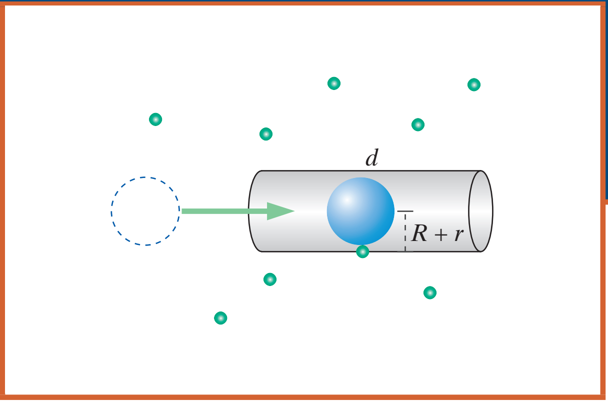
SUPPLEMENT

S1

Gases and Heat Engines



OBJECTIVES

After studying this supplement, you should be able to

- Determine the flow rate of a gas through a hole, given microscopic information about the gas
- Determine the change in temperature and pressure of a gas undergoing compression or expansion
- Determine the efficiency of a heat engine

S1.1 GASES, SOLIDS, AND LIQUIDS

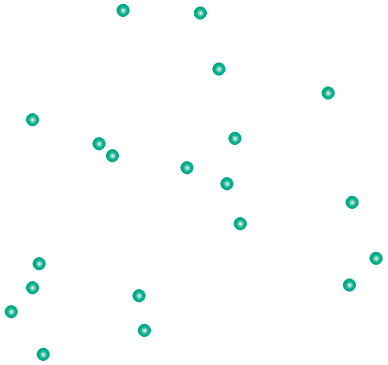


Figure S1.1 Molecules in a gas.

In contrast to a solid, a gas has no fixed structure. The gas molecules are not bound to each other but move around very freely, which is why a gas does not have a well-defined shape of its own; it fills whatever container you put it in (Figure S1.1). Think, for example, of the constantly shifting shape of a cloud, or the deformability of a balloon, in contrast with the rigidity of a block of aluminum. On average, gas molecules are sufficiently far apart that most of the time they hardly interact with each other. This low level of interaction is what makes it feasible to model a gas in some detail, using relatively simple concepts.

In a gas the molecular motion must be sufficiently violent that molecules can't stay stuck together. At high enough temperatures, any molecules that do manage to bind to each other temporarily soon get knocked apart again by high-speed collisions with other molecules. However, at a low enough temperature, molecules move sufficiently slowly that collisions are no longer violent enough to break intermolecular bonds. Rather, more and more molecules stick to each other in a growing mass as the gas turns into a liquid or, at still lower temperatures, a solid.

Liquids Are More Complex

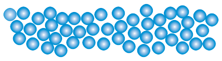


Figure S1.2 Molecules in a liquid.

A liquid is intermediate between a solid and a gas. The molecules in a liquid are sufficiently attracted to each other that the liquid doesn't fly apart like a gas (Figure S1.2), yet the attraction is not strong enough to keep each molecule near a fixed equilibrium position as in a solid. The molecules in a liquid can slide past each other, giving liquids their special property of fluid flow (unlike solids) with fixed volume (unlike gases).

The analysis of liquids in terms of atomic, microscopic models is quite difficult compared with gases, where the molecules only rarely come in contact with other atoms, or compared with solids, where the atoms never move very far away from their equilibrium positions. For this reason, in this introductory textbook with its emphasis on atomic-level description and analysis we concentrate mostly on understanding gases and solids.

An active field of research, called "molecular dynamics," models liquids, gases, and solids by computational modeling using the Momentum Principle and appropriate forces between the molecules. The difference between this work and the computational models you have made is that sophisticated programming techniques are required to deal with very large numbers of molecules, sometimes as many as a million, in a reasonable amount of computer time.

S1.2 GAS LEAKS THROUGH A HOLE

In Chapter 12 we used statistical mechanics to determine the average speed of a gas molecule. Here we'll see some interesting phenomena in which the average speed plays a role. We will model the gas molecules as little balls that don't attract each other and interact only in brief elastic collisions.

We will frequently use the symbol $n = N/V$ to stand for the number of gas molecules per unit volume, which we will express in SI units as number per cubic meter:

NUMBER DENSITY: NUMBER PER CUBIC METER

$$\text{Definition: } n \equiv \frac{N}{V}$$

N is the number of gas molecules in the volume V. The units of n are molecules per cubic meter.

