEA

Because the heat causes only a phase change and not a change in temperature, it is given fully by Eq. 18-16 ($Q = Lm$).

Calculation: Because the change is from liquid to gaseous phase, L is the heat of vaporization L_V , with the value given in Eq. 18-17 and Table 18-4. We find

$$\begin{aligned} Q &= L_V m = (2256 \text{ kJ/kg})(1.00 \text{ kg}) \\ &= 2256 \text{ kJ} \approx 2260 \text{ kJ.} \end{aligned} \quad (\text{Answer})$$

(c) What is the change in the system's internal energy during the process?

KEY IDEA

The change in the system's internal energy is related to the heat (here, this is energy transferred into the system) and the work (here, this is energy transferred out of the system) by the first law of thermodynamics (Eq. 18-26).

Calculation: We write the first law as

$$\begin{aligned} \Delta E_{\text{int}} &= Q - W = 2256 \text{ kJ} - 169 \text{ kJ} \\ &\approx 2090 \text{ kJ} = 2.09 \text{ MJ.} \end{aligned} \quad (\text{Answer})$$

This quantity is positive, indicating that the internal energy of the system has increased during the boiling process. The added energy goes into separating the H₂O molecules, which strongly attract one another in the liquid state. We see that, when water is boiled, about 7.5% (= 169 kJ/2260 kJ) of the heat goes into the work of pushing back the atmosphere. The rest of the heat goes into the internal energy of the system.

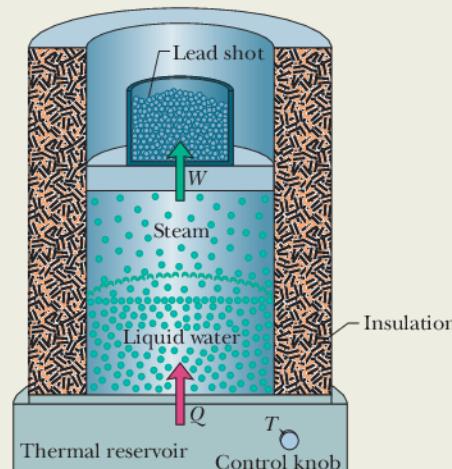


Figure 18-17 Water boiling at constant pressure. Energy is transferred from the thermal reservoir as heat until the liquid water has changed completely into steam. Work is done by the expanding gas as it lifts the loaded piston.



Additional examples, video, and practice available at WileyPLUS

18-6 HEAT TRANSFER MECHANISMS

Learning Objectives

After reading this module, you should be able to...

- 18.31 For thermal conduction through a layer, apply the relationship between the energy-transfer rate P_{cond} and the layer's area A , thermal conductivity k , thickness L , and temperature difference ΔT (between its two sides).
- 18.32 For a composite slab (two or more layers) that has reached the steady state in which temperatures are no longer changing, identify that (by the conservation of energy) the rates of thermal conduction P_{cond} through the layers must be equal.
- 18.33 For thermal conduction through a layer, apply the relationship between thermal resistance R , thickness L , and thermal conductivity k .
- 18.34 Identify that thermal energy can be transferred by

convection, in which a warmer fluid (gas or liquid) tends to rise in a cooler fluid.

- 18.35 In the *emission* of thermal radiation by an object, apply the relationship between the energy-transfer rate P_{rad} and the object's surface area A , emissivity ε , and *surface* temperature T (in kelvins).
- 18.36 In the *absorption* of thermal radiation by an object, apply the relationship between the energy-transfer rate P_{abs} and the object's surface area A and emissivity ε , and the *environmental* temperature T (in kelvins).
- 18.37 Calculate the net energy-transfer rate P_{net} of an object emitting radiation to its environment and absorbing radiation from that environment.

Key Ideas

- The rate P_{cond} at which energy is conducted through a slab for which one face is maintained at the higher temperature T_H and the other face is maintained at the lower temperature T_C is

$$P_{\text{cond}} = \frac{Q}{t} = kA \frac{T_H - T_C}{L}.$$

Here each face of the slab has area A , the length of the slab (the distance between the faces) is L , and k is the thermal conductivity of the material.

- Convection occurs when temperature differences cause an energy transfer by motion within a fluid.

- Radiation is an energy transfer via the emission of electromagnetic energy. The rate P_{rad} at which an object emits energy via thermal radiation is

$$P_{\text{rad}} = \sigma \varepsilon A T^4,$$

where $\sigma (= 5.6704 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4)$ is the Stefan – Boltzmann constant, ε is the emissivity of the object's surface, A is its surface area, and T is its surface temperature (in kelvins). The rate P_{abs} at which an object absorbs energy via thermal radiation from its environment, which is at the uniform temperature T_{env} (in kelvins), is

$$P_{\text{abs}} = \sigma \varepsilon A T_{\text{env}}^4.$$

Heat Transfer Mechanisms

We have discussed the transfer of energy as heat between a system and its environment, but we have not yet described how that transfer takes place. There are three transfer mechanisms: conduction, convection, and radiation. Let's next examine these mechanisms in turn.

Conduction

If you leave the end of a metal poker in a fire for enough time, its handle will get hot. Energy is transferred from the fire to the handle by (thermal) **conduction** along the length of the poker. The vibration amplitudes of the atoms and electrons of the metal at the fire end of the poker become relatively large because of the high temperature of their environment. These increased vibrational amplitudes, and thus the associated energy, are passed along the poker, from atom to atom, during collisions between adjacent atoms. In this way, a region of rising temperature extends itself along the poker to the handle.

Consider a slab of face area A and thickness L , whose faces are maintained at temperatures T_H and T_C by a hot reservoir and a cold reservoir, as in Fig. 18-18. Let Q be the energy that is transferred as heat through the slab, from its hot face to its cold face, in time t . Experiment shows that the *conduction rate* P_{cond} (the

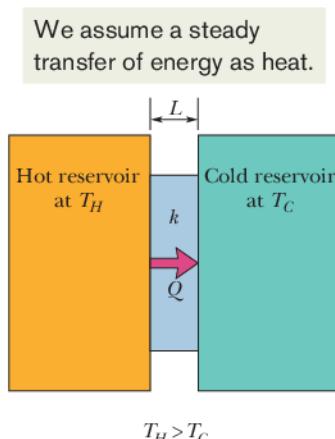


Figure 18-18 Thermal conduction. Energy is transferred as heat from a reservoir at temperature T_H to a cooler reservoir at temperature T_C through a conducting slab of thickness L and thermal conductivity k .

amount of energy transferred per unit time) is

$$P_{\text{cond}} = \frac{Q}{t} = kA \frac{T_H - T_C}{L}, \quad (18-32)$$

in which k , called the *thermal conductivity*, is a constant that depends on the material of which the slab is made. A material that readily transfers energy by conduction is a *good thermal conductor* and has a high value of k . Table 18-6 gives the thermal conductivities of some common metals, gases, and building materials.

Thermal Resistance to Conduction (R -Value)

If you are interested in insulating your house or in keeping cola cans cold on a picnic, you are more concerned with poor heat conductors than with good ones. For this reason, the concept of *thermal resistance* R has been introduced into engineering practice. The R -value of a slab of thickness L is defined as

$$R = \frac{L}{k}. \quad (18-33)$$

The lower the thermal conductivity of the material of which a slab is made, the higher the R -value of the slab; so something that has a high R -value is a *poor thermal conductor* and thus a *good thermal insulator*.

Note that R is a property attributed to a slab of a specified thickness, not to a material. The commonly used unit for R (which, in the United States at least, is almost never stated) is the square foot–Fahrenheit degree–hour per British thermal unit ($\text{ft}^2 \cdot \text{F}^\circ \cdot \text{h/Btu}$). (Now you know why the unit is rarely stated.)

Conduction Through a Composite Slab

Figure 18-19 shows a composite slab, consisting of two materials having different thicknesses L_1 and L_2 and different thermal conductivities k_1 and k_2 . The temperatures of the outer surfaces of the slab are T_H and T_C . Each face of the slab has area A . Let us derive an expression for the conduction rate through the slab under the assumption that the transfer is a *steady-state* process; that is, the temperatures everywhere in the slab and the rate of energy transfer do not change with time.

In the steady state, the conduction rates through the two materials must be equal. This is the same as saying that the energy transferred through one material in a certain time must be equal to that transferred through the other material in the same time. If this were not true, temperatures in the slab would be changing and we would not have a steady-state situation. Letting T_X be the temperature of the interface between the two materials, we can now use Eq. 18-32 to write

$$P_{\text{cond}} = \frac{k_2 A(T_H - T_X)}{L_2} = \frac{k_1 A(T_X - T_C)}{L_1}. \quad (18-34)$$

Solving Eq. 18-34 for T_X yields, after a little algebra,

$$T_X = \frac{k_1 L_2 T_C + k_2 L_1 T_H}{k_1 L_2 + k_2 L_1}. \quad (18-35)$$

Substituting this expression for T_X into either equality of Eq. 18-34 yields

$$P_{\text{cond}} = \frac{A(T_H - T_C)}{\frac{L_1}{k_1} + \frac{L_2}{k_2}}. \quad (18-36)$$

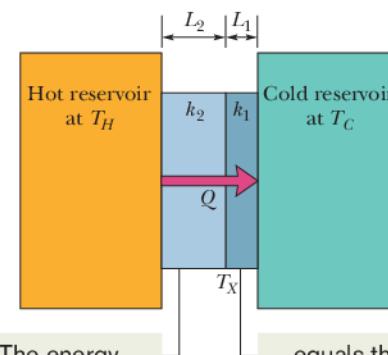
We can extend Eq. 18-36 to apply to any number n of materials making up a slab:

$$P_{\text{cond}} = \frac{A(T_H - T_C)}{\sum (L/k)}. \quad (18-37)$$

The summation sign in the denominator tells us to add the values of L/k for all the materials.

Table 18-6 Some Thermal Conductivities

Substance	k (W/m · K)
<i>Metals</i>	
Stainless steel	14
Lead	35
Iron	67
Brass	109
Aluminum	235
Copper	401
Silver	428
<i>Gases</i>	
Air (dry)	0.026
Helium	0.15
Hydrogen	0.18
<i>Building Materials</i>	
Polyurethane foam	0.024
Rock wool	0.043
Fiberglass	0.048
White pine	0.11
Window glass	1.0



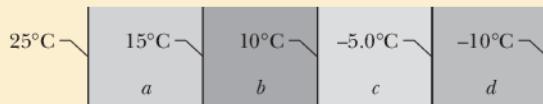
The energy transfer per second here equals the energy transfer per second here.

Figure 18-19 Heat is transferred at a steady rate through a composite slab made up of two different materials with different thicknesses and different thermal conductivities. The steady-state temperature at the interface of the two materials is T_X .



Checkpoint 7

The figure shows the face and interface temperatures of a composite slab consisting of four materials, of identical thicknesses, through which the heat transfer is steady. Rank the materials according to their thermal conductivities, greatest first.



Convection

When you look at the flame of a candle or a match, you are watching thermal energy being transported upward by **convection**. Such energy transfer occurs when a fluid, such as air or water, comes in contact with an object whose temperature is higher than that of the fluid. The temperature of the part of the fluid that is in contact with the hot object increases, and (in most cases) that fluid expands and thus becomes less dense. Because this expanded fluid is now lighter than the surrounding cooler fluid, buoyant forces cause it to rise. Some of the surrounding cooler fluid then flows so as to take the place of the rising warmer fluid, and the process can then continue.

Convection is part of many natural processes. Atmospheric convection plays a fundamental role in determining global climate patterns and daily weather variations. Glider pilots and birds alike seek rising thermals (convection currents of warm air) that keep them aloft. Huge energy transfers take place within the oceans by the same process. Finally, energy is transported to the surface of the Sun from the nuclear furnace at its core by enormous cells of convection, in which hot gas rises to the surface along the cell core and cooler gas around the core descends below the surface.

Radiation

The third method by which an object and its environment can exchange energy as heat is via electromagnetic waves (visible light is one kind of electromagnetic wave). Energy transferred in this way is often called **thermal radiation** to distinguish it from electromagnetic *signals* (as in, say, television broadcasts) and from nuclear radiation (energy and particles emitted by nuclei). (To “radiate” generally means to emit.) When you stand in front of a big fire, you are warmed by absorbing thermal radiation from the fire; that is, your thermal energy increases as the fire’s thermal energy decreases. No medium is required for heat transfer via radiation—the radiation can travel through vacuum from, say, the Sun to you.

The rate P_{rad} at which an object emits energy via electromagnetic radiation depends on the object’s surface area A and the temperature T of that area in kelvins and is given by

$$P_{\text{rad}} = \sigma \epsilon A T^4. \quad (18-38)$$

Here $\sigma = 5.6704 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$ is called the *Stefan–Boltzmann constant* after Josef Stefan (who discovered Eq. 18-38 experimentally in 1879) and Ludwig Boltzmann (who derived it theoretically soon after). The symbol ϵ represents the *emissivity* of the object’s surface, which has a value between 0 and 1, depending on the composition of the surface. A surface with the maximum emissivity of 1.0 is said to be a *blackbody radiator*, but such a surface is an ideal limit and does not occur in nature. Note again that the temperature in Eq. 18-38 must be in kelvins so that a temperature of absolute zero corresponds to no radiation. Note also that every object whose temperature is above 0 K—including you—emits thermal radiation. (See Fig. 18-20.)



Edward Kinsman/Photo Researchers, Inc.

Figure 18-20 A false-color thermogram reveals the rate at which energy is radiated by a cat. The rate is color-coded, with white and red indicating the greatest radiation rate. The nose is cool.

The rate P_{abs} at which an object absorbs energy via thermal radiation from its environment, which we take to be at uniform temperature T_{env} (in kelvins), is

$$P_{\text{abs}} = \sigma \epsilon A T_{\text{env}}^4. \quad (18-39)$$

The emissivity ϵ in Eq. 18-39 is the same as that in Eq. 18-38. An idealized blackbody radiator, with $\epsilon = 1$, will absorb all the radiated energy it intercepts (rather than sending a portion back away from itself through reflection or scattering).

Because an object both emits and absorbs thermal radiation, its net rate P_{net} of energy exchange due to thermal radiation is

$$P_{\text{net}} = P_{\text{abs}} - P_{\text{rad}} = \sigma \epsilon A (T_{\text{env}}^4 - T^4). \quad (18-40)$$

P_{net} is positive if net energy is being absorbed via radiation and negative if it is being lost via radiation.

Thermal radiation is involved in the numerous medical cases of a *dead* rattlesnake striking a hand reaching toward it. Pits between each eye and nostril of a rattlesnake (Fig. 18-21) serve as sensors of thermal radiation. When, say, a mouse moves close to a rattlesnake's head, the thermal radiation from the mouse triggers these sensors, causing a reflex action in which the snake strikes the mouse with its fangs and injects its venom. The thermal radiation from a reaching hand can cause the same reflex action even if the snake has been dead for as long as 30 min because the snake's nervous system continues to function. As one snake expert advised, if you must remove a recently killed rattlesnake, use a long stick rather than your hand.



© David A. Northcott/Corbis Images

Figure 18-21 A rattlesnake's face has thermal radiation detectors, allowing the snake to strike at an animal even in complete darkness.

Sample Problem 18.06 Thermal conduction through a layered wall

Figure 18-22 shows the cross section of a wall made of white pine of thickness L_a and brick of thickness L_d ($= 2.0L_a$), sandwiching two layers of unknown material with identical thicknesses and thermal conductivities. The thermal conductivity of the pine is k_a and that of the brick is k_d ($= 5.0k_a$). The face area A of the wall is unknown. Thermal conduction through the wall has reached the steady state; the only known interface temperatures are $T_1 = 25^\circ\text{C}$, $T_2 = 20^\circ\text{C}$, and $T_5 = -10^\circ\text{C}$. What is interface temperature T_4 ?

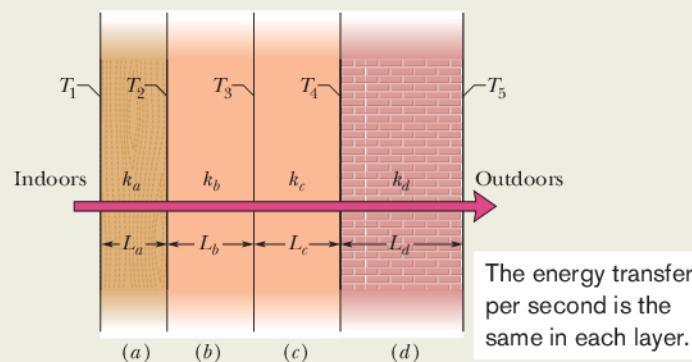


Figure 18-22 Steady-state heat transfer through a wall.

KEY IDEAS

- (1) Temperature T_4 helps determine the rate P_d at which energy is conducted through the brick, as given by Eq. 18-32. However, we lack enough data to solve Eq. 18-32 for T_4 .
- (2) Because the conduction is steady, the conduction rate P_d through the brick must equal the conduction rate P_a through the pine. That gets us going.

Calculations: From Eq. 18-32 and Fig. 18-22, we can write

$$P_a = k_a A \frac{T_1 - T_2}{L_a} \quad \text{and} \quad P_d = k_d A \frac{T_4 - T_5}{L_d}.$$

Setting $P_a = P_d$ and solving for T_4 yield

$$T_4 = \frac{k_a L_d}{k_d L_a} (T_1 - T_2) + T_5.$$

Letting $L_d = 2.0L_a$ and $k_d = 5.0k_a$, and inserting the known temperatures, we find

$$\begin{aligned} T_4 &= \frac{k_a (2.0L_a)}{(5.0k_a)L_a} (25^\circ\text{C} - 20^\circ\text{C}) + (-10^\circ\text{C}) \\ &= -8.0^\circ\text{C}. \end{aligned} \quad (\text{Answer})$$



Sample Problem 18.07 Thermal radiation by a skunk cabbage can melt surrounding snow

Unlike most other plants, a skunk cabbage can regulate its internal temperature (set at $T = 22^\circ\text{C}$) by altering the rate at which it produces energy. If it becomes covered with snow, it can increase that production so that its thermal radiation melts the snow in order to re-expose the plant to sunlight. Let's model a skunk cabbage with a cylinder of height $h = 5.0 \text{ cm}$ and radius $R = 1.5 \text{ cm}$ and assume it is surrounded by a snow wall at temperature $T_{\text{env}} = -3.0^\circ\text{C}$ (Fig. 18-23). If the emissivity ϵ is 0.80, what is the net rate of energy exchange via thermal radiation between the plant's curved side and the snow?

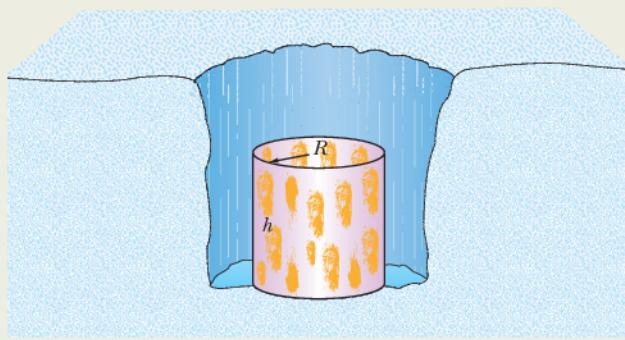


Figure 18-23 Model of skunk cabbage that has melted snow to uncover itself.

KEY IDEAS

- (1) In a steady-state situation, a surface with area A , emissivity ϵ , and temperature T loses energy to thermal radiation at the rate given by Eq. 18-38 ($P_{\text{rad}} = \sigma\epsilon AT^4$). (2) Simultaneously, it gains energy by thermal radiation from its environment at temperature T_{env} at the rate given by Eq. 18-39 ($P_{\text{env}} = \sigma\epsilon AT_{\text{env}}^4$).

Calculations: To find the net rate of energy exchange, we subtract Eq. 18-38 from Eq. 18-39 to write

$$\begin{aligned} P_{\text{net}} &= P_{\text{abs}} - P_{\text{rad}} \\ &= \sigma\epsilon A(T_{\text{env}}^4 - T^4). \end{aligned} \quad (18-41)$$

We need the area of the curved surface of the cylinder, which is $A = h(2\pi R)$. We also need the temperatures in kelvins: $T_{\text{env}} = 273 \text{ K} - 3 \text{ K} = 270 \text{ K}$ and $T = 273 \text{ K} + 22 \text{ K} = 295 \text{ K}$. Substituting in Eq. 18-41 for A and then substituting known values in SI units (which are not displayed here), we find

$$\begin{aligned} P_{\text{net}} &= (5.67 \times 10^{-8})(0.80)(0.050)(2\pi)(0.015)(270^4 - 295^4) \\ &= -0.48 \text{ W}. \end{aligned} \quad (\text{Answer})$$

Thus, the plant has a net loss of energy via thermal radiation of 0.48 W. The plant's energy production rate is comparable to that of a hummingbird in flight.



Additional examples, video, and practice available at WileyPLUS

Review & Summary

Temperature; Thermometers Temperature is an SI base quantity related to our sense of hot and cold. It is measured with a thermometer, which contains a working substance with a measurable property, such as length or pressure, that changes in a regular way as the substance becomes hotter or colder.

Zeroth Law of Thermodynamics When a thermometer and some other object are placed in contact with each other, they eventually reach thermal equilibrium. The reading of the thermometer is then taken to be the temperature of the other object. The process provides consistent and useful temperature measurements because of the **zeroth law of thermodynamics**: If bodies A and B are each in thermal equilibrium with a third body C (the thermometer), then A and B are in thermal equilibrium with each other.