Warning: You may be familiar from chemistry with the ideal gas law written in the form $PV = nRT$, where n is the number of moles. Here n means something else—the number of molecules per cubic meter, N/V.

EXAMPLE ***n* at Standard Temperature and Pressure**

Standard Temperature and Pressure (or STP) is defined for a gas to be $0\ ^\circ\text{C} = 273\ \text{K}$ and the average air pressure at sea level. Under STP conditions the ideal gas law can be used to show that one mole of a gas will occupy a volume of 22.4 liters $= 22.4 \times 10^3\ \text{cm}^3 = 22.4 \times 10^{-3}\ \text{m}^3$. What is the number density n of a gas at STP?

Solution One mole consists of 6.02×10^{23} molecules, so

$$n = \frac{6.02 \times 10^{23}\ \text{molecules}}{22.4 \times 10^{-3}\ \text{m}^3} = 2.68 \times 10^{25}\ \text{molecules/m}^3$$

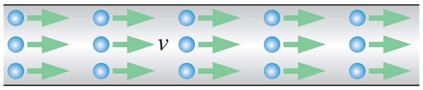


Figure S1.3 Side view of molecules all traveling to the right with speed v inside a tube. There are n molecules per cubic meter inside the tube.

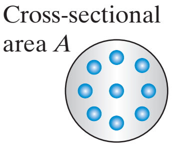


Figure S1.4 End view of molecules all traveling the same direction in a tube of cross-sectional area A.

One-Directional Gas

We will calculate the leakage rate of a gas through a small hole in a container filled with the gas. First we'll consider a simplified one-directional example, in order to understand the basic issues before stating the results for a real three-dimensional gas.

The chain of reasoning that we follow is basically geometric. Consider a situation in which many gas molecules are all traveling to the right inside a tube. For the moment, temporarily assume that they all have the same speed v (Figure S1.3). The cross-sectional area of the tube is A (Figure S1.4).

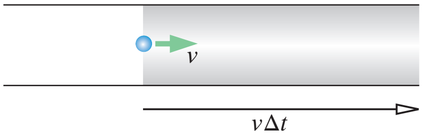


Figure S1.5 A molecule that will leave the tube in a time Δt must be within a distance $v\,\Delta t$ from the end.

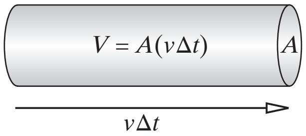


Figure S1.6 Volume containing the molecules that will leave the tube in time Δt.

Because eventually we want to be able to calculate how fast a gas will leak through a hole in a container, we will calculate how many molecules leave this tube in a short time interval Δt. For a molecule that is traveling at speed v to be able to reach the right end of the tube in this time interval Δt, it must be within a distance $v\Delta t$ of the end (Figure S1.5).

Since the cross-sectional area of the tube is A, the volume V of the tube that contains just those molecules that will leave the tube during the time interval Δt is simply $A(v\Delta t)$; see Figure S1.6.

There are n molecules per m^3 inside the tube, and $N = nV$ molecules inside the volume V. So the number N of molecules that will leave in the time interval Δt is

$$N = nV = n(Av\Delta t)$$

Dividing by the time interval Δt, we find the following result:

$$\text{number of molecules crossing area } A \text{ per second} = nAv$$

This is for the one-directional case; all molecules have the same speed.

> **QUESTION** Does this equation make sense? What would you expect if you increased the number of molecules per cubic meter, or the cross-sectional area, or the speed?

The equation does make sense. The more molecules per unit volume ($n = N/V$), the more molecules will reach the right end of the tube per unit time. The bigger the cross-sectional area (A), the more molecules that will pass through that area per unit time. The faster the molecules are moving (v), the more molecules from farther away that can reach the end of the tube in a given time interval. The units are right: (molecules/m^3)(m^2)(m/s) = molecules/s.

Effect of Different Speeds

We need to account for the fact that the gas molecules don't all have the same speed v. Suppose that n_1 molecules per unit volume have speeds of approximately v_1, n_2 molecules per unit volume have speeds of approximately v_2, and so on. The number of molecules crossing an area A per second is

$$n_1Av_1 + n_2Av_2 + \cdots$$

The average speed of all the molecules is by definition the following, where we weight each different speed by the number of molecules per cubic meter that have that approximate speed:

$$\bar{v} = \frac{n_1v_1 + n_2v_2 + \cdots}{n}$$

Therefore,

$$n_1Av_1 + n_2Av_2 + \cdots = nA\bar{v}$$

A horizontal bar over a symbol is a standard notation for "average," and $\bar{v}$ means average speed.