The Kelvin Temperature Scale In the SI system, temperature is measured on the **Kelvin scale**, which is based on the *triple point* of water (273.16 K). Other temperatures are then defined by

use of a *constant-volume gas thermometer*, in which a sample of gas is maintained at constant volume so its pressure is proportional to its temperature. We define the *temperature T* as measured with a gas thermometer to be

$$T = (273.16 \text{ K}) \left(\lim_{\text{gas} \rightarrow 0} \frac{p}{p_3} \right). \quad (18-6)$$

Here T is in kelvins, and p_3 and p are the pressures of the gas at 273.16 K and the measured temperature, respectively.

Celsius and Fahrenheit Scales The Celsius temperature scale is defined by

$$T_C = T - 273.15^\circ, \quad (18-7)$$

with T in kelvins. The Fahrenheit temperature scale is defined by

$$T_F = \frac{9}{5}T_C + 32^\circ. \quad (18-8)$$

Thermal Expansion All objects change size with changes in temperature. For a temperature change ΔT , a change ΔL in any linear dimension L is given by

$$\Delta L = L\alpha \Delta T, \quad (18-9)$$

in which α is the **coefficient of linear expansion**. The change ΔV in the volume V of a solid or liquid is

$$\Delta V = V\beta \Delta T. \quad (18-10)$$

Here $\beta = 3\alpha$ is the material's **coefficient of volume expansion**.

Heat Heat Q is energy that is transferred between a system and its environment because of a temperature difference between them. It can be measured in **joules** (J), **calories** (cal), **kilocalories** (Cal or kcal), or **British thermal units** (Btu), with

$$1 \text{ cal} = 3.968 \times 10^{-3} \text{ Btu} = 4.1868 \text{ J}. \quad (18-12)$$

Heat Capacity and Specific Heat If heat Q is absorbed by an object, the object's temperature change $T_f - T_i$ is related to Q by

$$Q = C(T_f - T_i), \quad (18-13)$$

in which C is the **heat capacity** of the object. If the object has mass m , then

$$Q = cm(T_f - T_i), \quad (18-14)$$

where c is the **specific heat** of the material making up the object. The **molar specific heat** of a material is the heat capacity per mole, which means per 6.02×10^{23} elementary units of the material.

Heat of Transformation Matter can exist in three common states: solid, liquid, and vapor. Heat absorbed by a material may change the material's physical state—for example, from solid to liquid or from liquid to gas. The amount of energy required per unit mass to change the state (but not the temperature) of a particular material is its **heat of transformation** L . Thus,

$$Q = Lm. \quad (18-16)$$

The **heat of vaporization** L_V is the amount of energy per unit mass that must be added to vaporize a liquid or that must be removed to condense a gas. The **heat of fusion** L_F is the amount of energy per unit mass that must be added to melt a solid or that must be removed to freeze a liquid.

Work Associated with Volume Change A gas may exchange energy with its surroundings through work. The amount of work W done by a gas as it expands or contracts from an initial volume V_i to a final volume V_f is given by

$$W = \int dW = \int_{V_i}^{V_f} p \, dV. \quad (18-25)$$

The integration is necessary because the pressure p may vary during the volume change.

First Law of Thermodynamics The principle of conservation of energy for a thermodynamic process is expressed in the **first law of thermodynamics**, which may assume either of the forms

$$\Delta E_{\text{int}} = E_{\text{int},f} - E_{\text{int},i} = Q - W \quad (\text{first law}) \quad (18-26)$$

$$\text{or} \quad dE_{\text{int}} = dQ - dW \quad (\text{first law}). \quad (18-27)$$

E_{int} represents the internal energy of the material, which depends only on the material's state (temperature, pressure, and volume). Q represents the energy exchanged as heat between the system and its surroundings; Q is positive if the system absorbs heat and negative if the system loses heat. W is the work done by the system; W is positive if the system expands against an external force from the surroundings and negative if the system contracts because of an external force. Q and W are path dependent; ΔE_{int} is path independent.

Applications of the First Law The first law of thermodynamics finds application in several special cases:

$$\text{adiabatic processes: } Q = 0, \quad \Delta E_{\text{int}} = -W$$

$$\text{constant-volume processes: } W = 0, \quad \Delta E_{\text{int}} = Q$$

$$\text{cyclical processes: } \Delta E_{\text{int}} = 0, \quad Q = W$$

$$\text{free expansions: } Q = W = \Delta E_{\text{int}} = 0$$

Conduction, Convection, and Radiation The rate P_{cond} at which energy is *conducted* through a slab for which one face is maintained at the higher temperature T_H and the other face is maintained at the lower temperature T_C is

$$P_{\text{cond}} = \frac{Q}{t} = kA \frac{T_H - T_C}{L} \quad (18-32)$$

Here each face of the slab has area A , the length of the slab (the distance between the faces) is L , and k is the thermal conductivity of the material.

Convection occurs when temperature differences cause an energy transfer by motion within a fluid.

Radiation is an energy transfer via the emission of electromagnetic energy. The rate P_{rad} at which an object emits energy via thermal radiation is

$$P_{\text{rad}} = \sigma \varepsilon A T^4, \quad (18-38)$$

where $\sigma (= 5.6704 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4)$ is the Stefan–Boltzmann constant, ε is the emissivity of the object's surface, A is its surface area, and T is its surface temperature (in kelvins). The rate P_{abs} at which an object absorbs energy via thermal radiation from its environment, which is at the uniform temperature T_{env} (in kelvins), is

$$P_{\text{abs}} = \sigma \varepsilon A T_{\text{env}}^4. \quad (18-39)$$


Questions

- 1** The initial length L , change in temperature ΔT , and change in length ΔL of four rods are given in the following table. Rank the rods according to their coefficients of thermal expansion, greatest first.

Rod	L (m)	ΔT ($^{\circ}$ C)	ΔL (m)
a	2	10	4×10^{-4}
b	1	20	4×10^{-4}
c	2	10	8×10^{-4}
d	4	5	4×10^{-4}

- 2** Figure 18-24 shows three linear temperature scales, with the freezing and boiling points of water indicated. Rank the three scales according to the size of one degree on them, greatest first.

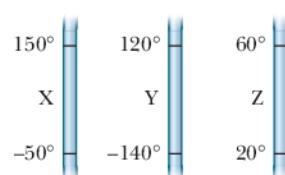


Figure 18-24 Question 2.

- 3** Materials A, B, and C are solids that are at their melting temperatures. Material A requires 200 J to melt 4 kg, material B requires 300 J to melt 5 kg, and material C requires 300 J to melt 6 kg. Rank the materials according to their heats of fusion, greatest first.

- 4** A sample A of liquid water and a sample B of ice, of identical mass, are placed in a thermally insulated container and allowed to come to thermal equilibrium. Figure 18-25a is a sketch of the temperature T of the samples versus time t . (a) Is the equilibrium temperature above, below, or at the freezing point of water? (b) In reaching equilibrium, does the liquid partly freeze, fully freeze, or undergo no freezing? (c) Does the ice partly melt, fully melt, or undergo no melting?

- 5** Question 4 continued: Graphs b through f of Fig. 18-25 are additional sketches of T versus t , of which one or more are impossible to produce. (a) Which is impossible and why? (b) In the possible ones, is the equilibrium temperature above, below, or at the freezing point of water? (c) As the possible situations reach equilibrium, does the liquid partly freeze, fully freeze, or undergo no freezing? Does the ice partly melt, fully melt, or undergo no melting?

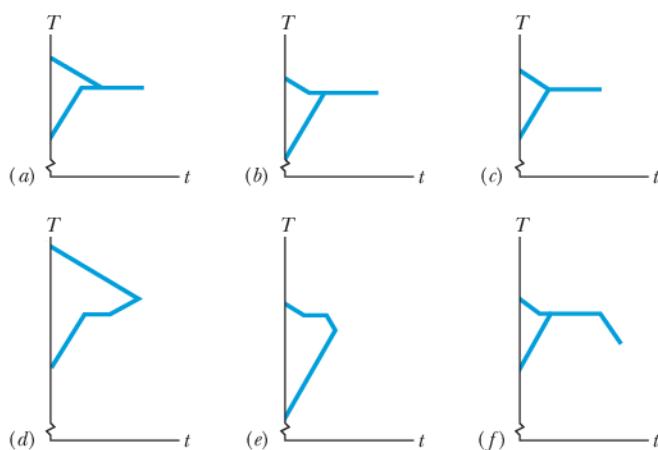


Figure 18-25 Questions 4 and 5.

- 6** Figure 18-26 shows three different arrangements of materials 1, 2, and 3 to form a wall. The thermal conductivities are $k_1 > k_2 > k_3$. The left side of the wall is 20° higher than the right side. Rank the arrangements according to (a) the (steady state) rate of energy conduction through the wall and (b) the temperature difference across material 1, greatest first.

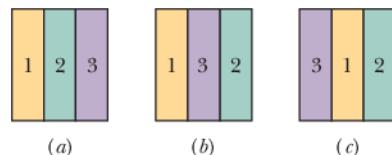


Figure 18-26 Question 6.

- 7** Figure 18-27 shows two closed cycles on p - V diagrams for a gas. The three parts of cycle 1 are of the same length and shape as those of cycle 2. For each cycle, should the cycle be traversed clockwise or counterclockwise if (a) the net work W done by the gas is to be positive and (b) the net energy transferred by the gas as heat Q is to be positive?

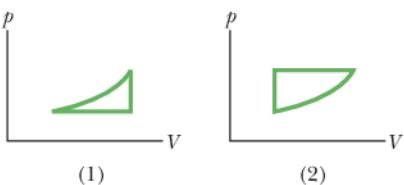


Figure 18-27 Questions 7 and 8.

- 8** For which cycle in Fig. 18-27, traversed clockwise, is (a) W greater and (b) Q greater?

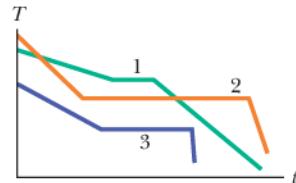


Figure 18-28 Question 9.

- 9** Three different materials of identical mass are placed one at a time in a special freezer that can extract energy from a material at a certain constant rate. During the cooling process, each material begins in the liquid state and ends in the solid state; Fig. 18-28 shows the temperature T versus time t . (a) For material 1, is the specific heat for the liquid state greater than or less than that for the solid state? Rank the materials according to (b) freezing-point temperature, (c) specific heat in the liquid state, (d) specific heat in the solid state, and (e) heat of fusion, all greatest first.

- 10** A solid cube of edge length r , a solid sphere of radius r , and a solid hemisphere of radius r , all made of the same material, are maintained at temperature 300 K in an environment at temperature 350 K . Rank the objects according to the net rate at which thermal radiation is exchanged with the environment, greatest first.

- 11** A hot object is dropped into a thermally insulated container of water, and the object and water are then allowed to come to thermal equilibrium. The experiment is repeated twice, with different hot objects. All three objects have the same mass and initial temperature, and the mass and initial temperature of the water are the same in the three experiments. For each of the experiments, Fig. 18-29 gives graphs of the temperatures T of the object and the water versus time t . Rank the graphs according to the specific heats of the objects, greatest first.

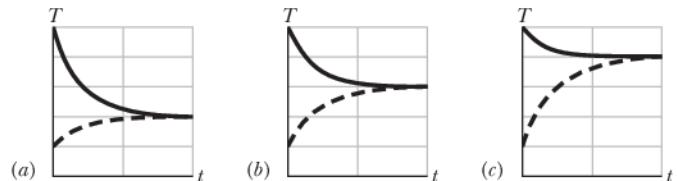


Figure 18-29 Question 11.

Problems



Tutoring problem available (at instructor's discretion) in WileyPLUS and WebAssign

SSM Worked-out solution available in Student Solutions Manual

••• Number of dots indicates level of problem difficulty

Additional information available in *The Flying Circus of Physics* and at flyingcircusofphysics.com

WWW Worked-out solution is at

ILW Interactive solution is at

<http://www.wiley.com/college/halliday>

Module 18-1 Temperature

- 1 Suppose the temperature of a gas is 373.15 K when it is at the boiling point of water. What then is the limiting value of the ratio of the pressure of the gas at that boiling point to its pressure at the triple point of water? (Assume the volume of the gas is the same at both temperatures.)

- 2 Two constant-volume gas thermometers are assembled, one with nitrogen and the other with hydrogen. Both contain enough gas so that $p_3 = 80 \text{ kPa}$. (a) What is the difference between the pressures in the two thermometers if both bulbs are in boiling water? (*Hint:* See Fig. 18-6.) (b) Which gas is at higher pressure?

- 3 A gas thermometer is constructed of two gas-containing bulbs, each in a water bath, as shown in Fig. 18-30. The pressure difference between the two bulbs is measured by a mercury manometer as shown. Appropriate reservoirs, not shown in the diagram, maintain constant gas volume in the two bulbs. There is no difference in pressure when both baths are at the triple point of water. The pressure difference is 120 torr when one bath is at the triple point and the other is at the boiling point of water. It is 90.0 torr when one bath is at the triple point and the other is at an unknown temperature to be measured. What is the unknown temperature?

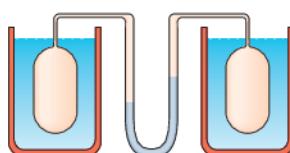


Figure 18-30 Problem 3.

Module 18-2 The Celsius and Fahrenheit Scales

- 4 (a) In 1964, the temperature in the Siberian village of Oymyakon reached -71°C . What temperature is this on the Fahrenheit scale? (b) The highest officially recorded temperature in the continental United States was 134°F in Death Valley, California. What is this temperature on the Celsius scale?

- 5 At what temperature is the Fahrenheit scale reading equal to (a) twice that of the Celsius scale and (b) half that of the Celsius scale?

- 6 On a linear X temperature scale, water freezes at -125.0°X and boils at 375.0°X . On a linear Y temperature scale, water freezes at -70.00°Y and boils at -30.00°Y . A temperature of 50.00°Y corresponds to what temperature on the X scale?

- 7 **ILW** Suppose that on a linear temperature scale X, water boils at -53.5°X and freezes at -170°X . What is a temperature of 340 K on the X scale? (Approximate water's boiling point as 373 K.)

Module 18-3 Thermal Expansion

- 8 At 20°C , a brass cube has edge length 30 cm. What is the increase in the surface area when it is heated from 20°C to 75°C ?

- 9 **ILW** A circular hole in an aluminum plate is 2.725 cm in diameter at 0.000°C . What is its diameter when the temperature of the plate is raised to 100.0°C ?

- 10 An aluminum flagpole is 33 m high. By how much does its length increase as the temperature increases by 15°C ?

- 11 What is the volume of a lead ball at 30.00°C if the ball's volume at 60.00°C is 50.00 cm^3 ?

- 12 An aluminum-alloy rod has a length of 10.000 cm at 20.000°C and a length of 10.015 cm at the boiling point of water. (a) What is the length of the rod at the freezing point of water? (b) What is the temperature if the length of the rod is 10.009 cm?

- 13 **SSM** Find the change in volume of an aluminum sphere with an initial radius of 10 cm when the sphere is heated from 0.0°C to 100°C .

- 14 When the temperature of a copper coin is raised by 100°C , its diameter increases by 0.18%. To two significant figures, give the percent increase in (a) the area of a face, (b) the thickness, (c) the volume, and (d) the mass of the coin. (e) Calculate the coefficient of linear expansion of the coin.

- 15 **ILW** A steel rod is 3.000 cm in diameter at 25.00°C . A brass ring has an interior diameter of 2.992 cm at 25.00°C . At what common temperature will the ring just slide onto the rod?

- 16 When the temperature of a metal cylinder is raised from 0.0°C to 100°C , its length increases by 0.23%. (a) Find the percent change in density. (b) What is the metal? Use Table 18-2.

- 17 **SSM** **WWW** An aluminum cup of 100 cm^3 capacity is completely filled with glycerin at 22°C . How much glycerin, if any, will spill out of the cup if the temperature of both the cup and the glycerin is increased to 28°C ? (The coefficient of volume expansion of glycerin is $5.1 \times 10^{-4}/^\circ\text{C}$.)

- 18 At 20°C , a rod is exactly 20.05 cm long on a steel ruler. Both are placed in an oven at 270°C , where the rod now measures 20.11 cm on the same ruler. What is the coefficient of linear expansion for the material of which the rod is made?

- 19 **GO** A vertical glass tube of length $L = 1.280\,000 \text{ m}$ is half filled with a liquid at $20.00\,000^\circ\text{C}$. How much will the height of the liquid column change when the tube and liquid are heated to $30.000\,000^\circ\text{C}$? Use coefficients $\alpha_{\text{glass}} = 1.000\,000 \times 10^{-5}/\text{K}$ and $\beta_{\text{liquid}} = 4.000\,000 \times 10^{-5}/\text{K}$.

- 20 **GO** In a certain experiment, a small radioactive source must move at selected, extremely slow speeds. This motion is accomplished by fastening the source to one end of an aluminum rod and heating the central section of the rod in a controlled way. If the effective heated section of the rod in Fig. 18-31 has length $d = 2.00 \text{ cm}$, at what constant rate must the temperature of the rod be changed if the source is to move at a constant speed of 100 nm/s ?

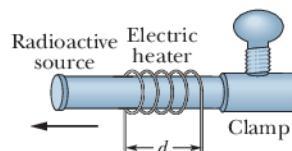


Figure 18-31 Problem 20.

- 21 **SSM** **ILW** As a result of a temperature rise of 32°C , a bar with a crack at its center buckles upward (Fig. 18-32). The fixed distance L_0 is 3.77 m and the coefficient of linear expansion of the bar is $25 \times 10^{-6}/^\circ\text{C}$. Find the rise x of the center.

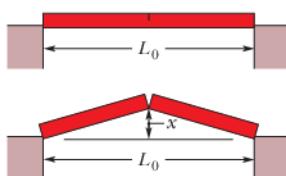


Figure 18-32 Problem 21.

Module 18-4 Absorption of Heat

•22 One way to keep the contents of a garage from becoming too cold on a night when a severe subfreezing temperature is forecast is to put a tub of water in the garage. If the mass of the water is 125 kg and its initial temperature is 20°C, (a) how much energy must the water transfer to its surroundings in order to freeze completely and (b) what is the lowest possible temperature of the water and its surroundings until that happens?

•23 SSM A small electric immersion heater is used to heat 100 g of water for a cup of instant coffee. The heater is labeled “200 watts” (it converts electrical energy to thermal energy at this rate). Calculate the time required to bring all this water from 23.0°C to 100°C, ignoring any heat losses.

•24 A certain substance has a mass per mole of 50.0 g/mol. When 314 J is added as heat to a 30.0 g sample, the sample’s temperature rises from 25.0°C to 45.0°C. What are the (a) specific heat and (b) molar specific heat of this substance? (c) How many moles are in the sample?

•25 A certain diet doctor encourages people to diet by drinking ice water. His theory is that the body must burn off enough fat to raise the temperature of the water from 0.00°C to the body temperature of 37.0°C. How many liters of ice water would have to be consumed to burn off 454 g (about 1 lb) of fat, assuming that burning this much fat requires 3500 Cal be transferred to the ice water? Why is it not advisable to follow this diet? (One liter = 10^3 cm³. The density of water is 1.00 g/cm³.)

•26 What mass of butter, which has a usable energy content of 6.0 Cal/g (= 6000 cal/g), would be equivalent to the change in gravitational potential energy of a 73.0 kg man who ascends from sea level to the top of Mt. Everest, at elevation 8.84 km? Assume that the average g for the ascent is 9.80 m/s².

•27 SSM Calculate the minimum amount of energy, in joules, required to completely melt 130 g of silver initially at 15.0°C.

•28 How much water remains unfrozen after 50.2 kJ is transferred as heat from 260 g of liquid water initially at its freezing point?

•29 In a solar water heater, energy from the Sun is gathered by water that circulates through tubes in a rooftop collector. The solar radiation enters the collector through a transparent cover and warms the water in the tubes; this water is pumped into a holding tank. Assume that the efficiency of the overall system is 20% (that is, 80% of the incident solar energy is lost from the system). What collector area is necessary to raise the temperature of 200 L of water in the tank from 20°C to 40°C in 1.0 h when the intensity of incident sunlight is 700 W/m²?

•30 A 0.400 kg sample is placed in a cooling apparatus that removes energy as heat at a constant rate. Figure 18-33 gives the temperature T of the sample versus time t ; the horizontal scale is set by $t_s = 80.0$ min. The sample freezes during the energy removal. The specific heat of the sample in its initial liquid phase is 3000 J/kg · K. What are (a) the sample’s heat of fusion and (b) its specific heat in the frozen phase?

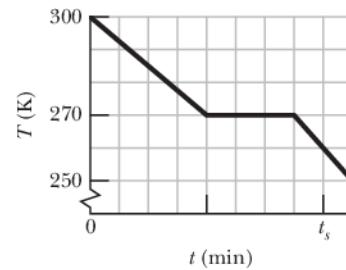


Figure 18-33 Problem 30.

•31 ILW What mass of steam at 100°C must be mixed with 150 g of ice at its melting point, in a thermally insulated container, to produce liquid water at 50°C?

•32 The specific heat of a substance varies with temperature according to the function $c = 0.20 + 0.14T + 0.023T^2$, with T in °C and c in cal/g · K. Find the energy required to raise the temperature of 2.0 g of this substance from 5.0°C to 15°C.

•33 Nonmetric version: (a) How long does a 2.0×10^5 Btu/h water heater take to raise the temperature of 40 gal of water from 70°F to 100°F? **Metric version:** (b) How long does a 59 kW water heater take to raise the temperature of 150 L of water from 21°C to 38°C?