Finally, we have a valid equation for the number of molecules in a one-directional flow leaving the right end of the tube, even in the situation where they have a distribution of different speeds:

NUMBER OF MOLECULES CROSSING AREA A PER SECOND (ONE-DIRECTIONAL)

$$\text{1-D flow rate} = nA\bar{v}$$

This is for one-directional flow; molecules have various speeds.

A "one-directional" gas may sound a bit silly, but this equation does apply to real one-directional flows such as the flow of water or gas through a pipe or the flow of electrons through a copper wire in an electric circuit.

A Three-Dimensional Gas

A more realistic model of a gas in a closed container would have approximately equal numbers of molecules heading to the left as well as to the right in the tube, in which case the number of molecules leaving the right end of the tube would be only $\frac{1}{2}nA\bar{v}$. In a real three-dimensional gas, molecules are moving in all directions. Only those molecules that are headed in the $+x$ direction can pass through a hole located to the right, not those moving in the $-x$ direction or in the $\pm y$ or $\pm z$ directions. The molecules are headed randomly in all six directions, so we might expect our equation would have a factor of $1/6$.

However, the actual factor is $1/4$, which comes from detailed averaging over all directions and is related to our use of the average speed (magnitude of velocity), rather than averages of velocity components v_x or v_y or v_z. We don't want to get bogged down in the rather heavyweight mathematics required to prove this, so we just state that the factor is $1/4$ rather than $1/6$. (You can find a full derivation in books on statistical mechanics.)

NUMBER OF MOLECULES CROSSING AREA *A* PER SECOND (THREE-DIMENSIONAL)

$$\text{3-D flow rate} = \frac{1}{4}nA\bar{v}$$

This is for three-dimensional flow; molecules have various velocities.

EXAMPLE **Leak Through a Hole in a Balloon**

At standard temperature and pressure, at what rate will helium escape from a balloon through a hole 1 mm in diameter? As we saw in Chapter 12, the average speed $\bar{v}$ of helium atoms at ordinary temperatures is about 1200 m/s.

Solution Earlier we calculated that at STP $n = 2.68 \times 10^{25}$ molecules per cubic meter. Therefore the leak rate is

$$\begin{aligned}\frac{1}{4}nA\bar{v} &= \frac{1}{4}\left(2.68 \times 10^{25}\frac{\text{molecules}}{\text{m}^3}\right)\left(\pi(0.5 \times 10^{-3}\ \text{m})^2\right)(1200\ \text{m/s}) \\ &= 6.3 \times 10^{21}\ \text{molecules/s; about 0.01 moles/s}\end{aligned}$$

Cooling of the Gas

There is an interesting and important effect of gas escaping through a hole. If you look back over the derivations of the equations, you can see that faster molecules escape disproportionately to their numbers. Faster molecules can be farther away from the hole than is true for slower molecules and still escape through the hole in the next short time interval. As a result, the distribution of speeds of molecules inside the container becomes somewhat depleted of high speeds.

Checkpoint 1 What can you say about the temperature of the gas inside the container as the gas escapes? Why?

EXAMPLE **Leakage from a Balloon**

A party balloon filled with helium is about one foot in diameter (about 30 cm). The volume of a sphere is $\frac{4}{3}\pi r^3$, where r is the radius of the sphere. In the previous example we calculated that the initial leak rate through a circular hole 1 mm in diameter is 6.3×10^{21} molecules/s. **(a)** If the helium were to escape at a constant rate equal to the initial rate, about how long would it take for all the helium to leak out? **(b)** As the helium escapes, the balloon shrinks, and the number of helium atoms per cubic meter n will stay roughly constant, in which case our analysis is pretty good. However, remember that the temperature of the gas drops due to a preferential loss of high-speed atoms. Would this effect make the amount of time to empty be more or less than the value you calculated in part (a)?