•34 GO Samples *A* and *B* are at different initial temperatures when they are placed in a thermally insulated container and allowed to come to thermal equilibrium. Figure 18-34a gives their temperatures T versus time t . Sample *A* has a mass of 5.0 kg; sample *B* has a mass of 1.5 kg. Figure 18-34b is a general plot for the material of sample *B*. It shows the temperature change ΔT that the material undergoes when energy is transferred to it as heat Q . The change ΔT is plotted versus the energy Q per unit mass of the material, and the scale of the vertical axis is set by $\Delta T_s = 4.0$ °C. What is the specific heat of sample *A*?

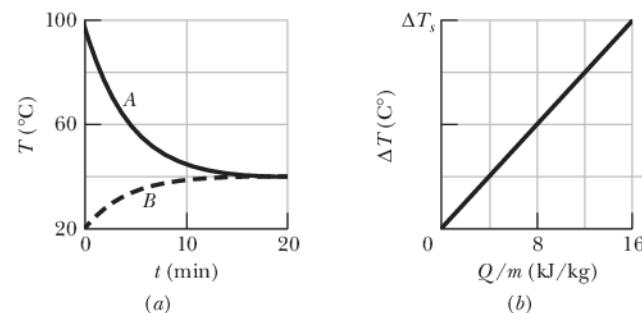


Figure 18-34 Problem 34.

•35 An insulated Thermos contains 130 cm³ of hot coffee at 80.0°C. You put in a 12.0 g ice cube at its melting point to cool the coffee. By how many degrees has your coffee cooled once the ice has melted and equilibrium is reached? Treat the coffee as though it were pure water and neglect energy exchanges with the environment.

•36 A 150 g copper bowl contains 220 g of water, both at 20.0°C. A very hot 300 g copper cylinder is dropped into the water, causing the water to boil, with 5.00 g being converted to steam. The final temperature of the system is 100°C. Neglect energy transfers with the environment. (a) How much energy (in calories) is transferred to the water as heat? (b) How much to the bowl? (c) What is the original temperature of the cylinder?

•37 A person makes a quantity of iced tea by mixing 500 g of hot tea (essentially water) with an equal mass of ice at its melting point. Assume the mixture has negligible energy exchanges with its environment. If the tea’s initial temperature is $T_i = 90^\circ\text{C}$, when thermal equilibrium is reached what are (a) the mixture’s temperature T_f and (b) the remaining mass m_f of ice? If $T_i = 70^\circ\text{C}$, when thermal equilibrium is reached what are (c) T_f and (d) m_f ?

•38 A 0.530 kg sample of liquid water and a sample of ice are placed in a thermally insulated container. The container also contains a device that transfers energy as heat from the liquid water to the ice at a constant rate P , until thermal equilibrium is

reached. The temperatures T of the liquid water and the ice are given in Fig. 18-35 as functions of time t ; the horizontal scale is set by $t_s = 80.0 \text{ min}$. (a) What is rate P ? (b) What is the initial mass of the ice in the container? (c) When thermal equilibrium is reached, what is the mass of the ice produced in this process?

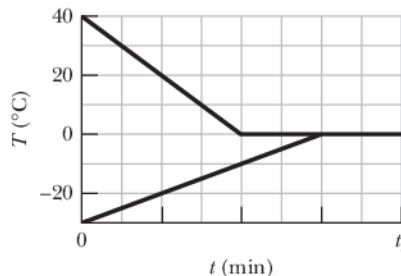


Figure 18-35 Problem 38.

••39 GO Ethyl alcohol has a boiling point of 78.0°C , a freezing point of -114°C , a heat of vaporization of 879 kJ/kg , a heat of fusion of 109 kJ/kg , and a specific heat of $2.43 \text{ kJ/kg}\cdot\text{K}$. How much energy must be removed from 0.510 kg of ethyl alcohol that is initially a gas at 78.0°C so that it becomes a solid at -114°C ?

••40 GO Calculate the specific heat of a metal from the following data. A container made of the metal has a mass of 3.6 kg and contains 14 kg of water. A 1.8 kg piece of the metal initially at a temperature of 180°C is dropped into the water. The container and water initially have a temperature of 16.0°C , and the final temperature of the entire (insulated) system is 18.0°C .

••41 SSM WWW (a) Two 50 g ice cubes are dropped into 200 g of water in a thermally insulated container. If the water is initially at 25°C , and the ice comes directly from a freezer at -15°C , what is the final temperature at thermal equilibrium? (b) What is the final temperature if only one ice cube is used?

••42 GO A 20.0 g copper ring at 0.000°C has an inner diameter of $D = 2.54000 \text{ cm}$. An aluminum sphere at 100.0°C has a diameter of $d = 2.54508 \text{ cm}$. The sphere is put on top of the ring (Fig. 18-36), and the two are allowed to come to thermal equilibrium, with no heat lost to the surroundings. The sphere just passes through the ring at the equilibrium temperature. What is the mass of the sphere?

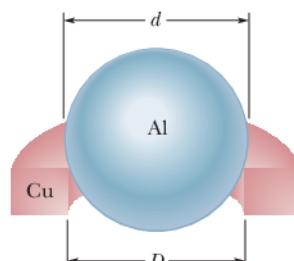


Figure 18-36 Problem 42.

Module 18-5 The First Law of Thermodynamics

•43 In Fig. 18-37, a gas sample expands from V_0 to $4.0V_0$ while its pressure decreases from p_0 to $p_0/4.0$. If $V_0 = 1.0 \text{ m}^3$ and $p_0 = 40 \text{ Pa}$, how much work is done by the gas if its pressure changes with volume via (a) path A, (b) path B, and (c) path C?

•44 GO A thermodynamic system is taken from state A to state B to

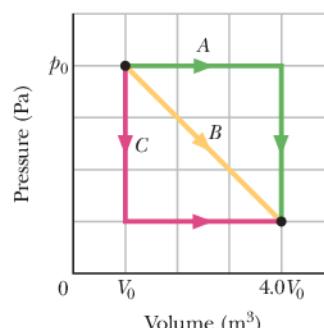


Figure 18-37 Problem 43.

state C , and then back to A , as shown in the p - V diagram of Fig. 18-38a. The vertical scale is set by $p_s = 40 \text{ Pa}$, and the horizontal scale is set by $V_s = 4.0 \text{ m}^3$. (a)–(g) Complete the table in Fig. 18-38b by inserting a plus sign, a minus sign, or a zero in each indicated cell. (h) What is the net work done by the system as it moves once through the cycle $ABCA$?

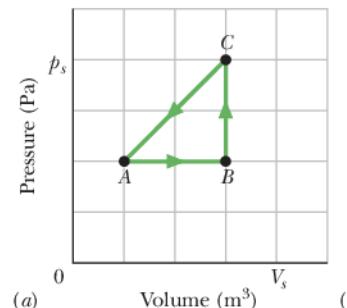


Figure 18-38 Problem 44.

	Q	W	ΔE_{int}
$A \rightarrow B$	(a)	(b)	+
$B \rightarrow C$	+	(c)	(d)
$C \rightarrow A$	(e)	(f)	(g)

•45 SSM ILW A gas within a closed chamber undergoes the cycle shown in the p - V diagram of Fig. 18-39. The horizontal scale is set by $V_s = 4.0 \text{ m}^3$. Calculate the net energy added to the system as heat during one complete cycle.

•46 Suppose 200 J of work is done on a system and 70.0 cal is extracted from the system as heat. In the sense of the first law of thermodynamics, what are the values (including algebraic signs) of (a) W , (b) Q , and (c) ΔE_{int} ?

•47 SSM WWW When a system is taken from state i to state f along path iaf in Fig. 18-40, $Q = 50 \text{ cal}$ and $W = 20 \text{ cal}$. Along path ibf , $Q = 36 \text{ cal}$. (a) What is W along path ibf ? (b) If $W = -13 \text{ cal}$ for the return path f_i , what is Q for this path? (c) If $E_{\text{int},i} = 10 \text{ cal}$, what is $E_{\text{int},f}$? If $E_{\text{int},b} = 22 \text{ cal}$, what is Q for (d) path ib and (e) path bf ?

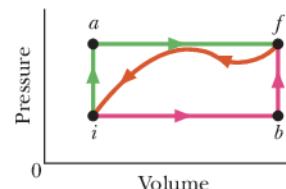


Figure 18-39 Problem 45.

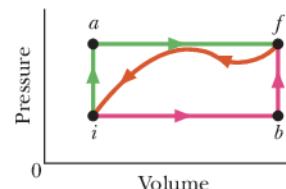


Figure 18-40 Problem 47.

•48 GO As a gas is held within a closed chamber, it passes through the cycle shown in Fig. 18-41. Determine the energy transferred by the system as heat during constant-pressure process CA if the energy added as heat Q_{AB} during constant-volume process AB is 20.0 J , no energy is transferred as heat during adiabatic process BC , and the net work done during the cycle is 15.0 J .

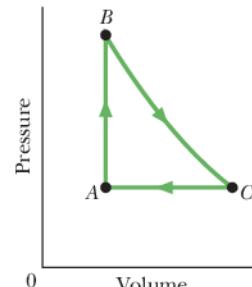


Figure 18-41 Problem 48.

- 49 GO** Figure 18-42 represents a closed cycle for a gas (the figure is not drawn to scale). The change in the internal energy of the gas as it moves from *a* to *c* along the path *abc* is -200 J . As it moves from *c* to *d*, 180 J must be transferred to it as heat. An additional transfer of 80 J to it as heat is needed as it moves from *d* to *a*. How much work is done on the gas as it moves from *c* to *d*?

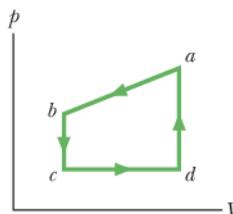


Figure 18-42 Problem 49.

- 50 GO** A lab sample of gas is taken through cycle *abca* shown in the *p*-*V* diagram of Fig. 18-43. The net work done is $+1.2\text{ J}$. Along path *ab*, the change in the internal energy is $+3.0\text{ J}$ and the magnitude of the work done is 5.0 J . Along path *ca*, the energy transferred to the gas as heat is $+2.5\text{ J}$. How much energy is transferred as heat along (a) path *ab* and (b) path *bc*?

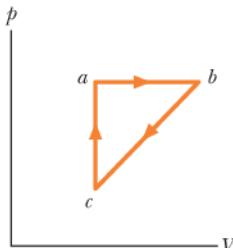


Figure 18-43 Problem 50.

Module 18-6 Heat Transfer Mechanisms

- 51** A sphere of radius 0.500 m , temperature 27.0°C , and emissivity 0.850 is located in an environment of temperature 77.0°C . At what rate does the sphere (a) emit and (b) absorb thermal radiation? (c) What is the sphere's net rate of energy exchange?

- 52** The ceiling of a single-family dwelling in a cold climate should have an *R*-value of 30 . To give such insulation, how thick would a layer of (a) polyurethane foam and (b) silver have to be?

- 53 SSM** Consider the slab shown in Fig. 18-18. Suppose that $L = 25.0\text{ cm}$, $A = 90.0\text{ cm}^2$, and the material is copper. If $T_H = 125^\circ\text{C}$, $T_C = 10.0^\circ\text{C}$, and a steady state is reached, find the conduction rate through the slab.

- 54** If you were to walk briefly in space without a spacesuit while far from the Sun (as an astronaut does in the movie *2001, A Space Odyssey*), you would feel the cold of space—while you radiated energy, you would absorb almost none from your environment. (a) At what rate would you lose energy? (b) How much energy would you lose in 30 s ? Assume that your emissivity is 0.90 , and estimate other data needed in the calculations.

- 55 ILW** A cylindrical copper rod of length 1.2 m and cross-sectional area 4.8 cm^2 is insulated along its side. The ends are held at a temperature difference of 100°C by having one end in a water–ice mixture and the other in a mixture of boiling water and steam. At what rate (a) is energy conducted by the rod and (b) does the ice melt?

- 56** The giant hornet *Vespa mandarinia japonica* preys on Japanese bees. However, if one of the hornets attempts to invade

Figure 18-44
Problem 56.

a beehive, several hundred of the bees quickly form a compact ball around the hornet to stop it. They don't sting, bite, crush, or suffocate it. Rather they overheat it by quickly raising their body temperatures from the normal 35°C to 47°C or 48°C , which is lethal to the hornet but not to the bees (Fig. 18-44). Assume the following: 500 bees form a ball of radius $R = 2.0\text{ cm}$ for a time $t = 20\text{ min}$, the primary loss of energy by the ball is by thermal radiation, the ball's surface has emissivity $\varepsilon = 0.80$, and the ball has a uniform temperature. On average, how much additional energy must each bee produce during the 20 min to maintain 47°C ?

- 57** (a) What is the rate of energy loss in watts per square meter through a glass window 3.0 mm thick if the outside temperature is -20°F and the inside temperature is $+72^\circ\text{F}$? (b) A storm window having the same thickness of glass is installed parallel to the first window, with an air gap of 7.5 cm between the two windows. What now is the rate of energy loss if conduction is the only important energy-loss mechanism?

- 58** A solid cylinder of radius $r_1 = 2.5\text{ cm}$, length $h_1 = 5.0\text{ cm}$, emissivity 0.85 , and temperature 30°C is suspended in an environment of temperature 50°C . (a) What is the cylinder's net thermal radiation transfer rate P_1 ? (b) If the cylinder is stretched until its radius is $r_2 = 0.50\text{ cm}$, its net thermal radiation transfer rate becomes P_2 . What is the ratio P_2/P_1 ?

- 59** In Fig. 18-45a, two identical rectangular rods of metal are welded end to end, with a temperature of $T_1 = 0^\circ\text{C}$ on the left side and a temperature of $T_2 = 100^\circ\text{C}$ on the right side. In 2.0 min , 10 J is conducted at a constant rate from the right side to the left side. How much time would be required to conduct 10 J if the rods were welded side to side as in Fig. 18-45b?

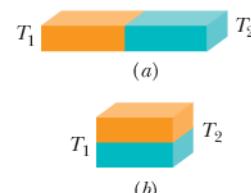


Figure 18-45 Problem 59.

- 60 GO** Figure 18-46 shows the cross section of a wall made of three layers. The layer thicknesses are L_1 , $L_2 = 0.700L_1$, and $L_3 = 0.350L_1$. The thermal conductivities are k_1 , $k_2 = 0.900k_1$, and $k_3 = 0.800k_1$. The temperatures at the left side and right side of the wall are $T_H = 30.0^\circ\text{C}$ and $T_C = -15.0^\circ\text{C}$, respectively. Thermal conduction is steady. (a) What is the temperature difference ΔT_2 across layer 2 (between the left and right sides of the layer)? If k_2 were, instead, equal to $1.1k_1$, (b) would the rate at which energy is conducted through the wall be greater than, less than, or the same as previously, and (c) what would be the value of ΔT_2 ?

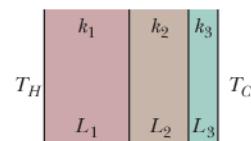


Figure 18-46 Problem 60.

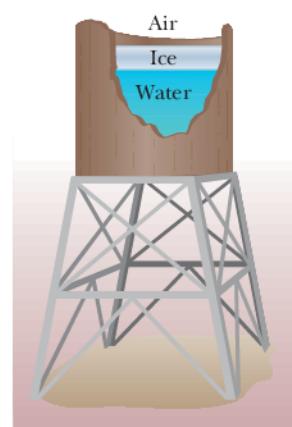


Figure 18-47 Problem 61.

- 61 SSM** A 5.0 cm slab has formed on an outdoor tank of water (Fig. 18-47). The air is at -10°C . Find the rate of ice formation (centimeters per hour). The ice has thermal conductivity $0.0040\text{ cal/s} \cdot \text{cm} \cdot {}^\circ\text{C}$ and density 0.92 g/cm^3 . Assume there is no energy transfer through the walls or bottom.

- 62** **Leidenfrost effect.** A water drop will last about 1 s on a hot skillet with a temperature between 100°C and about 200°C. However, if the skillet is much hotter, the drop can last several minutes, an effect named after an early investigator. The longer lifetime is due to the support of a thin layer of air and water vapor that separates the drop from the metal (by distance L in Fig. 18-48). Let $L = 0.100$ mm, and assume that the drop is flat with height $h = 1.50$ mm and bottom face area $A = 4.00 \times 10^{-6}$ m². Also assume that the skillet has a constant temperature $T_s = 300^\circ\text{C}$ and the drop has a temperature of 100°C. Water has density $\rho = 1000$ kg/m³, and the supporting layer has thermal conductivity $k = 0.026$ W/m·K. (a) At what rate is energy conducted from the skillet to the drop through the drop's bottom surface? (b) If conduction is the primary way energy moves from the skillet to the drop, how long will the drop last?



Figure 18-48 Problem 62.

- 63** Figure 18-49 shows (in cross section) a wall consisting of four layers, with thermal conductivities $k_1 = 0.060$ W/m·K, $k_3 = 0.040$ W/m·K, and $k_4 = 0.12$ W/m·K (k_2 is not known). The layer thicknesses are $L_1 = 1.5$ cm, $L_3 = 2.8$ cm, and $L_4 = 3.5$ cm (L_2 is not known). The known temperatures are $T_1 = 30^\circ\text{C}$, $T_{12} = 25^\circ\text{C}$, and $T_4 = -10^\circ\text{C}$. Energy transfer through the wall is steady. What is interface temperature T_{34} ?

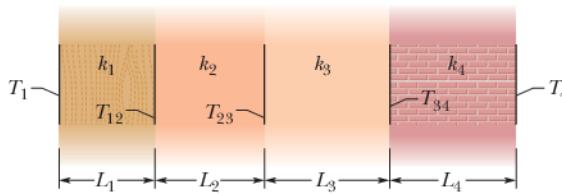


Figure 18-49 Problem 63.

- 64** **Penguin huddling.** To withstand the harsh weather of the Antarctic, emperor penguins huddle in groups (Fig. 18-50). Assume that a penguin is a circular cylinder with a top surface area $a = 0.34$ m² and height $h = 1.1$ m. Let P_r be the rate at which an individual penguin radiates energy to the environment (through the top and the sides); thus NP_r is the rate at which N identical, well-separated penguins radiate. If the penguins huddle closely to form



Alain Torterot/Peter Arnold/Photolibrary

Figure 18-50 Problem 64.

a *huddled cylinder* with top surface area Na and height h , the cylinder radiates at the rate P_h . If $N = 1000$, (a) what is the value of the fraction P_h/NP_r and (b) by what percentage does huddling reduce the total radiation loss?

- 65** Ice has formed on a shallow pond, and a steady state has been reached, with the air above the ice at -5.0°C and the bottom of the pond at 4.0°C . If the total depth of ice + water is 1.4 m, how thick is the ice? (Assume that the thermal conductivities of ice and water are 0.40 and 0.12 cal/m·C·s, respectively.)

- 66** **Evaporative cooling of beverages.** A cold beverage can be kept cold even on a warm day if it is slipped into a porous ceramic container that has been soaked in water. Assume that energy lost to evaporation matches the net energy gained via the radiation exchange through the top and side surfaces. The container and beverage have temperature $T = 15^\circ\text{C}$, the environment has temperature $T_{\text{env}} = 32^\circ\text{C}$, and the container is a cylinder with radius $r = 2.2$ cm and height 10 cm. Approximate the emissivity as $\epsilon = 1$, and neglect other energy exchanges. At what rate dm/dt is the container losing water mass?

Additional Problems

- 67** In the extrusion of cold chocolate from a tube, work is done on the chocolate by the pressure applied by a ram forcing the chocolate through the tube. The work per unit mass of extruded chocolate is equal to p/ρ , where p is the difference between the applied pressure and the pressure where the chocolate emerges from the tube, and ρ is the density of the chocolate. Rather than increasing the temperature of the chocolate, this work melts cocoa fats in the chocolate. These fats have a heat of fusion of 150 kJ/kg. Assume that all of the work goes into that melting and that these fats make up 30% of the chocolate's mass. What percentage of the fats melt during the extrusion if $p = 5.5$ MPa and $\rho = 1200$ kg/m³?

- 68** Icebergs in the North Atlantic present hazards to shipping, causing the lengths of shipping routes to be increased by about 30% during the iceberg season. Attempts to destroy icebergs include planting explosives, bombing, torpedoing, shelling, ramming, and coating with black soot. Suppose that direct melting of the iceberg by placing heat sources in the ice, is tried. How much energy as heat is required to melt 10% of an iceberg that has a mass of 200 000 metric tons? (Use 1 metric ton = 1000 kg.)

- 69** Figure 18-51 displays a closed cycle for a gas. The change in internal energy along path *ca* is -160 J. The energy transferred to the gas as heat is 200 J along path *ab*, and 40 J along path *bc*. How much work is done by the gas along (a) path *abc* and (b) path *ab*?

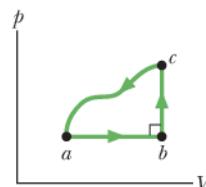


Figure 18-51
Problem 69.

- 70** In a certain solar house, energy from the Sun is stored in barrels filled with water. In a particular winter stretch of five cloudy days, 1.00×10^6 kcal is needed to maintain the inside of the house at 22.0°C . Assuming that the water in the barrels is at 50.0°C and that the water has a density of 1.00×10^3 kg/m³, what volume of water is required?

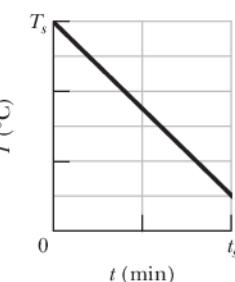


Figure 18-52 Problem 71.