Solution **(a)** The leak rate was 6.3×10^{21} atoms per second. Calculate the number of helium atoms in the balloon originally:

$$\frac{4}{3}\pi(0.3\text{ m})^3\left(\frac{6 \times 10^{23}\text{ atoms}}{22.4 \times 10^3\text{cm}^3}\right)\left(\frac{1 \times 10^6\text{cm}^3}{\text{m}^3}\right) = 3 \times 10^{24}\text{ atoms}$$

Assuming a constant rate:

$$\frac{3 \times 10^{24}\text{ atoms}}{6.3 \times 10^{21}\text{ atoms/s}} = 500\text{ s}$$

(b) With the preferential loss of high-speed atoms, the speed distribution inside the balloon shifts to lower speeds (corresponding to a lower temperature). If the average speed is lower, the leak rate is lower, and it should take longer for the balloon to empty than we calculated in part (a), where we assumed a constant leak rate.

We've implicitly done the analysis in vacuum. If the balloon is in air, air molecules enter the balloon through the same hole.

When you blow up an ordinary rubber balloon the pressure is higher than one atmosphere, which means higher number density n but also a correspondingly higher leak rate, which is proportional to n. To a first approximation the density doesn't matter in this estimate of the time to empty. Also note that often when you puncture a balloon the balloon rips, creating a large opening; this is not the case we are considering.

Checkpoint 2 A spacecraft containing air at STP is struck by a micrometeor that makes a hole 2 mm in diameter. Calculate the initial rate at which air escapes through the hole, in number of air molecules leaving the spacecraft per second. In Chapter 12 we found that the average speed of air molecules at STP is about 500 m/s.

S1.3 MEAN FREE PATH

Suppose that we place a special molecule somewhere in the helium gas, one whose movements we can trace. For example, it might be a molecule of perfume. On average, how far does this molecule go before it runs into a molecule of the gas? The average distance between collisions is called the "mean free path." It plays an important role in many phenomena, including the creation of electric sparks in air (discussed in Volume II of this textbook).

An approximate calculation of the mean free path depends on a simple geometrical argument. Draw a cylinder along the direction of motion of the

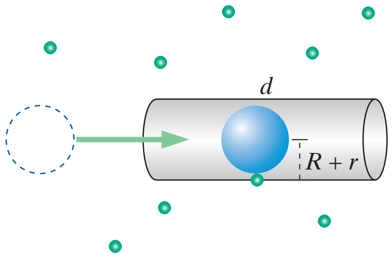


Figure S1.7 If a “special molecule” (blue) enters a cylinder of length d and radius $R + r$, it will collide with a gas molecule (green).

special molecule, with length d and radius $R + r$, where R is the radius of the molecule, and r is the radius of a gas molecule, as shown in Figure S1.7 and Figure S1.8.

The geometrical significance of this cylinder is that if the path of the special molecule comes within one molecular radius of a gas molecule, there will be a collision, so any gas molecule whose center is inside the cylinder will be hit. How long should the cylinder be for there to be a collision?

We define d to be the average distance the special molecule will travel before colliding with another molecule, so the cylinder drawn in Figure S1.7 should contain on average about one gas molecule. The cross-sectional area of the cylinder is $A \approx \pi(R + r)^2$ and the volume of the cylinder is Ad. If n stands for the number of gas molecules per cubic meter, we can write an equation involving the mean free path:

MEAN FREE PATH

$$d \approx \frac{1}{nA}$$

$A \approx \pi(R + r)^2$; see Figure S1.7.

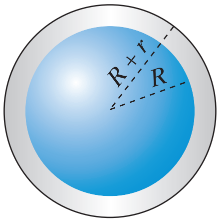


Figure S1.8 End view of cylinder.

We are ignoring some subtle effects in this calculation, but this analysis gives us the main picture: the mean free path is shorter for higher density or larger molecular size.

EXAMPLE

Mean Free Path in Air

To get an idea of the order of magnitude of a typical mean free path, assume that an N_2 molecule in the air has a radius of approximately 2×10^{-10} m (the radius of one of the N_2 atoms being about 1×10^{-10} m), and calculate approximately the mean free path d of an N_2 molecule moving through air.