- 71** A 0.300 kg sample is placed in a cooling apparatus that removes energy as heat at a constant rate of 2.81 W. Figure 18-52 gives the temperature T of the sam-

ple versus time t . The temperature scale is set by $T_s = 30^\circ\text{C}$ and the time scale is set by $t_s = 20 \text{ min}$. What is the specific heat of the sample?

72 The average rate at which energy is conducted outward through the ground surface in North America is 54.0 mW/m^2 , and the average thermal conductivity of the near-surface rocks is $2.50 \text{ W/m}\cdot\text{K}$. Assuming a surface temperature of 10.0°C , find the temperature at a depth of 35.0 km (near the base of the crust). Ignore the heat generated by the presence of radioactive elements.

73 What is the volume increase of an aluminum cube 5.00 cm on an edge when heated from 10.0°C to 60.0°C ?

74 In a series of experiments, block B is to be placed in a thermally insulated container with block A , which has the same mass as block B . In each experiment, block B is initially at a certain temperature T_B , but temperature T_A of block A is changed from experiment to experiment. Let T_f represent the final temperature of the two blocks when they reach thermal equilibrium in any of the experiments. Figure 18-53 gives temperature T_f versus the initial temperature T_A for a range of possible values of T_A , from $T_{A1} = 0 \text{ K}$ to $T_{A2} = 500 \text{ K}$. The vertical axis scale is set by $T_{fs} = 400 \text{ K}$. What are (a) temperature T_B and (b) the ratio c_B/c_A of the specific heats of the blocks?

75 Figure 18-54 displays a closed cycle for a gas. From c to b , 40 J is transferred from the gas as heat. From b to a , 130 J is transferred from the gas as heat, and the magnitude of the work done by the gas is 80 J . From a to c , 400 J is transferred to the gas as heat. What is the work done by the gas from a to c ? (Hint: You need to supply the plus and minus signs for the given data.)

76 Three equal-length straight rods, of aluminum, Invar, and steel, all at 20.0°C , form an equilateral triangle with hinge pins at the vertices. At what temperature will the angle opposite the Invar rod be 59.95° ? See Appendix E for needed trigonometric formulas and Table 18-2 for needed data.

77 SSM The temperature of a 0.700 kg cube of ice is decreased to -150°C . Then energy is gradually transferred to the cube as heat while it is otherwise thermally isolated from its environment. The total transfer is 0.6993 MJ . Assume the value of c_{ice} given in Table 18-3 is valid for temperatures from -150°C to 0°C . What is the final temperature of the water?

78 GO Icicles Liquid water coats an active (growing) icicle and extends up a short, narrow tube along the central axis (Fig. 18-55). Because the water–ice interface must have a temperature of 0°C , the water in the tube cannot lose energy through the

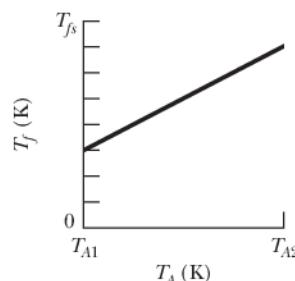


Figure 18-53 Problem 74.

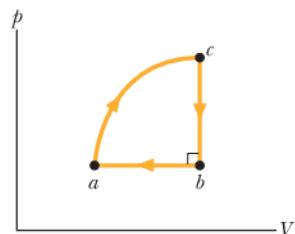


Figure 18-54 Problem 75.

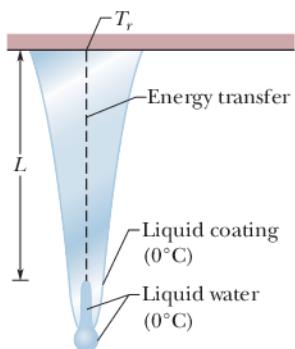


Figure 18-55 Problem 78.

sides of the icicle or down through the tip because there is no temperature change in those directions. It can lose energy and freeze only by sending energy up (through distance L) to the top of the icicle, where the temperature T_r can be below 0°C . Take $L = 0.12 \text{ m}$ and $T_r = -5^\circ\text{C}$. Assume that the central tube and the upward conduction path both have cross-sectional area A . In terms of A , what rate is (a) energy conducted upward and (b) mass converted from liquid to ice at the top of the central tube? (c) At what rate does the top of the tube move downward because of water freezing there? The thermal conductivity of ice is $0.400 \text{ W/m}\cdot\text{K}$, and the density of liquid water is 1000 kg/m^3 .

79 SSM A sample of gas expands from an initial pressure and volume of 10 Pa and 1.0 m^3 to a final volume of 2.0 m^3 . During the expansion, the pressure and volume are related by the equation $p = aV^2$, where $a = 10 \text{ N/m}^8$. Determine the work done by the gas during this expansion.

80 Figure 18-56a shows a cylinder containing gas and closed by a movable piston. The cylinder is kept submerged in an ice–water mixture. The piston is quickly pushed down from position 1 to position 2 and then held at position 2 until the gas is again at the temperature of the ice–water mixture; it then is slowly raised back to position 1. Figure 18-56b is a p – V diagram for the process. If 100 g of ice is melted during the cycle, how much work has been done on the gas?

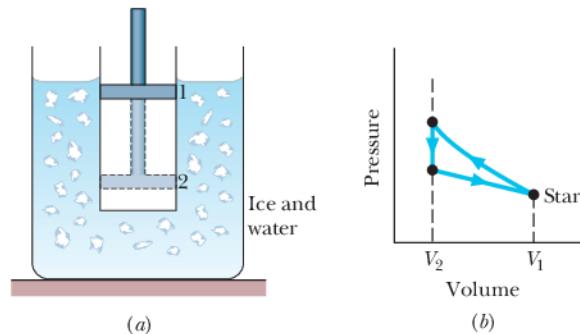


Figure 18-56 Problem 80.

81 SSM A sample of gas undergoes a transition from an initial state a to a final state b by three different paths (processes), as shown in the p – V diagram in Fig. 18-57, where $V_b = 5.00V_i$. The energy transferred to the gas as heat in process 1 is $10p_iV_i$. In terms of p_iV_i , what are (a) the energy transferred to the gas as heat in process 2 and (b) the change in internal energy that the gas undergoes in process 3?

82 A copper rod, an aluminum rod, and a brass rod, each of 6.00 m length and 1.00 cm diameter, are placed end to end with the aluminum rod between the other two. The free end of the copper rod is maintained at water's boiling point, and the free end of the brass rod is maintained at water's freezing point. What is the steady-state temperature of (a) the copper–aluminum junction and (b) the aluminum–brass junction?

83 SSM The temperature of a Pyrex disk is changed from 10.0°C to 60.0°C . Its initial radius is 8.00 cm ; its initial thickness is 0.500 cm . Take these data as being exact. What is the change in the volume of the disk? (See Table 18-2.)

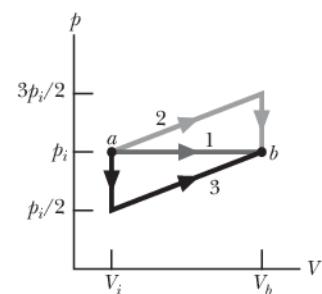


Figure 18-57 Problem 81.

84 (a) Calculate the rate at which body heat is conducted through the clothing of a skier in a steady-state process, given the following data: the body surface area is 1.8 m^2 , and the clothing is 1.0 cm thick; the skin surface temperature is 33°C and the outer surface of the clothing is at 1.0°C ; the thermal conductivity of the clothing is $0.040 \text{ W/m}\cdot\text{K}$. (b) If, after a fall, the skier's clothes became soaked with water of thermal conductivity $0.60 \text{ W/m}\cdot\text{K}$, by how much is the rate of conduction multiplied?

85 SSM A 2.50 kg lump of aluminum is heated to 92.0°C and then dropped into 8.00 kg of water at 5.00°C . Assuming that the lump–water system is thermally isolated, what is the system's equilibrium temperature?

86 A glass window pane is exactly 20 cm by 30 cm at 10°C . By how much has its area increased when its temperature is 40°C , assuming that it can expand freely?

87 A recruit can join the semi-secret “300 F” club at the Amundsen–Scott South Pole Station only when the outside temperature is below -70°C . On such a day, the recruit first basks in a hot sauna and then runs outside wearing only shoes. (This is, of course, extremely dangerous, but the rite is effectively a protest against the constant danger of the cold.)

Assume that upon stepping out of the sauna, the recruit's skin temperature is 102°F and the walls, ceiling, and floor of the sauna room have a temperature of 30°C . Estimate the recruit's surface area, and take the skin emissivity to be 0.80. (a) What is the approximate net rate P_{net} at which the recruit loses energy via thermal radiation exchanges with the room? Next, assume that when outdoors, half the recruit's surface area exchanges thermal radiation with the sky at a temperature of -25°C and the other half exchanges thermal radiation with the snow and ground at a temperature of -80°C . What is the approximate net rate at which the recruit loses energy via thermal radiation exchanges with (b) the sky and (c) the snow and ground?

88 A steel rod at 25.0°C is bolted at both ends and then cooled. At what temperature will it rupture? Use Table 12-1.

89 An athlete needs to lose weight and decides to do it by “pumping iron.” (a) How many times must an 80.0 kg weight be lifted a distance of 1.00 m in order to burn off 1.00 lb of fat, assuming that that much fat is equivalent to 3500 Cal? (b) If the weight is lifted once every 2.00 s, how long does the task take?

90 Soon after Earth was formed, heat released by the decay of radioactive elements raised the average internal temperature from 300 to 3000 K , at about which value it remains today. Assuming an average coefficient of volume expansion of $3.0 \times 10^{-5} \text{ K}^{-1}$, by how much has the radius of Earth increased since the planet was formed?

91 It is possible to melt ice by rubbing one block of it against another. How much work, in joules, would you have to do to get 1.00 g of ice to melt?

92 A rectangular plate of glass initially has the dimensions 0.200 m by 0.300 m . The coefficient of linear expansion for the glass is $9.00 \times 10^{-6}/\text{K}$. What is the change in the plate's area if its temperature is increased by 20.0 K ?

93 Suppose that you intercept 5.0×10^{-3} of the energy radiated by a hot sphere that has a radius of 0.020 m , an emissivity of 0.80, and a surface temperature of 500 K . How much energy do you intercept in 2.0 min?

94 A thermometer of mass 0.0550 kg and of specific heat $0.837 \text{ kJ/kg}\cdot\text{K}$ reads 15.0°C . It is then completely immersed in

0.300 kg of water, and it comes to the same final temperature as the water. If the thermometer then reads 44.4°C , what was the temperature of the water before insertion of the thermometer?

95 A sample of gas expands from $V_1 = 1.0 \text{ m}^3$ and $p_1 = 40 \text{ Pa}$ to $V_2 = 4.0 \text{ m}^3$ and $p_2 = 10 \text{ Pa}$ along path B in the p -V diagram in Fig. 18-58. It is then compressed back to V_1 along either path A or path C. Compute the net work done by the gas for the complete cycle along (a) path BA and (b) path BC.

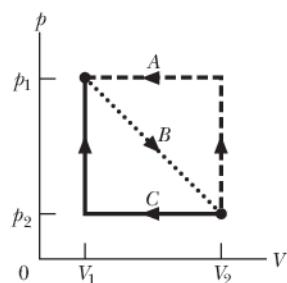


Figure 18-58 Problem 95.

96 Figure 18-59 shows a composite bar of length $L = L_1 + L_2$ and consisting of two materials. One material has length L_1 and coefficient of linear expansion α_1 ; the other has length L_2 and coefficient of linear expansion α_2 . (a) What is the coefficient of linear expansion α for the composite bar? For a particular composite bar, L is 52.4 cm , material 1 is steel, and material 2 is brass. If $\alpha = 1.3 \times 10^{-5}/\text{C}^\circ$, what are the lengths (b) L_1 and (c) L_2 ?

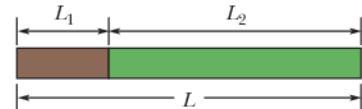


Figure 18-59 Problem 96.

97 On finding your stove out of order, you decide to boil the water for a cup of tea by shaking it in a thermos flask. Suppose that you use tap water at 19°C , the water falls 32 cm each shake, and you make 27 shakes each minute. Neglecting any loss of thermal energy by the flask, how long (in minutes) must you shake the flask until the water reaches 100°C ?

98 The p -V diagram in Fig. 18-60 shows two paths along which a sample of gas can be taken from state a to state b , where $V_b = 3.0V_1$. Path 1 requires that energy equal to $5.0p_1V_1$ be transferred to the gas as heat. Path 2 requires that energy equal to $5.5p_1V_1$ be transferred to the gas as heat. What is the ratio p_2/p_1 ?

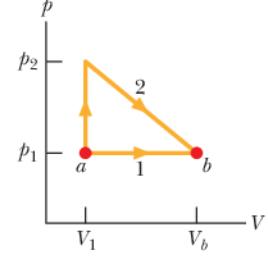


Figure 18-60 Problem 98.

99 A cube of edge length $6.0 \times 10^{-6} \text{ m}$, emissivity 0.75, and temperature -100°C floats in an environment at -150°C . What is the cube's net thermal radiation transfer rate?

100 A *flow calorimeter* is a device used to measure the specific heat of a liquid. Energy is added as heat at a known rate to a stream of the liquid as it passes through the calorimeter at a known rate. Measurement of the resulting temperature difference between the inflow and the outflow points of the liquid stream enables us to compute the specific heat of the liquid. Suppose a liquid of density 0.85 g/cm^3 flows through a calorimeter at the rate of $8.0 \text{ cm}^3/\text{s}$. When energy is added at the rate of 250 W by means of an electric heating coil, a temperature difference of 15 C° is established in steady-state conditions between the inflow and the outflow points. What is the specific heat of the liquid?

101 An object of mass 6.00 kg falls through a height of 50.0 m and, by means of a mechanical linkage, rotates a paddle wheel that stirs 0.600 kg of water. Assume that the initial gravitational potential energy of the object is fully transferred to thermal energy of the water, which is initially at 15.0°C . What is the temperature rise of the water?

102 The Pyrex glass mirror in a telescope has a diameter of 170 in. The temperature ranges from -16°C to 32°C on the location of the telescope. What is the maximum change in the diameter of the mirror, assuming that the glass can freely expand and contract?

103 The area A of a rectangular plate is $ab = 1.4 \text{ m}^2$. Its coefficient of linear expansion is $\alpha = 32 \times 10^{-6}/\text{C}^{\circ}$. After a temperature rise $\Delta T = 89^{\circ}\text{C}$, side a is longer by Δa and side b is longer by Δb (Fig. 18-61). Neglecting the small quantity $(\Delta a \Delta b)/ab$, find ΔA .

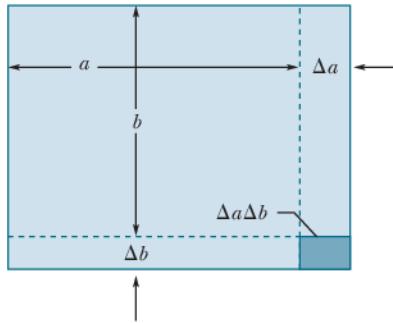


Figure 18-61 Problem 103.

104 Consider the liquid in a barometer whose coefficient of volume expansion is $6.6 \times 10^{-4}/\text{C}^{\circ}$. Find the relative change in the liquid's height if the temperature changes by 12°C while the pressure remains constant. Neglect the expansion of the glass tube.

105 A pendulum clock with a pendulum made of brass is designed to keep accurate time at 23°C . Assume it is a simple pendulum consisting of a bob at one end of a brass rod of negligible mass that is pivoted about the other end. If the clock operates at 0.0°C , (a) does it run too fast or too slow, and (b) what is the magnitude of its error in seconds per hour?

106 A room is lighted by four 100 W incandescent lightbulbs. (The power of 100 W is the rate at which a bulb converts electrical energy to heat and the energy of visible light.) Assuming that 73% of the energy is converted to heat, how much heat does the room receive in 6.9 h?

107 An energetic athlete can use up all the energy from a diet of 4000 Cal/day. If he were to use up this energy at a steady rate, what is the ratio of the rate of energy use compared to that of a 100 W bulb? (The power of 100 W is the rate at which the bulb converts electrical energy to heat and the energy of visible light.)

108 A 1700 kg Buick moving at 83 km/h brakes to a stop, at uniform deceleration and without skidding, over a distance of 93 m. At what average rate is mechanical energy transferred to thermal energy in the brake system?

The Kinetic Theory of Gases

19-1 AVOGADRO'S NUMBER

Learning Objectives

After reading this module, you should be able to . . .

19.01 Identify Avogadro's number N_A .

19.02 Apply the relationship between the number of moles n , the number of molecules N , and Avogadro's number N_A .

19.03 Apply the relationships between the mass m of a sample, the molar mass M of the molecules in the sample, the number of moles n in the sample, and Avogadro's number N_A .

Key Ideas

- The kinetic theory of gases relates the macroscopic properties of gases (for example, pressure and temperature) to the microscopic properties of gas molecules (for example, speed and kinetic energy).
- One mole of a substance contains N_A (Avogadro's number) elementary units (usually atoms or molecules), where N_A is found experimentally to be

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro's number}).$$

One molar mass M of any substance is the mass of one mole of the substance.

- A mole is related to the mass m of the individual molecules of the substance by

$$M = mN_A.$$

- The number of moles n contained in a sample of mass M_{sam} consisting of N molecules, is related to the molar mass M of the molecules and to Avogadro's number N_A as given by

$$n = \frac{N}{N_A} = \frac{M_{\text{sam}}}{M} = \frac{M_{\text{sam}}}{mN_A}.$$

What Is Physics?

One of the main subjects in thermodynamics is the physics of gases. A gas consists of atoms (either individually or bound together as molecules) that fill their container's volume and exert pressure on the container's walls. We can usually assign a temperature to such a contained gas. These three variables associated with a gas—volume, pressure, and temperature—are all a consequence of the motion of the atoms. The volume is a result of the freedom the atoms have to spread throughout the container, the pressure is a result of the collisions of the atoms with the container's walls, and the temperature has to do with the kinetic energy of the atoms. The **kinetic theory of gases**, the focus of this chapter, relates the motion of the atoms to the volume, pressure, and temperature of the gas.

Applications of the kinetic theory of gases are countless. Automobile engineers are concerned with the combustion of vaporized fuel (a gas) in the automobile engines. Food engineers are concerned with the production rate of the fermentation gas that causes bread to rise as it bakes. Beverage engineers are concerned with how gas can produce the head in a glass of beer or shoot a cork from a champagne bottle. Medical engineers and physiologists are concerned with calculating how long a scuba diver must pause during ascent to eliminate nitrogen gas from the bloodstream (to avoid the *bends*). Environmental scientists are concerned with how heat exchanges between the oceans and the atmosphere can affect weather conditions.

The first step in our discussion of the kinetic theory of gases deals with measuring the amount of a gas present in a sample, for which we use Avogadro's number.

Avogadro's Number

When our thinking is slanted toward atoms and molecules, it makes sense to measure the sizes of our samples in moles. If we do so, we can be certain that we are comparing samples that contain the same number of atoms or molecules. The *mole* is one of the seven SI base units and is defined as follows:



One mole is the number of atoms in a 12 g sample of carbon-12.

The obvious question now is: “How many atoms or molecules are there in a mole?” The answer is determined experimentally and, as you saw in Chapter 18, is

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro's number}), \quad (19-1)$$

where mol^{-1} represents the inverse mole or “per mole,” and mol is the abbreviation for mole. The number N_A is called **Avogadro's number** after Italian scientist Amedeo Avogadro (1776–1856), who suggested that all gases occupying the same volume under the same conditions of temperature and pressure contain the same number of atoms or molecules.

The number of moles n contained in a sample of any substance is equal to the ratio of the number of molecules N in the sample to the number of molecules N_A in 1 mol:

$$n = \frac{N}{N_A}. \quad (19-2)$$

(Caution: The three symbols in this equation can easily be confused with one another, so you should sort them with their meanings now, before you end in “N-confusion.”) We can find the number of moles n in a sample from the mass M_{sam} of the sample and either the *molar mass* M (the mass of 1 mol) or the molecular mass m (the mass of one molecule):

$$n = \frac{M_{\text{sam}}}{M} = \frac{M_{\text{sam}}}{mN_A}. \quad (19-3)$$

In Eq. 19-3, we used the fact that the mass M of 1 mol is the product of the mass m of one molecule and the number of molecules N_A in 1 mol:

$$M = mN_A. \quad (19-4)$$

19-2 IDEAL GASES

Learning Objectives

After reading this module, you should be able to . . .

- 19.04** Identify why an ideal gas is said to be ideal.
- 19.05** Apply either of the two forms of the ideal gas law, written in terms of the number of moles n or the number of molecules N .
- 19.06** Relate the ideal gas constant R and the Boltzmann constant k .
- 19.07** Identify that the temperature in the ideal gas law must be in kelvins.
- 19.08** Sketch p - V diagrams for a constant-temperature expansion of a gas and a constant-temperature contraction.
- 19.09** Identify the term isotherm.
- 19.10** Calculate the work done by a gas, including the algebraic sign, for an expansion and a contraction along an isotherm.
- 19.11** For an isothermal process, identify that the change in internal energy ΔE is zero and that the energy Q transferred as heat is equal to the work W done.
- 19.12** On a p - V diagram, sketch a constant-volume process and identify the amount of work done in terms of area on the diagram.
- 19.13** On a p - V diagram, sketch a constant-pressure process and determine the work done in terms of area on the diagram.

Key Ideas

- An ideal gas is one for which the pressure p , volume V , and temperature T are related by

$$pV = nRT \quad (\text{ideal gas law}).$$

Here n is the number of moles of the gas present and R is a constant ($8.31 \text{ J/mol} \cdot \text{K}$) called the gas constant.

- The ideal gas law can also be written as

$$pV = NkT,$$

where the Boltzmann constant k is

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K}.$$

- The work done by an ideal gas during an isothermal (constant-temperature) change from volume V_i to volume V_f is

$$W = nRT \ln \frac{V_f}{V_i} \quad (\text{ideal gas, isothermal process}).$$

Ideal Gases

Our goal in this chapter is to explain the macroscopic properties of a gas—such as its pressure and its temperature—in terms of the behavior of the molecules that make it up. However, there is an immediate problem: which gas? Should it be hydrogen, oxygen, or methane, or perhaps uranium hexafluoride? They are all different. Experimenters have found, though, that if we confine 1 mol samples of various gases in boxes of identical volume and hold the gases at the same temperature, then their measured pressures are almost the same, and at lower densities the differences tend to disappear. Further experiments show that, at low enough densities, all real gases tend to obey the relation

$$pV = nRT \quad (\text{ideal gas law}), \quad (19-5)$$

in which p is the absolute (not gauge) pressure, n is the number of moles of gas present, and T is the temperature in kelvins. The symbol R is a constant called the **gas constant** that has the same value for all gases—namely,

$$R = 8.31 \text{ J/mol} \cdot \text{K}. \quad (19-6)$$

Equation 19-5 is called the **ideal gas law**. Provided the gas density is low, this law holds for any single gas or for any mixture of different gases. (For a mixture, n is the total number of moles in the mixture.)

We can rewrite Eq. 19-5 in an alternative form, in terms of a constant called the **Boltzmann constant** k , which is defined as

$$k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K}. \quad (19-7)$$

This allows us to write $R = kN_A$. Then, with Eq. 19-2 ($n = N/N_A$), we see that

$$nR = Nk. \quad (19-8)$$

Substituting this into Eq. 19-5 gives a second expression for the ideal gas law:

$$pV = NkT \quad (\text{ideal gas law}). \quad (19-9)$$

(Caution: Note the difference between the two expressions for the ideal gas law—Eq. 19-5 involves the number of moles n , and Eq. 19-9 involves the number of molecules N .)

You may well ask, “What is an *ideal gas*, and what is so ‘ideal’ about it?” The answer lies in the simplicity of the law (Eqs. 19-5 and 19-9) that governs its macroscopic properties. Using this law—as you will see—we can deduce many properties of the ideal gas in a simple way. Although there is no such thing in nature as a truly ideal gas, *all real* gases approach the ideal state at low enough densities—that is, under conditions in which their molecules are far enough apart that they do not interact with one another. Thus, the ideal gas concept allows us to gain useful insights into the limiting behavior of real gases.



Courtesy www.doctorslime.com

Figure 19-1 (a) Before and (b) after images of a large steel tank crushed by atmospheric pressure after internal steam cooled and condensed.

Figure 19-1 gives a dramatic example of the ideal gas law. A stainless-steel tank with a volume of 18 m^3 was filled with steam at a temperature of 110°C through a valve at one end. The steam supply was then turned off and the valve closed, so that the steam was trapped inside the tank (Fig. 19-1a). Water from a fire hose was then poured onto the tank to rapidly cool it. Within less than a minute, the enormously sturdy tank was crushed (Fig. 19-1b), as if some giant invisible creature from a grade B science fiction movie had stepped on it during a rampage.

Actually, it was the atmosphere that crushed the tank. As the tank was cooled by the water steam, the steam cooled and much of it condensed, which means that the number N of gas molecules and the temperature T of the gas inside the tank both decreased. Thus, the right side of Eq. 19-9 decreased, and because volume V was constant, the gas pressure p on the left side also decreased. The gas pressure decreased so much that the external atmospheric pressure was able to crush the tank's steel wall. Figure 19-1 was staged, but this type of crushing sometimes occurs in industrial accidents (photos and videos can be found on the web).



Work Done by an Ideal Gas at Constant Temperature

Suppose we put an ideal gas in a piston–cylinder arrangement like those in Chapter 18. Suppose also that we allow the gas to expand from an initial volume V_i to a final volume V_f while we keep the temperature T of the gas constant. Such a process, at *constant temperature*, is called an **isothermal expansion** (and the reverse is called an **isothermal compression**).

On a p - V diagram, an *isotherm* is a curve that connects points that have the same temperature. Thus, it is a graph of pressure versus volume for a gas whose temperature T is held constant. For n moles of an ideal gas, it is a graph of the equation

$$p = nRT \frac{1}{V} = (\text{a constant}) \frac{1}{V}. \quad (19-10)$$

Figure 19-2 shows three isotherms, each corresponding to a different (constant) value of T . (Note that the values of T for the isotherms increase upward to the right.) Superimposed on the middle isotherm is the path followed by a gas during an isothermal expansion from state i to state f at a constant temperature of 310 K .

To find the work done by an ideal gas during an isothermal expansion, we start with Eq. 18-25,

$$W = \int_{V_i}^{V_f} p \, dV. \quad (19-11)$$

This is a general expression for the work done during any change in volume of any gas. For an ideal gas, we can use Eq. 19-5 ($pV = nRT$) to substitute for p , obtaining

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} \, dV. \quad (19-12)$$

Because we are considering an isothermal expansion, T is constant, so we can move it in front of the integral sign to write

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \left[\ln V \right]_{V_i}^{V_f}. \quad (19-13)$$

By evaluating the expression in brackets at the limits and then using the relationship $\ln a - \ln b = \ln(a/b)$, we find that

$$W = nRT \ln \frac{V_f}{V_i} \quad (\text{ideal gas, isothermal process}). \quad (19-14)$$

Recall that the symbol \ln specifies a *natural* logarithm, which has base e .

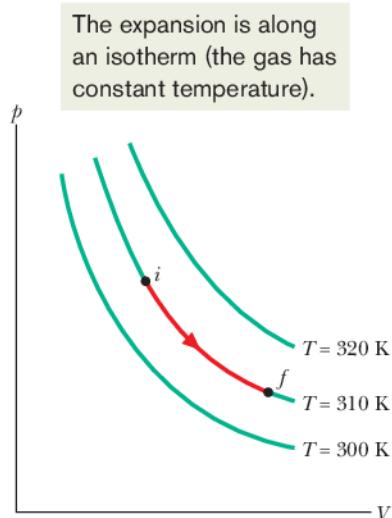


Figure 19-2 Three isotherms on a p - V diagram. The path shown along the middle isotherm represents an isothermal expansion of a gas from an initial state i to a final state f . The path from f to i along the isotherm would represent the reverse process—that is, an isothermal compression.

For an expansion, V_f is greater than V_i , so the ratio V_f/V_i in Eq. 19-14 is greater than unity. The natural logarithm of a quantity greater than unity is positive, and so the work W done by an ideal gas during an isothermal expansion is positive, as we expect. For a compression, V_f is less than V_i , so the ratio of volumes in Eq. 19-14 is less than unity. The natural logarithm in that equation—hence the work W —is negative, again as we expect.

Work Done at Constant Volume and at Constant Pressure

Equation 19-14 does not give the work W done by an ideal gas during *every* thermodynamic process. Instead, it gives the work only for a process in which the temperature is held constant. If the temperature varies, then the symbol T in Eq. 19-12 cannot be moved in front of the integral symbol as in Eq. 19-13, and thus we do not end up with Eq. 19-14.

However, we can always go back to Eq. 19-11 to find the work W done by an ideal gas (or any other gas) during any process, such as a constant-volume process and a constant-pressure process. If the volume of the gas is constant, then Eq. 19-11 yields

$$W = 0 \quad (\text{constant-volume process}). \quad (19-15)$$

If, instead, the volume changes while the pressure p of the gas is held constant, then Eq. 19-11 becomes

$$W = p(V_f - V_i) = p \Delta V \quad (\text{constant-pressure process}). \quad (19-16)$$



Checkpoint 1

An ideal gas has an initial pressure of 3 pressure units and an initial volume of 4 volume units. The table gives the final pressure and volume of the gas (in those same units) in five processes. Which processes start and end on the same isotherm?

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>p</i>	12	6	5	4	1
<i>V</i>	1	2	7	3	12

Sample Problem 19.01 Ideal gas and changes of temperature, volume, and pressure

A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume is reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

KEY IDEA

Because the gas is ideal, we can use the ideal gas law to relate its parameters, both in the initial state *i* and in the final state *f*.

Calculations: From Eq. 19-5 we can write

$$p_i V_i = nRT_i \quad \text{and} \quad p_f V_f = nRT_f.$$

Dividing the second equation by the first equation and solving for p_f yields

$$p_f = \frac{p_i T_f V_i}{T_i V_f}. \quad (19-17)$$

Note here that if we converted the given initial and final volumes from liters to the proper units of cubic meters, the multiplying conversion factors would cancel out of Eq. 19-17. The same would be true for conversion factors that convert the pressures from atmospheres to the proper pascals. However, to convert the given temperatures to kelvins requires the addition of an amount that would not cancel and thus must be included. Hence, we must write

$$T_i = (273 + 20) \text{ K} = 293 \text{ K}$$

$$\text{and} \quad T_f = (273 + 35) \text{ K} = 308 \text{ K}.$$

Inserting the given data into Eq. 19-17 then yields

$$p_f = \frac{(15 \text{ atm})(308 \text{ K})(12 \text{ L})}{(293 \text{ K})(8.5 \text{ L})} = 22 \text{ atm.} \quad (\text{Answer})$$



Additional examples, video, and practice available at WileyPLUS



Sample Problem 19.02 Work by an ideal gas

One mole of oxygen (assume it to be an ideal gas) expands at a constant temperature T of 310 K from an initial volume V_i of 12 L to a final volume V_f of 19 L. How much work is done by the gas during the expansion?

KEY IDEA

Generally we find the work by integrating the gas pressure with respect to the gas volume, using Eq. 19-11. However, because the gas here is ideal and the expansion is isothermal, that integration leads to Eq. 19-14.

Calculation: Therefore, we can write

$$\begin{aligned} W &= nRT \ln \frac{V_f}{V_i} \\ &= (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(310 \text{ K}) \ln \frac{19 \text{ L}}{12 \text{ L}} \\ &= 1180 \text{ J.} \quad (\text{Answer}) \end{aligned}$$

The expansion is graphed in the p - V diagram of Fig. 19-3. The work done by the gas during the expansion is represented by the area beneath the curve if .

You can show that if the expansion is now reversed, with the gas undergoing an isothermal compression from 19 L to 12 L, the work done by the gas will be -1180 J . Thus, an external force would have to do 1180 J of work on the gas to compress it.

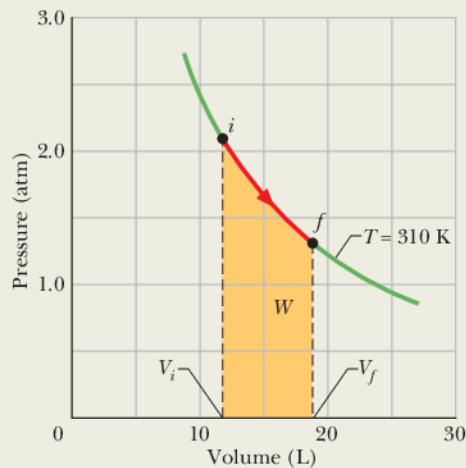


Figure 19-3 The shaded area represents the work done by 1 mol of oxygen in expanding from V_i to V_f at a temperature T of 310 K.

 Additional examples, video, and practice available at WileyPLUS

19-3 PRESSURE, TEMPERATURE, AND RMS SPEED

Learning Objectives

After reading this module, you should be able to . . .

- 19.14 Identify that the pressure on the interior walls of a gas container is due to the molecular collisions with the walls.
- 19.15 Relate the pressure on a container wall to the momentum of the gas molecules and the time intervals between their collisions with the wall.
- 19.16 For the molecules of an ideal gas, relate the root-

- mean-square speed v_{rms} and the average speed v_{avg} .
- 19.17 Relate the pressure of an ideal gas to the rms speed v_{rms} of the molecules.
- 19.18 For an ideal gas, apply the relationship between the gas temperature T and the rms speed v_{rms} and molar mass M of the molecules.

Key Ideas

- In terms of the speed of the gas molecules, the pressure exerted by n moles of an ideal gas is

$$P = \frac{nMv_{\text{rms}}^2}{3V},$$

where $v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}}$ is the root-mean-square speed of the

molecules, M is the molar mass, and V is the volume.

- The rms speed can be written in terms of the temperature as

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}.$$

Pressure, Temperature, and RMS Speed

Here is our first kinetic theory problem. Let n moles of an ideal gas be confined in a cubical box of volume V , as in Fig. 19-4. The walls of the box are held at temperature T . What is the connection between the pressure P exerted by the gas on the walls and the speeds of the molecules?

The molecules of gas in the box are moving in all directions and with various speeds, bumping into one another and bouncing from the walls of the box like balls in a racquetball court. We ignore (for the time being) collisions of the molecules with one another and consider only elastic collisions with the walls.

Figure 19-4 shows a typical gas molecule, of mass m and velocity \vec{v} , that is about to collide with the shaded wall. Because we assume that any collision of a molecule with a wall is elastic, when this molecule collides with the shaded wall, the only component of its velocity that is changed is the x component, and that component is reversed. This means that the only change in the particle's momentum is along the x axis, and that change is

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x.$$

Hence, the momentum Δp_x delivered to the wall by the molecule during the collision is $+2mv_x$. (Because in this book the symbol p represents both momentum and pressure, we must be careful to note that here p represents momentum and is a vector quantity.)

The molecule of Fig. 19-4 will hit the shaded wall repeatedly. The time Δt between collisions is the time the molecule takes to travel to the opposite wall and back again (a distance $2L$) at speed v_x . Thus, Δt is equal to $2L/v_x$. (Note that this result holds even if the molecule bounces off any of the other walls along the way, because those walls are parallel to x and so cannot change v_x .) Therefore, the average rate at which momentum is delivered to the shaded wall by this single molecule is

$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$

From Newton's second law ($\vec{F} = d\vec{p}/dt$), the rate at which momentum is delivered to the wall is the force acting on that wall. To find the total force, we must add up the contributions of all the molecules that strike the wall, allowing for the possibility that they all have different speeds. Dividing the magnitude of the total force F_x by the area of the wall ($= L^2$) then gives the pressure p on that wall, where now and in the rest of this discussion, p represents pressure. Thus, using the expression for $\Delta p_x/\Delta t$, we can write this pressure as

$$\begin{aligned} p &= \frac{F_x}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \cdots + mv_{xN}^2/L}{L^2} \\ &= \left(\frac{m}{L^3} \right) (v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2), \end{aligned} \quad (19-18)$$

where N is the number of molecules in the box.

Since $N = nN_A$, there are nN_A terms in the second set of parentheses of Eq. 19-18. We can replace that quantity by $nN_A(v_x^2)_{\text{avg}}$, where $(v_x^2)_{\text{avg}}$ is the average value of the square of the x components of all the molecular speeds. Equation 19-18 then becomes

$$p = \frac{nM N_A}{L^3} (v_x^2)_{\text{avg}}.$$

However, $M N_A$ is the molar mass M of the gas (that is, the mass of 1 mol of the gas). Also, L^3 is the volume of the box, so

$$p = \frac{nM(v_x^2)_{\text{avg}}}{V}. \quad (19-19)$$

For any molecule, $v^2 = v_x^2 + v_y^2 + v_z^2$. Because there are many molecules and because they are all moving in random directions, the average values of the squares of their velocity components are equal, so that $v_x^2 = \frac{1}{3}v^2$. Thus, Eq. 19-19 becomes

$$p = \frac{nM(v^2)_{\text{avg}}}{3V}. \quad (19-20)$$

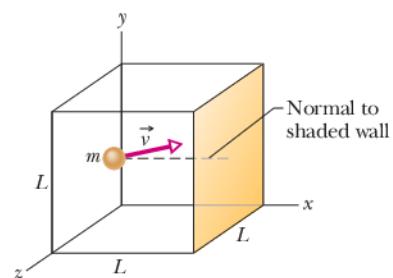


Figure 19-4 A cubical box of edge length L , containing n moles of an ideal gas. A molecule of mass m and velocity \vec{v} is about to collide with the shaded wall of area L^2 . A normal to that wall is shown.

Table 19-1 Some RMS Speeds at Room Temperature ($T = 300\text{ K}$)^a

Gas	Molar Mass (10^{-3} kg/mol)	v_{rms} (m/s)
Hydrogen (H_2)	2.02	1920
Helium (He)	4.0	1370
Water vapor (H_2O)	18.0	645
Nitrogen (N_2)	28.0	517
Oxygen (O_2)	32.0	483
Carbon dioxide (CO_2)	44.0	412
Sulfur dioxide (SO_2)	64.1	342

^aFor convenience, we often set room temperature equal to 300 K even though (at 27°C or 81°F) that represents a fairly warm room.

The square root of $(v^2)_{\text{avg}}$ is a kind of average speed, called the **root-mean-square speed** of the molecules and symbolized by v_{rms} . Its name describes it rather well: You *square* each speed, you find the *mean* (that is, the average) of all these squared speeds, and then you take the square *root* of that mean. With $\sqrt{(v^2)_{\text{avg}}} = v_{\text{rms}}$, we can then write Eq. 19-20 as

$$p = \frac{nMv_{\text{rms}}^2}{3V}. \quad (19-21)$$

This tells us how the pressure of the gas (a purely macroscopic quantity) depends on the speed of the molecules (a purely microscopic quantity).

We can turn Eq. 19-21 around and use it to calculate v_{rms} . Combining Eq. 19-21 with the ideal gas law ($pV = nRT$) leads to

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \quad (19-22)$$

Table 19-1 shows some rms speeds calculated from Eq. 19-22. The speeds are surprisingly high. For hydrogen molecules at room temperature (300 K), the rms speed is 1920 m/s, or 4300 mi/h—faster than a speeding bullet! On the surface of the Sun, where the temperature is 2×10^6 K, the rms speed of hydrogen molecules would be 82 times greater than at room temperature were it not for the fact that at such high speeds, the molecules cannot survive collisions among themselves. Remember too that the rms speed is only a kind of average speed; many molecules move much faster than this, and some much slower.

The speed of sound in a gas is closely related to the rms speed of the molecules of that gas. In a sound wave, the disturbance is passed on from molecule to molecule by means of collisions. The wave cannot move any faster than the “average” speed of the molecules. In fact, the speed of sound must be somewhat less than this “average” molecular speed because not all molecules are moving in exactly the same direction as the wave. As examples, at room temperature, the rms speeds of hydrogen and nitrogen molecules are 1920 m/s and 517 m/s, respectively. The speeds of sound in these two gases at this temperature are 1350 m/s and 350 m/s, respectively.

A question often arises: If molecules move so fast, why does it take as long as a minute or so before you can smell perfume when someone opens a bottle across a room? The answer is that, as we shall discuss in Module 19-5, each perfume molecule may have a high speed but it moves away from the bottle only very slowly because its repeated collisions with other molecules prevent it from moving directly across the room to you.



Sample Problem 19.03 Average and rms values

Here are five numbers: 5, 11, 32, 67, and 89.

- (a) What is the average value n_{avg} of these numbers?

Calculation: We find this from

$$n_{\text{avg}} = \frac{5 + 11 + 32 + 67 + 89}{5} = 40.8. \quad (\text{Answer})$$

- (b) What is the rms value n_{rms} of these numbers?

Calculation: We find this from

$$\begin{aligned} n_{\text{rms}} &= \sqrt{\frac{5^2 + 11^2 + 32^2 + 67^2 + 89^2}{5}} \\ &= 52.1. \end{aligned} \quad (\text{Answer})$$

The rms value is greater than the average value because the larger numbers—being squared—are relatively more important in forming the rms value.



Additional examples, video, and practice available at WileyPLUS

19-4 TRANSLATIONAL KINETIC ENERGY

Learning Objectives

After reading this module, you should be able to . . .

19.19 For an ideal gas, relate the average kinetic energy of the molecules to their rms speed.

19.20 Apply the relationship between the average kinetic energy and the temperature of the gas.

19.21 Identify that a measurement of a gas temperature is effectively a measurement of the average kinetic energy of the gas molecules.

Key Ideas

- The average translational kinetic energy per molecule in an ideal gas is

$$K_{\text{avg}} = \frac{1}{2}mv_{\text{rms}}^2.$$

- The average translational kinetic energy is related to the temperature of the gas:

$$K_{\text{avg}} = \frac{3}{2}kT.$$

Translational Kinetic Energy

We again consider a single molecule of an ideal gas as it moves around in the box of Fig. 19-4, but we now assume that its speed changes when it collides with other molecules. Its translational kinetic energy at any instant is $\frac{1}{2}mv^2$. Its *average* translational kinetic energy over the time that we watch it is

$$K_{\text{avg}} = \left(\frac{1}{2}mv^2\right)_{\text{avg}} = \frac{1}{2}m(v^2)_{\text{avg}} = \frac{1}{2}mv_{\text{rms}}^2, \quad (19-23)$$

in which we make the assumption that the average speed of the molecule during our observation is the same as the average speed of all the molecules at any given time. (Provided the total energy of the gas is not changing and provided we observe our molecule for long enough, this assumption is appropriate.) Substituting for v_{rms} from Eq. 19-22 leads to

$$K_{\text{avg}} = \left(\frac{1}{2}m\right) \frac{3RT}{M}.$$

However, M/m , the molar mass divided by the mass of a molecule, is simply Avogadro's number. Thus,

$$K_{\text{avg}} = \frac{3RT}{2N_A}.$$

Using Eq. 19-7 ($k = R/N_A$), we can then write

$$K_{\text{avg}} = \frac{3}{2}kT. \quad (19-24)$$

This equation tells us something unexpected:



At a given temperature T , all ideal gas molecules—no matter what their mass—have the same average translational kinetic energy—namely, $\frac{3}{2}kT$. When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.