Solution

$$n = 2.68 \times 10^{25} \, \frac{\text{molecules}}{\text{m}^3}$$

$$A \approx \pi(2 \times 2 \times 10^{-10} \text{ m})^2 = 5 \times 10^{-19} \text{ m}^2$$

$$d \approx \frac{1}{nA} \approx \frac{1}{\left(2.68 \times 10^{25} \, \frac{\text{molecules}}{\text{m}^3}\right)(5 \times 10^{-19} \text{ m}^2)}$$

$$d \approx 7 \times 10^{-8} \text{ m}$$

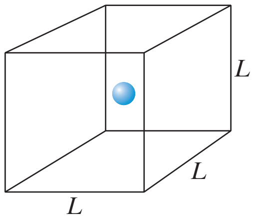


Figure S1.9 The volume of air occupied on average by one molecule.

Checkpoint 3 It is interesting to compare the mean free path of about 7×10^{-8} m to the average spacing L between air molecules, which is the cube root of the volume occupied on average by one molecule (Figure S1.9). Calculate L. You may be surprised to find that the mean free path d is much larger than the average molecular spacing L. The molecules represent rather small targets.

S1.4 PRESSURE AND TEMPERATURE

We can use statistical ideas to relate what we know about the motion of molecules in a gas to the pressure that the gas exerts on its container. We’ll consider a closed container, with the energy of the gas not changing.

In a party balloon, helium atoms are continually hitting the rubber walls of the balloon. In an earlier example we found that at STP (standard temperature and pressure) about 6×10^{21} helium atoms per second escape through a

1-mm-diameter section of the balloon. That means that in a closed container 6×10^{21} helium atoms per second strike every 1-mm-diameter portion of the container's walls.

The time- and space-averaged effect of this bombardment is an average force exerted on every square millimeter of the container. This average force per unit area is called the "pressure" P and is measured in $\mathrm{N/m^2}$, also called a "pascal." We are going to calculate how big the pressure is in terms of the average speed of the helium atoms, thus building a link between the microscopic behavior of the helium atoms and the macroscopic time- and space-averaged pressure.

On average, a helium atom bounces off the wall with no change of kinetic energy. We emphasize that this is the average behavior. Any individual atom may happen to gain or lose energy in the collision with a vibrating atom in the container wall, but if the container is not being warmed up or cooled down, the velocity distribution in the gas does not change, and on average the helium atoms rebound from the wall with the same kinetic energy they had just before hitting the wall (Figure S1.10).

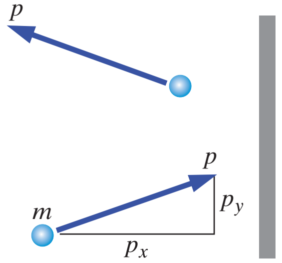


Figure S1.10 On average, an atom bounces off the wall without changing speed.

> **QUESTION** If the kinetic energy doesn't change when an atom bounces off the wall, is there any change in the atom's momentum?

Unlike speed or kinetic energy, momentum is a vector quantity, and there is a large change in the x component of momentum, from $+p_x$ to $-p_x$. (There is no change in the y component.) Therefore the momentum change of the helium atom is $\Delta p_{x,\text{helium}} = -2p_x$.

> **QUESTION** What caused this change in the momentum of the helium atom?

A force is required to change the momentum of an object. In this case the force was applied by the wall of the container (or in more detail, by an atom in the wall of the container). By the principle of reciprocity (Newton's third law), the helium atom must have applied an equal and opposite force to the wall (or more precisely, to an atom in the wall of the container). Therefore the wall must have acquired an amount of momentum $\Delta p_{x,\text{ wall}} = 2p_x$.

If we could calculate the average time Δt between collisions of helium atoms with a small area A of the wall, we could express the pressure (force per unit area) as follows, since $d\vec{p}/dt = \vec{F}$:

$$P = \frac{F}{A} = \frac{1}{A}\frac{\Delta p_x}{\Delta t}$$

Assuming One Direction and One Speed

We already know that if there are n_+ helium atoms per unit volume that have an x component of velocity equal to $v_x > 0$ (that is, moving in the $+x$ direction toward the wall), the number of such atoms that hit an area A of the wall in a time Δt is $n_+ A v_x \Delta t$. Therefore the average time between collisions is

$$\Delta t = 1/(n_+ A v_x)$$

and we find

$$P = \frac{F}{A} = \frac{1}{A}\frac{\Delta p_x}{\left(\dfrac{1}{n_+ A v_x}\right)} = (n_+ v_x)(2p_x) = 2n_+\left(\frac{p_x}{m}\right)p_x = 2n_+\frac{p_x^2}{m}$$