Checkpoint 2

A gas mixture consists of molecules of types 1, 2, and 3, with molecular masses $m_1 > m_2 > m_3$. Rank the three types according to (a) average kinetic energy and (b) rms speed, greatest first.

19-5 MEAN FREE PATH

Learning Objectives

After reading this module, you should be able to...

19.22 Identify what is meant by mean free path.

19.23 Apply the relationship between the mean free path, the

diameter of the molecules, and the number of molecules per unit volume.

Key Idea

- The mean free path λ of a gas molecule is its average path length between collisions and is given by

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V},$$

where N/V is the number of molecules per unit volume and d is the molecular diameter.

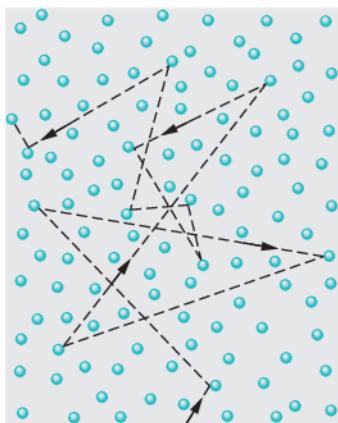


Figure 19-5 A molecule traveling through a gas, colliding with other gas molecules in its path. Although the other molecules are shown as stationary, they are also moving in a similar fashion.

Mean Free Path

We continue to examine the motion of molecules in an ideal gas. Figure 19-5 shows the path of a typical molecule as it moves through the gas, changing both speed and direction abruptly as it collides elastically with other molecules. Between collisions, the molecule moves in a straight line at constant speed. Although the figure shows the other molecules as stationary, they are (of course) also moving.

One useful parameter to describe this random motion is the **mean free path** λ of the molecules. As its name implies, λ is the average distance traversed by a molecule between collisions. We expect λ to vary inversely with N/V , the number of molecules per unit volume (or density of molecules). The larger N/V is, the more collisions there should be and the smaller the mean free path. We also expect λ to vary inversely with the size of the molecules—with their diameter d , say. (If the molecules were points, as we have assumed them to be, they would never collide and the mean free path would be infinite.) Thus, the larger the molecules are, the smaller the mean free path. We can even predict that λ should vary (inversely) as the *square* of the molecular diameter because the cross section of a molecule—not its diameter—determines its effective target area.

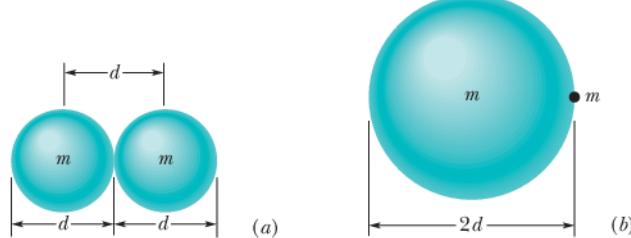
The expression for the mean free path does, in fact, turn out to be

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V} \quad (\text{mean free path}). \quad (19-25)$$

To justify Eq. 19-25, we focus attention on a single molecule and assume—as Fig. 19-5 suggests—that our molecule is traveling with a constant speed v and that all the other molecules are at rest. Later, we shall relax this assumption.

We assume further that the molecules are spheres of diameter d . A collision will then take place if the centers of two molecules come within a distance d of each other, as in Fig. 19-6a. Another, more helpful way to look at the situation is

Figure 19-6 (a) A collision occurs when the centers of two molecules come within a distance d of each other, d being the molecular diameter. (b) An equivalent but more convenient representation is to think of the moving molecule as having a radius d and all other molecules as being points. The condition for a collision is unchanged.



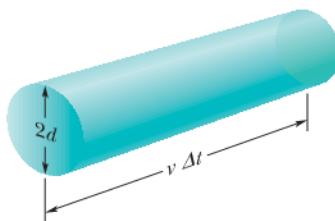


Figure 19-7 In time Δt the moving molecule effectively sweeps out a cylinder of length $v \Delta t$ and radius d .

to consider our single molecule to have a *radius* of d and all the other molecules to be *points*, as in Fig. 19-6b. This does not change our criterion for a collision.

As our single molecule zigzags through the gas, it sweeps out a short cylinder of cross-sectional area πd^2 between successive collisions. If we watch this molecule for a time interval Δt , it moves a distance $v \Delta t$, where v is its assumed speed. Thus, if we align all the short cylinders swept out in interval Δt , we form a composite cylinder (Fig. 19-7) of length $v \Delta t$ and volume $(\pi d^2)(v \Delta t)$. The number of collisions that occur in time Δt is then equal to the number of (point) molecules that lie within this cylinder.

Since N/V is the number of molecules per unit volume, the number of molecules in the cylinder is N/V times the volume of the cylinder, or $(N/V)(\pi d^2 v \Delta t)$. This is also the number of collisions in time Δt . The mean free path is the length of the path (and of the cylinder) divided by this number:

$$\begin{aligned}\lambda &= \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} \approx \frac{v \Delta t}{\pi d^2 v \Delta t N/V} \\ &= \frac{1}{\pi d^2 N/V}.\end{aligned}\quad (19-26)$$

This equation is only approximate because it is based on the assumption that all the molecules except one are at rest. In fact, *all* the molecules are moving; when this is taken properly into account, Eq. 19-25 results. Note that it differs from the (approximate) Eq. 19-26 only by a factor of $1/\sqrt{2}$.

The approximation in Eq. 19-26 involves the two v symbols we canceled. The v in the numerator is v_{avg} , the mean speed of the molecules *relative to the container*. The v in the denominator is v_{rel} , the mean speed of our single molecule *relative to the other molecules*, which are moving. It is this latter average speed that determines the number of collisions. A detailed calculation, taking into account the actual speed distribution of the molecules, gives $v_{\text{rel}} = \sqrt{2} v_{\text{avg}}$ and thus the factor $\sqrt{2}$.

The mean free path of air molecules at sea level is about $0.1 \mu\text{m}$. At an altitude of 100 km, the density of air has dropped to such an extent that the mean free path rises to about 16 cm. At 300 km, the mean free path is about 20 km. A problem faced by those who would study the physics and chemistry of the upper atmosphere in the laboratory is the unavailability of containers large enough to hold gas samples (of Freon, carbon dioxide, and ozone) that simulate upper atmospheric conditions.



Checkpoint 3

One mole of gas *A*, with molecular diameter $2d_0$ and average molecular speed v_0 , is placed inside a certain container. One mole of gas *B*, with molecular diameter d_0 and average molecular speed $2v_0$ (the molecules of *B* are smaller but faster), is placed in an identical container. Which gas has the greater average collision rate within its container?

**Sample Problem 19.04 Mean free path, average speed, collision frequency**

(a) What is the mean free path λ for oxygen molecules at temperature $T = 300\text{ K}$ and pressure $p = 1.0\text{ atm}$? Assume that the molecular diameter is $d = 290\text{ pm}$ and the gas is ideal.

KEY IDEA

Each oxygen molecule moves among other *moving* oxygen molecules in a zigzag path due to the resulting collisions. Thus, we use Eq. 19-25 for the mean free path.

Calculation: We first need the number of molecules per unit volume, N/V . Because we assume the gas is ideal, we can use the ideal gas law of Eq. 19-9 ($pV = NkT$) to write $N/V = p/kT$. Substituting this into Eq. 19-25, we find

$$\begin{aligned}\lambda &= \frac{1}{\sqrt{2}\pi d^2 N/V} = \frac{kT}{\sqrt{2}\pi d^2 p} \\ &= \frac{(1.38 \times 10^{-23}\text{ J/K})(300\text{ K})}{\sqrt{2}\pi(2.9 \times 10^{-10}\text{ m})^2(1.01 \times 10^5\text{ Pa})} \\ &= 1.1 \times 10^{-7}\text{ m.} \quad (\text{Answer})\end{aligned}$$

This is about 380 molecular diameters.

(b) Assume the average speed of the oxygen molecules is $v = 450\text{ m/s}$. What is the average time t between successive

collisions for any given molecule? At what rate does the molecule collide; that is, what is the frequency f of its collisions?

KEY IDEAS

(1) Between collisions, the molecule travels, on average, the mean free path λ at speed v . (2) The average rate or frequency at which the collisions occur is the inverse of the time t between collisions.

Calculations: From the first key idea, the average time between collisions is

$$t = \frac{\text{distance}}{\text{speed}} = \frac{\lambda}{v} = \frac{1.1 \times 10^{-7}\text{ m}}{450\text{ m/s}}$$

$$= 2.44 \times 10^{-10}\text{ s} \approx 0.24\text{ ns.} \quad (\text{Answer})$$

This tells us that, on average, any given oxygen molecule has less than a nanosecond between collisions.

From the second key idea, the collision frequency is

$$f = \frac{1}{t} = \frac{1}{2.44 \times 10^{-10}\text{ s}} = 4.1 \times 10^9\text{ s}^{-1}. \quad (\text{Answer})$$

This tells us that, on average, any given oxygen molecule makes about 4 billion collisions per second.



Additional examples, video, and practice available at WileyPLUS

19-6 THE DISTRIBUTION OF MOLECULAR SPEEDS

Learning Objectives

After reading this module, you should be able to...

19.24 Explain how Maxwell's speed distribution law is used to find the fraction of molecules with speeds in a certain speed range.

19.25 Sketch a graph of Maxwell's speed distribution, showing the probability distribution versus speed and indicating the relative positions of the average speed v_{avg} , the most probable speed v_p , and the rms speed v_{rms} .

Key Ideas

• The Maxwell speed distribution $P(v)$ is a function such that $P(v) dv$ gives the fraction of molecules with speeds in the interval dv at speed v :

$$P(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}.$$

• Three measures of the distribution of speeds among the molecules of a gas are

19.26 Explain how Maxwell's speed distribution is used to find the average speed, the rms speed, and the most probable speed.

19.27 For a given temperature T and molar mass M , calculate the average speed v_{avg} , the most probable speed v_p , and the rms speed v_{rms} .

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad (\text{average speed}),$$

$$v_p = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}),$$

and $v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (\text{rms speed}).$

The Distribution of Molecular Speeds

The root-mean-square speed v_{rms} gives us a general idea of molecular speeds in a gas at a given temperature. We often want to know more. For example, what fraction of the molecules have speeds greater than the rms value? What fraction have speeds greater than twice the rms value? To answer such questions, we need to know how the possible values of speed are distributed among the molecules. Figure 19-8a shows this distribution for oxygen molecules at room temperature ($T = 300 \text{ K}$); Fig. 19-8b compares it with the distribution at $T = 80 \text{ K}$.

In 1852, Scottish physicist James Clerk Maxwell first solved the problem of finding the speed distribution of gas molecules. His result, known as **Maxwell's speed distribution law**, is

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}. \quad (19-27)$$

Here M is the molar mass of the gas, R is the gas constant, T is the gas temperature, and v is the molecular speed. It is this equation that is plotted in Fig. 19-8a, b. The quantity $P(v)$ in Eq. 19-27 and Fig. 19-8 is a *probability distribution function*: For any speed v , the product $P(v) dv$ (a dimensionless quantity) is the fraction of molecules with speeds in the interval dv centered on speed v .

As Fig. 19-8a shows, this fraction is equal to the area of a strip with height $P(v)$ and width dv . The total area under the distribution curve corresponds to the fraction of the molecules whose speeds lie between zero and infinity. All molecules fall into this category, so the value of this total area is unity; that is,

$$\int_0^\infty P(v) dv = 1. \quad (19-28)$$

The fraction (frac) of molecules with speeds in an interval of, say, v_1 to v_2 is then

$$\text{frac} = \int_{v_1}^{v_2} P(v) dv. \quad (19-29)$$

Average, RMS, and Most Probable Speeds

In principle, we can find the **average speed** v_{avg} of the molecules in a gas with the following procedure: We *weight* each value of v in the distribution; that is, we multiply it

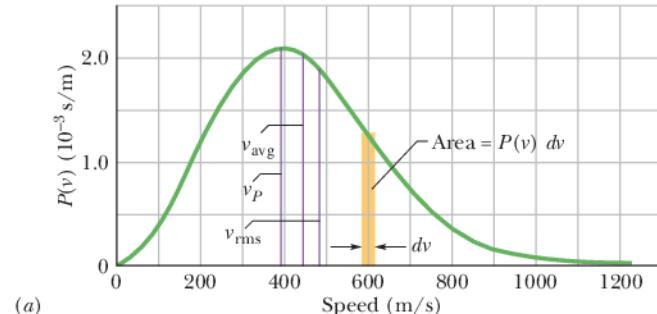
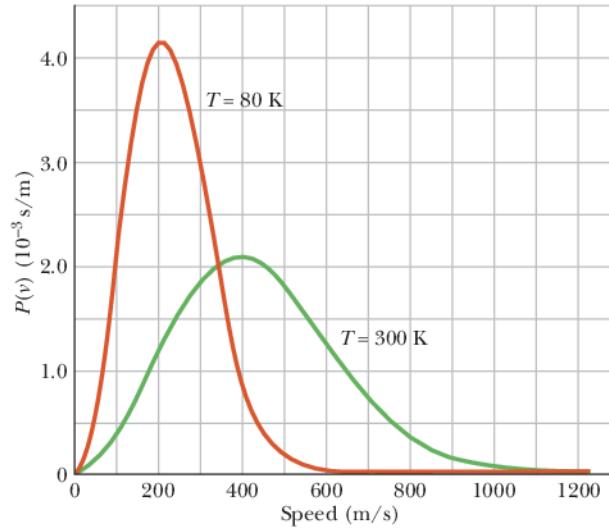


Figure 19-8 (a) The Maxwell speed distribution for oxygen molecules at $T = 300 \text{ K}$. The three characteristic speeds are marked. (b) The curves for 300 K and 80 K. Note that the molecules move more slowly at the lower temperature. Because these are probability distributions, the area under each curve has a numerical value of unity.



by the fraction $P(v) dv$ of molecules with speeds in a differential interval dv centered on v . Then we add up all these values of $v P(v) dv$. The result is v_{avg} . In practice, we do all this by evaluating

$$v_{\text{avg}} = \int_0^{\infty} v P(v) dv. \quad (19-30)$$

Substituting for $P(v)$ from Eq. 19-27 and using generic integral 20 from the list of integrals in Appendix E, we find

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad (\text{average speed}). \quad (19-31)$$

Similarly, we can find the average of the square of the speeds $(v^2)_{\text{avg}}$ with

$$(v^2)_{\text{avg}} = \int_0^{\infty} v^2 P(v) dv. \quad (19-32)$$

Substituting for $P(v)$ from Eq. 19-27 and using generic integral 16 from the list of integrals in Appendix E, we find

$$(v^2)_{\text{avg}} = \frac{3RT}{M}. \quad (19-33)$$

The square root of $(v^2)_{\text{avg}}$ is the root-mean-square speed v_{rms} . Thus,

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (\text{rms speed}), \quad (19-34)$$

which agrees with Eq. 19-22.

The **most probable speed** v_p is the speed at which $P(v)$ is maximum (see Fig. 19-8a). To calculate v_p , we set $dP/dv = 0$ (the slope of the curve in Fig. 19-8a is zero at the maximum of the curve) and then solve for v . Doing so, we find

$$v_p = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}). \quad (19-35)$$

A molecule is more likely to have speed v_p than any other speed, but some molecules will have speeds that are many times v_p . These molecules lie in the *high-speed tail* of a distribution curve like that in Fig. 19-8a. Such higher speed molecules make possible both rain and sunshine (without which we could not exist):

Rain The speed distribution of water molecules in, say, a pond at summer-time temperatures can be represented by a curve similar to that of Fig. 19-8a. Most of the molecules lack the energy to escape from the surface. However, a few of the molecules in the high-speed tail of the curve can do so. It is these water molecules that evaporate, making clouds and rain possible.

As the fast water molecules leave the surface, carrying energy with them, the temperature of the remaining water is maintained by heat transfer from the surroundings. Other fast molecules—produced in particularly favorable collisions—quickly take the place of those that have left, and the speed distribution is maintained.

Sunshine Let the distribution function of Eq. 19-27 now refer to protons in the core of the Sun. The Sun's energy is supplied by a nuclear fusion process that starts with the merging of two protons. However, protons repel each other because of their electrical charges, and protons of average speed do not have enough kinetic energy to overcome the repulsion and get close enough to merge. Very fast protons with speeds in the high-speed tail of the distribution curve can do so, however, and for that reason the Sun can shine.



Sample Problem 19.05 Speed distribution in a gas

In oxygen (molar mass $M = 0.0320 \text{ kg/mol}$) at room temperature (300 K), what fraction of the molecules have speeds in the interval 599 to 601 m/s?

KEY IDEAS

- The speeds of the molecules are distributed over a wide range of values, with the distribution $P(v)$ of Eq. 19-27.
- The fraction of molecules with speeds in a differential interval dv is $P(v) dv$.
- For a larger interval, the fraction is found by integrating $P(v)$ over the interval.
- However, the interval $\Delta v = 2 \text{ m/s}$ here is small compared to the speed $v = 600 \text{ m/s}$ on which it is centered.

Calculations: Because Δv is small, we can avoid the integration by approximating the fraction as

$$\text{frac} = P(v) \Delta v = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} \Delta v.$$

Sample Problem 19.06 Average speed, rms speed, most probable speed

The molar mass M of oxygen is 0.0320 kg/mol.

- (a) What is the average speed v_{avg} of oxygen gas molecules at $T = 300 \text{ K}$?

KEY IDEA

To find the average speed, we must weight speed v with the distribution function $P(v)$ of Eq. 19-27 and then integrate the resulting expression over the range of possible speeds (from zero to the limit of an infinite speed).

Calculation: We end up with Eq. 19-31, which gives us

$$\begin{aligned} v_{\text{avg}} &= \sqrt{\frac{8RT}{\pi M}} \\ &= \sqrt{\frac{8(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})}{\pi(0.0320 \text{ kg/mol})}} \\ &= 445 \text{ m/s.} \end{aligned} \quad (\text{Answer})$$

This result is plotted in Fig. 19-8a.

- (b) What is the root-mean-square speed v_{rms} at 300 K?

KEY IDEA

To find v_{rms} , we must first find $(v^2)_{\text{avg}}$ by weighting v^2 with the distribution function $P(v)$ of Eq. 19-27 and then integrating the expression over the range of possible speeds. Then we must take the square root of the result.

The total area under the plot of $P(v)$ in Fig. 19-8a is the total fraction of molecules (unity), and the area of the thin gold strip (not to scale) is the fraction we seek. Let's evaluate frac in parts:

$$\text{frac} = (4\pi)(A)(v^2)(e^B)(\Delta v), \quad (19-36)$$

where

$$\begin{aligned} A &= \left(\frac{M}{2\pi RT} \right)^{3/2} = \left(\frac{0.0320 \text{ kg/mol}}{(2\pi)(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})} \right)^{3/2} \\ &= 2.92 \times 10^{-9} \text{ s}^3/\text{m}^3 \end{aligned}$$

$$\text{and } B = -\frac{Mv^2}{2RT} = -\frac{(0.0320 \text{ kg/mol})(600 \text{ m/s})^2}{(2)(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})} = -2.31.$$

Substituting A and B into Eq. 19-36 yields

$$\begin{aligned} \text{frac} &= (4\pi)(A)(v^2)(e^B)(\Delta v) \\ &= (4\pi)(2.92 \times 10^{-9} \text{ s}^3/\text{m}^3)(600 \text{ m/s})^2(e^{-2.31})(2 \text{ m/s}) \\ &= 2.62 \times 10^{-3} = 0.262\%. \end{aligned} \quad (\text{Answer})$$

Calculation: We end up with Eq. 19-34, which gives us

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})}{0.0320 \text{ kg/mol}}} \\ &= 483 \text{ m/s.} \end{aligned} \quad (\text{Answer})$$

This result, plotted in Fig. 19-8a, is greater than v_{avg} because the greater speed values influence the calculation more when we integrate the v^2 values than when we integrate the v values.

- (c) What is the most probable speed v_P at 300 K?

KEY IDEA

Speed v_P corresponds to the maximum of the distribution function $P(v)$, which we obtain by setting the derivative $dP/dv = 0$ and solving the result for v .

Calculation: We end up with Eq. 19-35, which gives us

$$\begin{aligned} v_P &= \sqrt{\frac{2RT}{M}} \\ &= \sqrt{\frac{2(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})}{0.0320 \text{ kg/mol}}} \\ &= 395 \text{ m/s.} \end{aligned} \quad (\text{Answer})$$

This result is also plotted in Fig. 19-8a.



Additional examples, video, and practice available at WileyPLUS



19-7 THE MOLAR SPECIFIC HEATS OF AN IDEAL GAS

Learning Objectives

After reading this module, you should be able to . . .

- 19.28 Identify that the internal energy of an ideal monatomic gas is the sum of the translational kinetic energies of its atoms.
- 19.29 Apply the relationship between the internal energy E_{int} of a monatomic ideal gas, the number of moles n , and the gas temperature T .
- 19.30 Distinguish between monatomic, diatomic, and polyatomic ideal gases.
- 19.31 For monatomic, diatomic, and polyatomic ideal gases, evaluate the molar specific heats for a constant-volume process and a constant-pressure process.
- 19.32 Calculate a molar specific heat at constant pressure C_p by adding R to the molar specific heat at constant volume C_V , and explain why (physically) C_p is greater.
- 19.33 Identify that the energy transferred to an ideal gas as heat in a constant-volume process goes entirely into the internal energy (the random translational motion) but that

in a constant-pressure process energy also goes into the work done to expand the gas.

- 19.34 Identify that for a given change in temperature, the change in the internal energy of an ideal gas is the same for *any* process and is most easily calculated by assuming a constant-volume process.
- 19.35 For an ideal gas, apply the relationship between heat Q , number of moles n , and temperature change ΔT , using the appropriate molar specific heat.
- 19.36 Between two isotherms on a p - V diagram, sketch a constant-volume process and a constant-pressure process, and for each identify the work done in terms of area on the graph.
- 19.37 Calculate the work done by an ideal gas for a constant-pressure process.
- 19.38 Identify that work is zero for constant volume.

Key Ideas

- The molar specific heat C_V of a gas at constant volume is defined as

$$C_V = \frac{Q}{n \Delta T} = \frac{\Delta E_{\text{int}}}{n \Delta T},$$

in which Q is the energy transferred as heat to or from a sample of n moles of the gas, ΔT is the resulting temperature change of the gas, and ΔE_{int} is the resulting change in the internal energy of the gas.

- For an ideal monatomic gas,

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol} \cdot \text{K}.$$

- The molar specific heat C_p of a gas at constant pressure is

defined to be

$$C_p = \frac{Q}{n \Delta T},$$

in which Q , n , and ΔT are defined as above. C_p is also given by

$$C_p = C_V + R.$$

- For n moles of an ideal gas,

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (\text{ideal gas}).$$

- If n moles of a confined ideal gas undergo a temperature change ΔT due to *any* process, the change in the internal energy of the gas is

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (\text{ideal gas, any process}).$$

The Molar Specific Heats of an Ideal Gas

In this module, we want to derive from molecular considerations an expression for the internal energy E_{int} of an ideal gas. In other words, we want an expression for the energy associated with the random motions of the atoms or molecules in the gas. We shall then use that expression to derive the molar specific heats of an ideal gas.

Internal Energy E_{int}

Let us first assume that our ideal gas is a *monatomic gas* (individual atoms rather than molecules), such as helium, neon, or argon. Let us also assume that the internal energy E_{int} is the sum of the translational kinetic energies of the atoms. (Quantum theory disallows rotational kinetic energy for individual atoms.)

The average translational kinetic energy of a single atom depends only on the gas temperature and is given by Eq. 19-24 as $K_{\text{avg}} = \frac{3}{2}kT$. A sample of n moles of such a gas contains nN_A atoms. The internal energy E_{int} of the sample is then

$$E_{\text{int}} = (nN_A)K_{\text{avg}} = (nN_A)\left(\frac{3}{2}kT\right). \quad (19-37)$$

Using Eq. 19-7 ($k = R/N_A$), we can rewrite this as

$$E_{\text{int}} = \frac{3}{2}nRT \quad (\text{monatomic ideal gas}). \quad (19-38)$$



The internal energy E_{int} of an ideal gas is a function of the gas temperature *only*; it does not depend on any other variable.

With Eq. 19-38 in hand, we are now able to derive an expression for the molar specific heat of an ideal gas. Actually, we shall derive two expressions. One is for the case in which the volume of the gas remains constant as energy is transferred to or from it as heat. The other is for the case in which the pressure of the gas remains constant as energy is transferred to or from it as heat. The symbols for these two molar specific heats are C_V and C_p , respectively. (By convention, the capital letter C is used in both cases, even though C_V and C_p represent types of specific heat and not heat capacities.)

Molar Specific Heat at Constant Volume

Figure 19-9a shows n moles of an ideal gas at pressure p and temperature T , confined to a cylinder of fixed volume V . This *initial state i* of the gas is marked on the p - V diagram of Fig. 19-9b. Suppose now that you add a small amount of energy to the gas as heat Q by slowly turning up the temperature of the thermal reservoir. The gas temperature rises a small amount to $T + \Delta T$, and its pressure rises to $p + \Delta p$, bringing the gas to *final state f*. In such experiments, we would find that the heat Q is related to the temperature change ΔT by

$$Q = nC_V\Delta T \quad (\text{constant volume}), \quad (19-39)$$

where C_V is a constant called the **molar specific heat at constant volume**. Substituting this expression for Q into the first law of thermodynamics as given by Eq. 18-26 ($\Delta E_{\text{int}} = Q - W$) yields

$$\Delta E_{\text{int}} = nC_V\Delta T - W. \quad (19-40)$$

With the volume held constant, the gas cannot expand and thus cannot do any work. Therefore, $W = 0$, and Eq. 19-40 gives us

$$C_V = \frac{\Delta E_{\text{int}}}{n \Delta T}. \quad (19-41)$$

From Eq. 19-38, the change in internal energy must be

$$\Delta E_{\text{int}} = \frac{3}{2}nR\Delta T. \quad (19-42)$$

Substituting this result into Eq. 19-41 yields

$$C_V = \frac{3}{2}R = 12.5 \text{ J/mol}\cdot\text{K} \quad (\text{monatomic gas}). \quad (19-43)$$

As Table 19-2 shows, this prediction of the kinetic theory (for ideal gases) agrees very well with experiment for real monatomic gases, the case that we have assumed. The (predicted and) experimental values of C_V for *diatomic gases* (which have molecules with two atoms) and *polyatomic gases* (which have molecules with more than two atoms) are greater than those for monatomic gases for reasons that will be suggested in Module 19-8. Here we make the preliminary assumption that the C_V values for diatomic and polyatomic gases are greater than for monatomic gases because the more complex molecules can rotate and thus have rotational kinetic energy. So, when Q is transferred to a diatomic or polyatomic gas, only part of it goes into the translational kinetic energy, increasing the

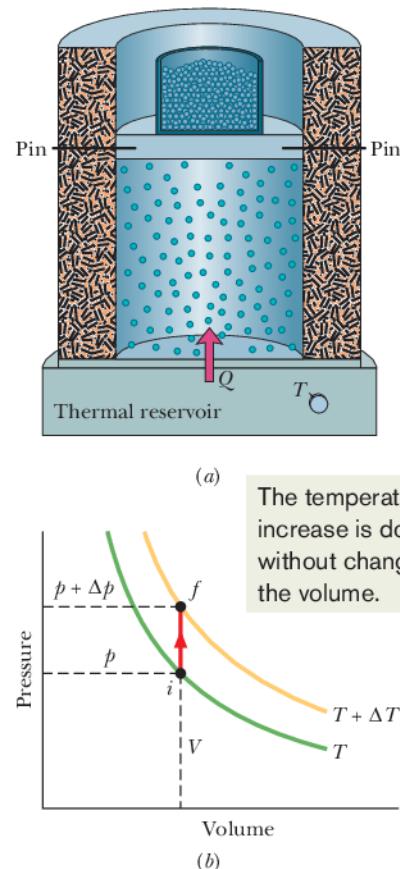


Figure 19-9 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-volume process. Heat is added, but no work is done. (b) The process on a p - V diagram.

Table 19-2 Molar Specific Heats at Constant Volume

Molecule	Example	C_V (J/mol·K)
Monatomic	Ideal	$\frac{3}{2}R = 12.5$
	Real	He 12.5 Ar 12.6
Diatomeric	Ideal	$\frac{5}{2}R = 20.8$
	Real	N ₂ 20.7 O ₂ 20.8
Polyatomic	Ideal	$3R = 24.9$
	Real	NH ₄ 29.0 CO ₂ 29.7

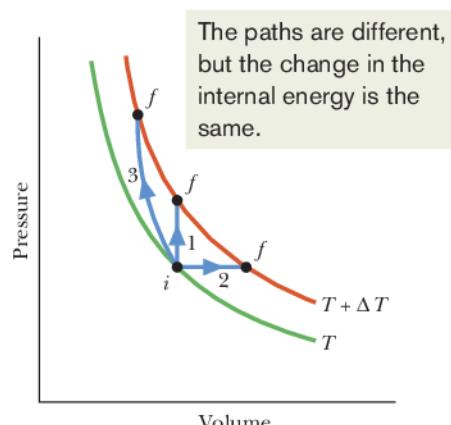


Figure 19-10 Three paths representing three different processes that take an ideal gas from an initial state i at temperature T to some final state f at temperature $T + \Delta T$. The change ΔE_{int} in the internal energy of the gas is the same for these three processes and for any others that result in the same change of temperature.

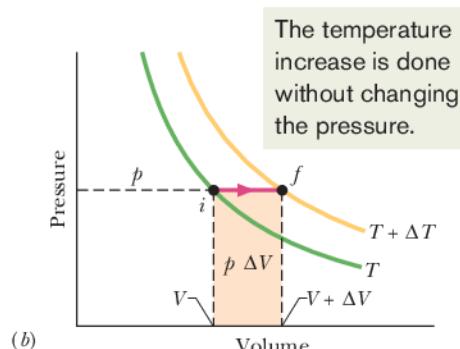
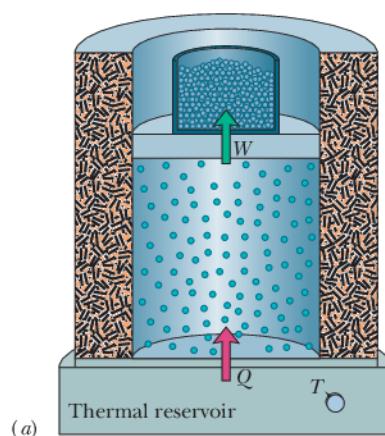


Figure 19-11 (a) The temperature of an ideal gas is raised from T to $T + \Delta T$ in a constant-pressure process. Heat is added and work is done in lifting the loaded piston. (b) The process on a p - V diagram. The work $p \Delta V$ is given by the shaded area.

temperature. (For now we neglect the possibility of also putting energy into oscillations of the molecules.)

We can now generalize Eq. 19-38 for the internal energy of any ideal gas by substituting C_V for $\frac{3}{2}R$; we get

$$E_{\text{int}} = nC_V T \quad (\text{any ideal gas}). \quad (19-44)$$

This equation applies not only to an ideal monatomic gas but also to diatomic and polyatomic ideal gases, provided the appropriate value of C_V is used. Just as with Eq. 19-38, we see that the internal energy of a gas depends on the temperature of the gas but not on its pressure or density.

When a confined ideal gas undergoes temperature change ΔT , then from either Eq. 19-41 or Eq. 19-44 the resulting change in its internal energy is

$$\Delta E_{\text{int}} = nC_V \Delta T \quad (\text{ideal gas, any process}). \quad (19-45)$$

This equation tells us:



A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, *not* on what type of process produces the change.

As examples, consider the three paths between the two isotherms in the p - V diagram of Fig. 19-10. Path 1 represents a constant-volume process. Path 2 represents a constant-pressure process (we examine it next). Path 3 represents a process in which no heat is exchanged with the system's environment (we discuss this in Module 19-9). Although the values of heat Q and work W associated with these three paths differ, as do p_f and V_f , the values of ΔE_{int} associated with the three paths are identical and are all given by Eq. 19-45, because they all involve the same temperature change ΔT . Therefore, no matter what path is actually taken between T and $T + \Delta T$, we can *always* use path 1 and Eq. 19-45 to compute ΔE_{int} easily.

Molar Specific Heat at Constant Pressure

We now assume that the temperature of our ideal gas is increased by the same small amount ΔT as previously but now the necessary energy (heat Q) is added with the gas under constant pressure. An experiment for doing this is shown in Fig. 19-11a; the p - V diagram for the process is plotted in Fig. 19-11b. From such experiments we find that the heat Q is related to the temperature change ΔT by

$$Q = nC_p \Delta T \quad (\text{constant pressure}), \quad (19-46)$$

where C_p is a constant called the **molar specific heat at constant pressure**. This C_p is *greater* than the molar specific heat at constant volume C_V , because energy must now be supplied not only to raise the temperature of the gas but also for the gas to do work—that is, to lift the weighted piston of Fig. 19-11a.

To relate molar specific heats C_p and C_V , we start with the first law of thermodynamics (Eq. 18-26):

$$\Delta E_{\text{int}} = Q - W. \quad (19-47)$$

We next replace each term in Eq. 19-47. For ΔE_{int} , we substitute from Eq. 19-45. For Q , we substitute from Eq. 19-46. To replace W , we first note that since the pressure remains constant, Eq. 19-16 tells us that $W = p \Delta V$. Then we note that, using the ideal gas equation ($pV = nRT$), we can write

$$W = p \Delta V = nR \Delta T. \quad (19-48)$$

Making these substitutions in Eq. 19-47 and then dividing through by $n \Delta T$, we find

$$C_V = C_p - R$$

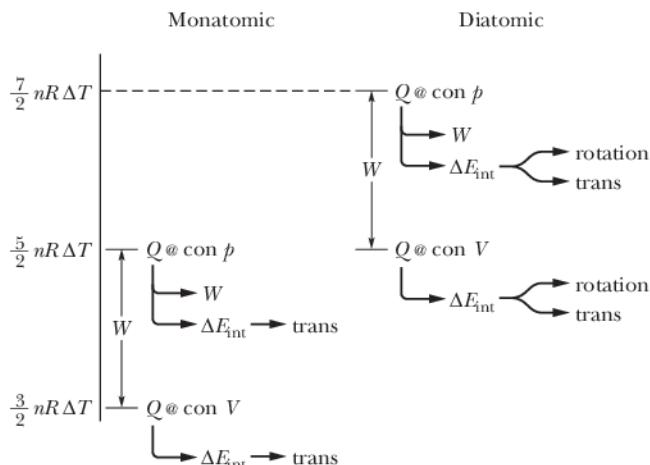


Figure 19-12 The relative values of Q for a monatomic gas (left side) and a diatomic gas undergoing a constant-volume process (labeled “con V ”) and a constant-pressure process (labeled “con p ”). The transfer of the energy into work W and internal energy (ΔE_{int}) is noted.

and then

$$C_p = C_V + R. \quad (19-49)$$

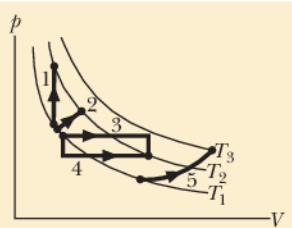
This prediction of kinetic theory agrees well with experiment, not only for monatomic gases but also for gases in general, as long as their density is low enough so that we may treat them as ideal.

The left side of Fig. 19-12 shows the relative values of Q for a monatomic gas undergoing either a constant-volume process ($Q = \frac{3}{2}nR \Delta T$) or a constant-pressure process ($Q = \frac{5}{2}nR \Delta T$). Note that for the latter, the value of Q is higher by the amount W , the work done by the gas in the expansion. Note also that for the constant-volume process, the energy added as Q goes entirely into the change in internal energy ΔE_{int} and for the constant-pressure process, the energy added as Q goes into both ΔE_{int} and the work W .



Checkpoint 4

The figure here shows five paths traversed by a gas on a p - V diagram. Rank the paths according to the change in internal energy of the gas, greatest first.



Sample Problem 19.07 Monatomic gas, heat, internal energy, and work

A bubble of 5.00 mol of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase ΔT of 20.0 $^{\circ}\text{C}$ at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal.

- (a) How much energy is added to the helium as heat during the increase and expansion?

KEY IDEA

Heat Q is related to the temperature change ΔT by a molar specific heat of the gas.

Calculations: Because the pressure p is held constant during the addition of energy, we use the molar specific heat at

constant pressure C_p and Eq. 19-46,

$$Q = nC_p \Delta T, \quad (19-50)$$

to find Q . To evaluate C_p we go to Eq. 19-49, which tells us that for any ideal gas, $C_p = C_V + R$. Then from Eq. 19-43, we know that for any monatomic gas (like the helium here), $C_V = \frac{3}{2}R$. Thus, Eq. 19-50 gives us

$$\begin{aligned} Q &= n(C_V + R) \Delta T = n(\frac{3}{2}R + R) \Delta T = n(\frac{5}{2}R) \Delta T \\ &= (5.00 \text{ mol})(2.5)(8.31 \text{ J/mol}\cdot\text{K})(20.0 \text{ }^{\circ}\text{C}) \\ &= 2077.5 \text{ J} \approx 2080 \text{ J}. \end{aligned} \quad (\text{Answer})$$

- (b) What is the change ΔE_{int} in the internal energy of the helium during the temperature increase?

KEY IDEA

Because the bubble expands, this is not a constant-volume process. However, the helium is nonetheless confined (to the bubble). Thus, the change ΔE_{int} is the same as *would occur* in a constant-volume process with the same temperature change ΔT .

Calculation: We can now easily find the constant-volume change ΔE_{int} with Eq. 19-45:

$$\begin{aligned}\Delta E_{\text{int}} &= nC_V \Delta T = n\left(\frac{3}{2}R\right) \Delta T \\ &= (5.00 \text{ mol})(1.5)(8.31 \text{ J/mol} \cdot \text{K})(20.0 \text{ }^{\circ}\text{C}) \\ &= 1246.5 \text{ J} \approx 1250 \text{ J.} \quad (\text{Answer})\end{aligned}$$

(c) How much work W is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?

KEY IDEAS

The work done by *any* gas expanding against the pressure from its environment is given by Eq. 19-11, which tells us to in-



Additional examples, video, and practice available at WileyPLUS

tegrate $p dV$. When the pressure is constant (as here), we can simplify that to $W = p \Delta V$. When the gas is *ideal* (as here), we can use the ideal gas law (Eq. 19-5) to write $p \Delta V = nR \Delta T$.

Calculation: We end up with

$$\begin{aligned}W &= nR \Delta T \\ &= (5.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(20.0 \text{ }^{\circ}\text{C}) \\ &= 831 \text{ J.} \quad (\text{Answer})\end{aligned}$$

Another way: Because we happen to know Q and ΔE_{int} , we can work this problem another way: We can account for the energy changes of the gas with the first law of thermodynamics, writing

$$\begin{aligned}W &= Q - \Delta E_{\text{int}} = 2077.5 \text{ J} - 1246.5 \text{ J} \\ &= 831 \text{ J.} \quad (\text{Answer})\end{aligned}$$

The transfers: Let's follow the energy. Of the 2077.5 J transferred to the helium as heat Q , 831 J goes into the work W required for the expansion and 1246.5 J goes into the internal energy E_{int} , which, for a monatomic gas, is entirely the kinetic energy of the atoms in their translational motion. These several results are suggested on the left side of Fig. 19-12.

19-8 DEGREES OF FREEDOM AND MOLAR SPECIFIC HEATS

Learning Objectives

After reading this module, you should be able to . . .

- 19.39 Identify that a degree of freedom is associated with each way a gas can store energy (translation, rotation, and oscillation).
- 19.40 Identify that an energy of $\frac{1}{2}kT$ per molecule is associated with each degree of freedom.
- 19.41 Identify that a monatomic gas can have an internal energy consisting of only translational motion.

Key Ideas

- We find C_V by using the equipartition of energy theorem, which states that every degree of freedom of a molecule (that is, every independent way it can store energy) has associated with it—an average—an energy $\frac{1}{2}kT$ per molecule ($= \frac{1}{2}RT$ per mole).

- If f is the number of degrees of freedom, then

- 19.42 Identify that at low temperatures a diatomic gas has energy in only translational motion, at higher temperatures it also has energy in molecular rotation, and at even higher temperatures it can also have energy in molecular oscillations.

- 19.43 Calculate the molar specific heat for monatomic and diatomic ideal gases in a constant-volume process and a constant-pressure process.

$$E_{\text{int}} = (f/2)nRT \text{ and}$$

$$C_V = \left(\frac{f}{2}\right)R = 4.16f \text{ J/mol} \cdot \text{K.}$$

- For monatomic gases $f = 3$ (three translational degrees); for diatomic gases $f = 5$ (three translational and two rotational degrees).

Degrees of Freedom and Molar Specific Heats

As Table 19-2 shows, the prediction that $C_V = \frac{3}{2}R$ agrees with experiment for monatomic gases but fails for diatomic and polyatomic gases. Let us try to explain the discrepancy by considering the possibility that molecules with more than one atom can store internal energy in forms other than translational kinetic energy.

Figure 19-13 shows common models of helium (a *monatomic* molecule, containing a single atom), oxygen (a *diatomic* molecule, containing two atoms), and

Table 19-3 Degrees of Freedom for Various Molecules

Molecule	Example	Degrees of Freedom			Predicted Molar Specific Heats	
		Translational	Rotational	Total (<i>f</i>)	<i>C_V</i> (Eq. 19-51)	<i>C_p</i> = <i>C_V</i> + <i>R</i>
Monatomic	He	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomeric	O ₂	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	CH ₄	3	3	6	$3R$	$4R$

methane (a *polyatomic* molecule). From such models, we would assume that all three types of molecules can have translational motions (say, moving left-right and up-down) and rotational motions (spinning about an axis like a top). In addition, we would assume that the diatomic and polyatomic molecules can have oscillatory motions, with the atoms oscillating slightly toward and away from one another, as if attached to opposite ends of a spring.

To keep account of the various ways in which energy can be stored in a gas, James Clerk Maxwell introduced the theorem of the **equipartition of energy**:



Every kind of molecule has a certain number *f* of *degrees of freedom*, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it—on average—an energy of $\frac{1}{2}kT$ per molecule (or $\frac{1}{2}RT$ per mole).