An Alternative Argument

Alternatively, we can say that n_+Av_x helium atoms with this x component of velocity hit the area A every second, and each of them delivers $2p_x$ of momentum to the wall, so that the total momentum transfer to the wall per second is

$$\text{(number of hits per second) (momentum transfer per hit)} = (n_+Av_x)(2p_x)$$

Divide by A to get the force per unit area, and you again get

$$P = (n_+v_x)(2p_x) = 2n_+\frac{p_x^2}{m}$$

Taking the Velocity Distribution into Account

Actually, this is just the contribution to the pressure made by those atoms that happened to have this particular value of $v_x > 0$. On average, only half the atoms are headed in the $+x$ direction, so we replace n_+ by $n/2$, where n is the number of atoms per cubic meter (going in either the $+x$ or $-x$ direction).

$$P = 2n_+\frac{p_x^2}{m} = n\frac{p_x^2}{m}$$

We also need to average over the slow and fast atoms:

$$P = n\frac{\overline{p_x^2}}{m}$$

We'll explain what we mean by this average. Suppose that n_1 atoms per unit volume have x components of momentum of approximately p_{x1}, n_2 atoms per unit volume have x components of momentum of approximately p_{x2}, and so on. The pressure is

$$P = n_1\left(\frac{p_{x1}^2}{m}\right) + n_2\left(\frac{p_{x2}^2}{m}\right) + \cdots$$

The average value of p_x^2 for all the atoms is by definition the following, where we weight each different value of p_x^2 by the number of atoms per cubic meter that have that approximate value:

$$\overline{p_x^2} = \frac{n_1p_{x1}^2 + n_2p_{x2}^2 + \cdots}{n}$$

so we have $n_1p_{x1}^2 + n_2p_{x2}^2 + \cdots = n\overline{p_x^2}$. Therefore we can write this:

$$P = n_1\left(\frac{p_{x1}^2}{m}\right) + n_2\left(\frac{p_{x2}^2}{m}\right) + \cdots = n\frac{\overline{p_x^2}}{m}$$

Taking Direction into Account

We can re-express the pressure in terms of the magnitude of momentum p rather than p_x by the following steps:

> First, note that $p = \sqrt{p_x^2 + p_y^2 + p_z^2}$, or $p^2 = p_x^2 + p_y^2 + p_z^2$.
>
> Second, since the atoms are flying around in random directions, there should be no difference in averaging in the x, y, or z direction, so $\overline{p_x^2} = \overline{p_y^2} = \overline{p_z^2}$, which implies that $\overline{p^2} = 3\overline{p_x^2}$.

Taking these factors into account, instead of $P = n\dfrac{\overline{p_x^2}}{m}$ we can write the following important result:

GAS PRESSURE IN TERMS OF ATOMIC QUANTITIES

$$P = \frac{1}{3}n\frac{\overline{p^2}}{m}$$

> **QUESTION** Look back over the line of reasoning that led us to this result, and reflect on the nature of the argument. Stripped of the details, try to summarize the major steps leading to this result.

We reached this result by combining two effects: the number of molecules hitting an area per second is proportional to v, and the momentum transfer is also proportional to v. Hence the force per unit area is proportional to v^2.

We derived the pressure by considering the effects of molecules hitting the walls, but the result applies throughout the gas, since if you put some object anywhere in the gas it will experience this same pressure.

The Ideal Gas Law

It is useful to rewrite our result for the pressure, factoring out the term $\overline{p^2}/(2m)$, which is the average translational kinetic energy K_{trans} of a molecule of mass m:

$$P = \frac{2}{3}n\left(\frac{\overline{p^2}}{2m}\right) = \frac{2}{3}n\overline{K}_{\text{trans}}$$

The pressure of a gas is proportional to the number density (number of molecules per cubic meter, N/V), and proportional to the average translational kinetic energy of the gas molecules. This gives us a connection to temperature, because we found in Chapter 12 that $\overline{K}_{\text{trans}} = \frac{3}{2}k_BT$.

Substituting into the pressure equation, $P = \frac{2}{3}n\overline{K}_{\text{trans}} = \frac{2}{3}n(\frac{3}{2}k_BT) = nk_BT$, which relates pressure to temperature and is called the ideal gas law:

MICROSCOPIC VERSION OF THE IDEAL GAS LAW

$$P = nk_BT$$

Checkpoint 4 We found that at STP, $n = 2.68 \times 10^{25}$ molecules per m^3. Calculate the value of one atmosphere of pressure in units of N/m^2.