Let us apply the theorem to the translational and rotational motions of the molecules in Fig. 19-13. (We discuss oscillatory motion below.) For the translational motion, superimpose an *xyz* coordinate system on any gas. The molecules will, in general, have velocity components along all three axes. Thus, gas molecules of all types have three degrees of translational freedom (three ways to move in translation) and, on average, an associated energy of $3(\frac{1}{2}kT)$ per molecule.

For the rotational motion, imagine the origin of our *xyz* coordinate system at the center of each molecule in Fig. 19-13. In a gas, each molecule should be able to rotate with an angular velocity component along each of the three axes, so each gas should have three degrees of rotational freedom and, on average, an additional energy of $3(\frac{1}{2}kT)$ per molecule. However, experiment shows this is true only for the polyatomic molecules. According to *quantum theory*, the physics dealing with the allowed motions and energies of molecules and atoms, a monatomic gas molecule does not rotate and so has no rotational energy (a single atom cannot rotate like a top). A diatomic molecule can rotate like a top only about axes perpendicular to the line connecting the atoms (the axes are shown in Fig. 19-13b) and not about that line itself. Therefore, a diatomic molecule can have only two degrees of rotational freedom and a rotational energy of only $2(\frac{1}{2}kT)$ per molecule.

To extend our analysis of molar specific heats (*C_p* and *C* in Module 19-7) to ideal diatomic and polyatomic gases, it is necessary to retrace the derivations of that analysis in detail. First, we replace Eq. 19-38 ($E_{\text{int}} = \frac{3}{2}nRT$) with $E_{\text{int}} = (f/2)nRT$, where *f* is the number of degrees of freedom listed in Table 19-3. Doing so leads to the prediction

$$C_V = \left(\frac{f}{2} \right) R = 4.16f \text{ J/mol} \cdot \text{K}, \quad (19-51)$$

which agrees—as it must—with Eq. 19-43 for monatomic gases (*f* = 3). As Table 19-2 shows, this prediction also agrees with experiment for diatomic gases (*f* = 5), but it is too low for polyatomic gases (*f* = 6 for molecules comparable to CH₄).

Sample Problem 19.08 Diatomic gas, heat, temperature, internal energy

We transfer 1000 J as heat *Q* to a diatomic gas, allowing the gas to expand with the pressure held constant. The gas molecules

each rotate around an internal axis but do not oscillate. How much of the 1000 J goes into the increase of the gas's internal

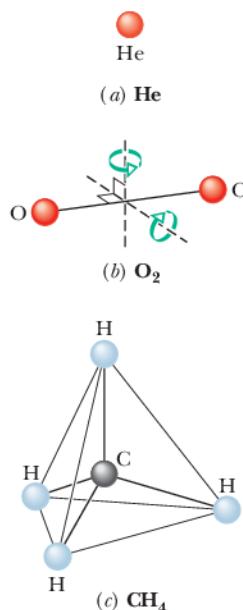


Figure 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen molecule.



energy? Of that amount, how much goes into ΔK_{tran} (the kinetic energy of the translational motion of the molecules) and ΔK_{rot} (the kinetic energy of their rotational motion)?

KEY IDEAS

- The transfer of energy as heat Q to a gas under constant pressure is related to the resulting temperature increase ΔT via Eq. 19-46 ($Q = nC_p \Delta T$).
- Because the gas is diatomic with molecules undergoing rotation but not oscillation, the molar specific heat is, from Fig. 19-12 and Table 19-3, $C_p = \frac{7}{2}R$.
- The increase ΔE_{int} in the internal energy is the same as would occur with a constant-volume process resulting in the same ΔT . Thus, from Eq. 19-45, $\Delta E_{\text{int}} = nC_V \Delta T$. From Fig. 19-12 and Table 19-3, we see that $C_V = \frac{5}{2}R$.
- For the same n and ΔT , ΔE_{int} is greater for a diatomic gas than for a monatomic gas because additional energy is required for rotation.

Increase in E_{int} : Let's first get the temperature change ΔT due to the transfer of energy as heat. From Eq. 19-46, substituting $\frac{7}{2}R$ for C_p , we have

$$\Delta T = \frac{Q}{\frac{7}{2}nR}. \quad (19-52)$$

We next find ΔE_{int} from Eq. 19-45, substituting the molar specific heat $C_V (= \frac{5}{2}R)$ for a constant-volume process and using the same ΔT . Because we are dealing with a diatomic gas, let's call this change $\Delta E_{\text{int,dia}}$. Equation 19-45 gives us

$$\begin{aligned}\Delta E_{\text{int,dia}} &= nC_V \Delta T = n\frac{5}{2}R\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{5}{7}Q \\ &= 0.71428Q = 714.3 \text{ J.} \quad (\text{Answer})\end{aligned}$$

In words, about 71% of the energy transferred to the gas goes into the internal energy. The rest goes into the work required to increase the volume of the gas, as the gas pushes the walls of its container outward.

Increases in K : If we were to increase the temperature of a monatomic gas (with the same value of n) by the amount given in Eq. 19-52, the internal energy would change by a smaller amount, call it $\Delta E_{\text{int,mon}}$, because rotational motion is not involved. To calculate that smaller amount, we still use Eq. 19-45 but now we substitute the value of C_V for a monatomic gas—namely, $C_V = \frac{3}{2}R$. So,

$$\Delta E_{\text{int,mon}} = n\frac{3}{2}R \Delta T.$$

Substituting for ΔT from Eq. 19-52 leads us to

$$\begin{aligned}\Delta E_{\text{int,mon}} &= n\frac{3}{2}R\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{3}{7}Q \\ &= 0.42857Q = 428.6 \text{ J.}\end{aligned}$$

For the monatomic gas, all this energy would go into the kinetic energy of the translational motion of the atoms. The important point here is that for a diatomic gas with the same values of n and ΔT , the same amount of energy goes into the kinetic energy of the translational motion of the molecules. The rest of $\Delta E_{\text{int,dia}}$ (that is, the additional 285.7 J) goes into the rotational motion of the molecules. Thus, for the diatomic gas,

$$\Delta K_{\text{trans}} = 428.6 \text{ J} \quad \text{and} \quad \Delta K_{\text{rot}} = 285.7 \text{ J.} \quad (\text{Answer})$$



Additional examples, video, and practice available at WileyPLUS

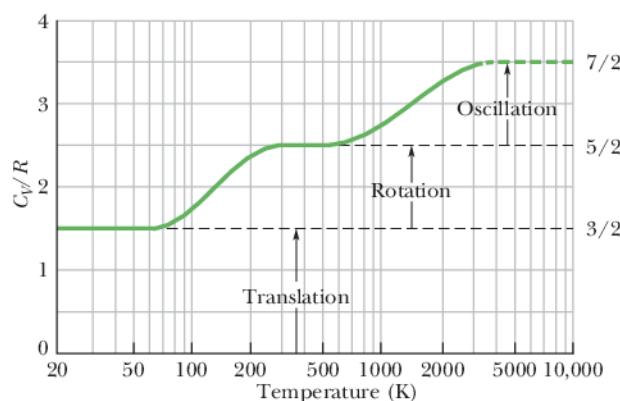


Figure 19-14 C_V/R versus temperature for (diatomic) hydrogen gas. Because rotational and oscillatory motions begin at certain energies, only translation is possible at very low temperatures. As the temperature increases, rotational motion can begin. At still higher temperatures, oscillatory motion can begin.

A Hint of Quantum Theory

We can improve the agreement of kinetic theory with experiment by including the oscillations of the atoms in a gas of diatomic or polyatomic molecules. For example, the two atoms in the O_2 molecule of Fig. 19-13b can oscillate toward and away from each other, with the interconnecting bond acting like a spring. However, experiment shows that such oscillations occur only at relatively high temperatures of the gas—the motion is “turned on” only when the gas molecules have relatively large energies. Rotational motion is also subject to such “turning on,” but at a lower temperature.

Figure 19-14 is of help in seeing this turning on of rotational motion and oscillatory motion. The ratio C_V/R for diatomic hydrogen gas (H_2) is plotted there against temperature, with the temperature scale logarithmic to cover several orders of magnitude. Below about 80 K, we find that $C_V/R = 1.5$. This result implies that only the three translational degrees of freedom of hydrogen are involved in the specific heat.

As the temperature increases, the value of C_V/R gradually increases to 2.5, implying that two additional degrees of freedom have become involved. Quantum theory shows that these two degrees of freedom are associated with the rotational motion of the hydrogen molecules and that this motion requires a certain minimum amount of energy. At very low temperatures (below 80 K), the molecules do not have enough energy to rotate. As the temperature increases from 80 K, first a few molecules and then more and more of them obtain enough energy to rotate, and the value of C_V/R increases, until all of the molecules are rotating and $C_V/R = 2.5$.

Similarly, quantum theory shows that oscillatory motion of the molecules requires a certain (higher) minimum amount of energy. This minimum amount is not met until the molecules reach a temperature of about 1000 K, as shown in Fig. 19-14. As the temperature increases beyond 1000 K, more and more molecules have enough energy to oscillate and the value of C_V/R increases, until all of the molecules are oscillating and $C_V/R = 3.5$. (In Fig. 19-14, the plotted curve stops at 3200 K because there the atoms of a hydrogen molecule oscillate so much that they overwhelm their bond, and the molecule then *dissociates* into two separate atoms.)

The turning on of the rotation and vibration of the diatomic and polyatomic molecules is due to the fact that the energies of these motions are quantized, that is, restricted to certain values. There is a lowest allowed value for each type of motion. Unless the thermal agitation of the surrounding molecules provides those lowest amounts, a molecule simply cannot rotate or vibrate.

19-9 THE ADIABATIC EXPANSION OF AN IDEAL GAS

Learning Objectives

After reading this module, you should be able to . . .

- 19.44** On a p - V diagram, sketch an adiabatic expansion (or contraction) and identify that there is no heat exchange Q with the environment.
- 19.45** Identify that in an adiabatic expansion, the gas does work on the environment, decreasing the gas's internal energy, and that in an adiabatic contraction, work is done on the gas, increasing the internal energy.
- 19.46** In an adiabatic expansion or contraction, relate the initial pressure and volume to the final pressure and volume.

Key Ideas

- When an ideal gas undergoes a slow adiabatic volume change (a change for which $Q = 0$),

$$pV^\gamma = \text{a constant} \quad (\text{adiabatic process}),$$

- 19.47** In an adiabatic expansion or contraction, relate the initial temperature and volume to the final temperature and volume.

- 19.48** Calculate the work done in an adiabatic process by integrating the pressure with respect to volume.

- 19.49** Identify that a free expansion of a gas into a vacuum is adiabatic but no work is done and thus, by the first law of thermodynamics, the internal energy and temperature of the gas do not change.

in which $\gamma (= C_p/C_V)$ is the ratio of molar specific heats for the gas.

- For a free expansion, $pV = \text{a constant}$.

The Adiabatic Expansion of an Ideal Gas

We saw in Module 17-2 that sound waves are propagated through air and other gases as a series of compressions and expansions; these variations in the transmission medium take place so rapidly that there is no time for energy to be transferred from one part of the medium to another as heat. As we saw in Module 18-5, a process for which $Q = 0$ is an *adiabatic process*. We can ensure that $Q = 0$ either by carrying out the process very quickly (as in sound waves) or by doing it (at any rate) in a well-insulated container.

Figure 19-15a shows our usual insulated cylinder, now containing an ideal gas and resting on an insulating stand. By removing mass from the piston, we can allow the gas to expand adiabatically. As the volume increases, both the pressure and the temperature drop. We shall prove next that the relation between the pressure and the volume during such an adiabatic process is

$$pV^\gamma = \text{a constant} \quad (\text{adiabatic process}), \quad (19-53)$$

in which $\gamma = C_p/C_V$, the ratio of the molar specific heats for the gas. On a p - V diagram such as that in Fig. 19-15b, the process occurs along a line (called an *adiabat*) that has the equation $p = (\text{a constant})/V^\gamma$. Since the gas goes from an initial state i to a final state f , we can rewrite Eq. 19-53 as

$$p_i V_i^\gamma = p_f V_f^\gamma \quad (\text{adiabatic process}). \quad (19-54)$$

To write an equation for an adiabatic process in terms of T and V , we use the ideal gas equation ($pV = nRT$) to eliminate p from Eq. 19-53, finding

$$\left(\frac{nRT}{V}\right)V^\gamma = \text{a constant}.$$

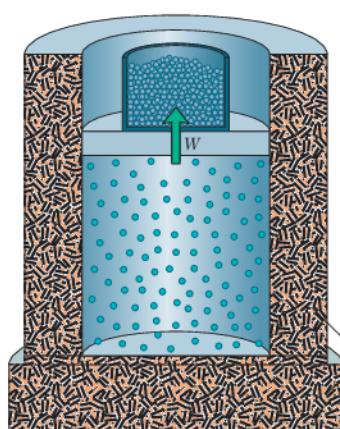
Because n and R are constants, we can rewrite this in the alternative form

$$TV^{\gamma-1} = \text{a constant} \quad (\text{adiabatic process}), \quad (19-55)$$

in which the constant is different from that in Eq. 19-53. When the gas goes from an initial state i to a final state f , we can rewrite Eq. 19-55 as

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad (\text{adiabatic process}). \quad (19-56)$$

Understanding adiabatic processes allows you to understand why popping the cork on a cold bottle of champagne or the tab on a cold can of soda causes a slight fog to form at the opening of the container. At the top of any unopened carbonated drink sits a gas of carbon dioxide and water vapor. Because the pressure of that gas is much greater than atmospheric pressure, the gas expands out into the atmosphere when the container is opened. Thus, the gas volume increases, but that means the gas must do work pushing against the atmosphere. Because the expansion is rapid, it is adiabatic, and the only source of energy for the work is the internal energy of the gas. Because the internal energy decreases,



(a)

We slowly remove lead shot, allowing an expansion without any heat transfer.

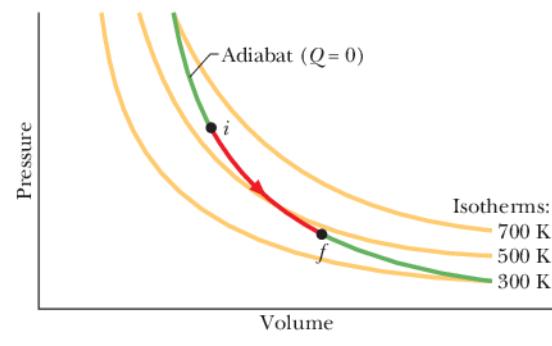


Figure 19-15 (a) The volume of an ideal gas is increased by removing mass from the piston. The process is adiabatic ($Q = 0$). (b) The process proceeds from i to f along an adiabat on a p - V diagram.

the temperature of the gas also decreases and so does the number of water molecules that can remain as a vapor. So, lots of the water molecules condense into tiny drops of fog.

Proof of Eq. 19-53

Suppose that you remove some shot from the piston of Fig. 19-15a, allowing the ideal gas to push the piston and the remaining shot upward and thus to increase the volume by a differential amount dV . Since the volume change is tiny, we may assume that the pressure p of the gas on the piston is constant during the change. This assumption allows us to say that the work dW done by the gas during the volume increase is equal to $p dV$. From Eq. 18-27, the first law of thermodynamics can then be written as

$$dE_{\text{int}} = Q - p dV. \quad (19-57)$$

Since the gas is thermally insulated (and thus the expansion is adiabatic), we substitute 0 for Q . Then we use Eq. 19-45 to substitute $nC_V dT$ for dE_{int} . With these substitutions, and after some rearranging, we have

$$n dT = -\left(\frac{p}{C_V}\right) dV. \quad (19-58)$$

Now from the ideal gas law ($pV = nRT$) we have

$$p dV + V dp = nR dT. \quad (19-59)$$

Replacing R with its equal, $C_p - C_V$, in Eq. 19-59 yields

$$n dT = \frac{p dV + V dp}{C_p - C_V}. \quad (19-60)$$

Equating Eqs. 19-58 and 19-60 and rearranging then give

$$\frac{dp}{p} + \left(\frac{C_p}{C_V}\right) \frac{dV}{V} = 0.$$

Replacing the ratio of the molar specific heats with γ and integrating (see integral 5 in Appendix E) yield

$$\ln p + \gamma \ln V = \text{a constant.}$$

Rewriting the left side as $\ln pV^\gamma$ and then taking the antilog of both sides, we find

$$pV^\gamma = \text{a constant.} \quad (19-61)$$

Free Expansions

Recall from Module 18-5 that a free expansion of a gas is an adiabatic process with *no* work or change in internal energy. Thus, a free expansion differs from the adiabatic process described by Eqs. 19-53 through 19-61, in which work is done and the internal energy changes. Those equations then do *not* apply to a free expansion, even though such an expansion is adiabatic.

Also recall that in a free expansion, a gas is in equilibrium only at its initial and final points; thus, we can plot only those points, but not the expansion itself, on a p - V diagram. In addition, because $\Delta E_{\text{int}} = 0$, the temperature of the final state must be that of the initial state. Thus, the initial and final points on a p - V diagram must be on the same isotherm, and instead of Eq. 19-56 we have

$$T_i = T_f \quad (\text{free expansion}). \quad (19-62)$$

If we next assume that the gas is ideal (so that $pV = nRT$), then because there is no change in temperature, there can be no change in the product pV . Thus, instead of Eq. 19-53 a free expansion involves the relation

$$p_i V_i = p_f V_f \quad (\text{free expansion}). \quad (19-63)$$



Sample Problem 19.09 Work done by a gas in an adiabatic expansion

Initially an ideal diatomic gas has pressure $p_i = 2.00 \times 10^5 \text{ Pa}$ and volume $V_i = 4.00 \times 10^{-6} \text{ m}^3$. How much work W does it do, and what is the change ΔE_{int} in its internal energy if it expands adiabatically to volume $V_f = 8.00 \times 10^{-6} \text{ m}^3$? Throughout the process, the molecules have rotation but not oscillation.

KEY IDEA

- (1) In an adiabatic expansion, no heat is exchanged between the gas and its environment, and the energy for the work done by the gas comes from the internal energy.
- (2) The final pressure and volume are related to the initial pressure and volume by Eq. 19-54 ($p_i V_i^\gamma = p_f V_f^\gamma$).
- (3) The work done by a gas in any process can be calculated by integrating the pressure with respect to the volume (the work is due to the gas pushing the walls of its container outward).

Calculations: We want to calculate the work by filling out this integration,

$$W = \int_{V_i}^{V_f} p \, dV, \quad (19-64)$$

but we first need an expression for the pressure as a function of volume (so that we integrate the expression with respect to volume). So, let's rewrite Eq. 19-54 with indefinite symbols (dropping the subscripts f) as

$$p = \frac{1}{V^\gamma} p_i V_i^\gamma = V^{-\gamma} p_i V_i^\gamma. \quad (19-65)$$

The initial quantities are given constants but the pressure p is a function of the variable volume V . Substituting this

expression into Eq. 19-64 and integrating lead us to

$$\begin{aligned} W &= \int_{V_i}^{V_f} p \, dV = \int_{V_i}^{V_f} V^{-\gamma} p_i V_i^\gamma \, dV \\ &= p_i V_i^\gamma \int_{V_i}^{V_f} V^{-\gamma} \, dV = \frac{1}{-\gamma + 1} p_i V_i^\gamma [V^{-\gamma+1}]_{V_i}^{V_f} \\ &= \frac{1}{-\gamma + 1} p_i V_i^\gamma [V_f^{-\gamma+1} - V_i^{-\gamma+1}]. \end{aligned} \quad (19-66)$$

Before we substitute in given data, we must determine the ratio γ of molar specific heats for a gas of diatomic molecules with rotation but no oscillation. From Table 19-3 we find

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{7}{5}R}{\frac{5}{2}R} = 1.4. \quad (19-67)$$

We can now write the work done by the gas as the following (with volume in cubic meters and pressure in pascals):

$$\begin{aligned} W &= \frac{1}{-1.4 + 1} (2.00 \times 10^5)(4.00 \times 10^{-6})^{1.4} \\ &\quad \times [(8.00 \times 10^{-6})^{-1.4+1} - (4.00 \times 10^{-6})^{-1.4+1}] \\ &= 0.48 \text{ J}. \end{aligned} \quad (\text{Answer})$$

The first law of thermodynamics (Eq. 18-26) tells us that $\Delta E_{\text{int}} = Q - W$. Because $Q = 0$ in the adiabatic expansion, we see that

$$\Delta E_{\text{int}} = -0.48 \text{ J}. \quad (\text{Answer})$$

With this decrease in internal energy, the gas temperature must also decrease because of the expansion.

Sample Problem 19.10 Adiabatic expansion, free expansion

Initially, 1 mol of oxygen (assumed to be an ideal gas) has temperature 310 K and volume 12 L. We will allow it to expand to volume 19 L.

- (a) What would be the final temperature if the gas expands adiabatically? Oxygen (O_2) is diatomic and here has rotation but not oscillation.

KEY IDEAS

- 1. When a gas expands against the pressure of its environment, it must do work.

- 2. When the process is adiabatic (no energy is transferred as heat), then the energy required for the work can come only from the internal energy of the gas.
- 3. Because the internal energy decreases, the temperature T must also decrease.

Calculations: We can relate the initial and final temperatures and volumes with Eq. 19-56:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}. \quad (19-68)$$

Because the molecules are diatomic and have rotation but not oscillation, we can take the molar specific heats from