The Macroscopic Ideal Gas Law

We can compare our microscopic version of the gas law with experiments that measure the macroscopic properties of gases. For gases with fairly low densities, measurements of the pressure for all gases (helium, oxygen, nitrogen, carbon dioxide, etc.) are well summarized by the macroscopic ideal gas law, which is probably familiar to you from chemistry, and which describes the observed behavior of any low-density gas:

MACROSCOPIC VERSION OF THE IDEAL GAS LAW

$$PV = (\text{number of moles})RT$$

R is the "gas constant" (8.3 J/K/mole).

To compare with our microscopic prediction, we can convert this macroscopic version of the ideal gas law to a version involving microscopic quantities:

$$P = \frac{(\text{number of moles})RT}{V}$$

$$\text{number of moles} = \frac{(\text{number of molecules})}{(6.02 \times 10^{23}\,\text{molecules/mole})} = \frac{N}{6.02 \times 10^{23}}$$

where N is the number of molecules in the gas. Therefore we have

$$P = \left(\frac{N}{6.02 \times 10^{23}}\right)\frac{RT}{V} = \left(\frac{N}{V}\right)\left(\frac{R}{6.02 \times 10^{23}}\right)T$$

This is simply $P = nk_BT$, where $n = N/V$ and $R/6.02 \times 10^{23}$ is the Boltzmann constant k_B:

$$k_B = \frac{R}{6.02 \times 10^{23}} = \frac{8.3\,\text{J/K/mole}}{6.02 \times 10^{23}\,\text{molecules/mole}} = 1.38 \times 10^{-23}\,\text{J/K}$$

Warning about the Meaning of *n*

Sometimes the ideal gas law is written in the form $PV = nRT$, where n is the number of moles rather than the number of molecules per cubic meter, $n = N/V$. On the rare occasions when we need to refer to the number of moles, we'll write it out as "number of moles."

Temperature from Entropy or from the Ideal Gas Law

In Chapter 12 we found the relationship $\overline{K}_{\text{trans}} = \frac{3}{2}k_BT$, based on the Boltzmann distribution as applied to a low-density gas. The Boltzmann distribution in turn was based on the statistical mechanics definition of temperature in terms of entropy as $1/T = dS/dE$.

When we inserted $\overline{K}_{\text{trans}} = \frac{3}{2}k_BT$ into the kinetic theory result for pressure, $P = \frac{1}{3}n(\overline{p^2/m})$, we obtained the molecular version of the ideal gas law, $P = nk_BT$, which we showed was equivalent to the macroscopic version of the ideal gas law, $P = (\text{number of moles})RT/V$.

Low-density gases are described well by the ideal gas law, and for that reason gases are used to make accurate thermometers. You measure the pressure P and volume V of a known number of moles of a low-density gas and determine the temperature from the macroscopic gas law:

$$T = \frac{PV}{(\text{number of moles})R} \quad \text{(gas thermometer)}$$

The fact that we could start from $1/T = dS/dE$ and derive the ideal gas law proves that the temperature measured by a gas thermometer is exactly the same as the "thermodynamic temperature" defined in terms of entropy.

Real Gases

Our analysis works well for low-density gases. For high-density gases, there are two major complications. First, the molecules themselves take up a considerable fraction of the space, so the effective volume is less than the geometrical volume, and V in the gas law must be replaced by a smaller value.

Second, at high densities the short-range electric forces between molecules have some effect. In this context these intermolecular forces are called "van der Waals" forces, which are the gradient of the interatomic potential energy discussed in Chapter 7. In a low-density gas almost all of the energy is kinetic energy, but in a high-density gas some of the energy goes into configurational energy associated with the interatomic potential energy. The effect is that in the gas law P must be replaced by a smaller value.

When these two effects are taken into effect, the resulting "van der Waals" equation fits the experimental data quite well for all densities of a gas, although the corrections are different for different gases due to differences in molecular sizes and intermolecular forces.

Energy of a Diatomic Gas

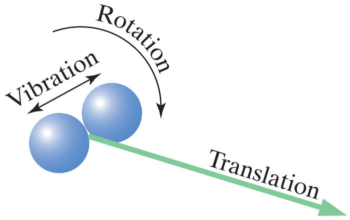


Figure S1.11 Energy of an oxygen molecule.

The equation for the average translational kinetic energy $\overline{K}_{\text{trans}} = \frac{3}{2}k_B T$ is valid even for a gas with multiatom molecules such as nitrogen (N_2) or oxygen (O_2). However, as you will recall from Chapter 9, this translational kinetic energy is only a part of the total energy of the molecule. In addition to translational energy, a diatomic molecule can have rotational and vibrational energy relative to the center of mass (Figure S1.11), so the energy contains additional terms. We write the energy of a diatomic molecule in the following way:

$$K_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}} + Mgy_{\text{CM}}$$

The key point, as we discussed in Chapter 12, is that the average energy of a diatomic molecule is greater than the average energy of an atom in a monatomic gas at the same temperature. For a monatomic gas such as helium the average total energy per molecule is just $\overline{K}_{\text{trans}} = \frac{3}{2}k_B T$.

Application: Weight of a Gas in a Box

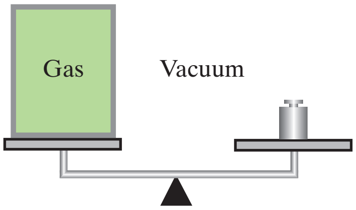


Figure S1.12 Weighing a box containing a gas.

In Chapter 12 we used the Boltzmann factor to find the number density as a function of height, $n \propto e^{-mgy/k_B T}$. From this we can determine the pressure as a function of height, which makes it possible to understand something that otherwise might be rather odd about weighing a box that contains a gas (Figure S1.12). Let's do the weighing in a vacuum so we don't have to worry about buoyancy forces due to surrounding air. The box definitely weighs more on the scales if there is gas in it than if there is a vacuum in it. In fact, if the mass of the gas is M, the additional weight is Mg, because the Momentum Principle for multiparticle systems refers to the net force on a system, and the gravitational contribution to the net force is the sum of the gravitational forces on each individual gas molecule in the box, Mg.

That seems reasonable until you think about the details of what is going on inside the box. At any given instant, the vast majority of the gas molecules are not touching the box! Also, some of the gas molecules are colliding with the top of the box, exerting an upward force on the box. How can these molecules possibly contribute to the weight measured by the scales? What is the mechanism for the Momentum Principle working out correctly for this multiparticle system?

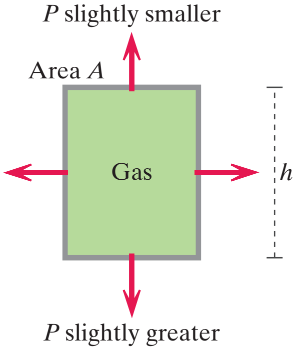


Figure S1.13 The force due to gas pressure on the top of the box differs slightly from the force on the bottom of the box.

The number density n at the bottom of the box is slightly larger than the number density at the top of the box, if all the gas is at the same temperature, which is a good assumption in most situations. Therefore the pressure, $P = nk_B T$, is larger at the bottom than at the top. Let's calculate the y components of the forces associated with these slightly different pressures, where A is the area of the top (and bottom) of the box, and h is the height of the box (Figure S1.13).

$$F_{\text{net},y} = P_{\text{top}}A - P_{\text{bottom}}A = A\,\Delta P$$

where ΔP is the pressure difference from bottom to top inside the box. We can calculate ΔP directly, by starting from the fact that for a small height change Δy, we have this:

$$\frac{\Delta P}{\Delta y} \approx \frac{dP}{dy}, \quad \text{so} \quad \Delta P \approx \frac{dP}{dy}\Delta y$$

If we can evaluate dP/dy, we can determine the small pressure difference ΔP. Since $P = nk_BT$, the height dependence of the pressure is the same as for the number density (for constant temperature), and we can write this:

$$\frac{dP}{dy} = \frac{d}{dy}\left(P_{\text{bottom}}e^{-mgy/k_BT}\right)$$
$$\frac{dP}{dy} = P_{\text{bottom}}e^{-mgy/k_BT}\left(-\frac{mg}{k_BT}\right) \approx -P_{\text{bottom}}\left(\frac{mg}{k_BT}\right)$$

because the factor e^{-mgy/k_BT} is very close to 1. The result is negative because the force the gas exerts on the top of the box is smaller than the force on the bottom. Choosing $\Delta y = h$, and writing $P_{\text{bottom}} = nk_BT$, we have this result for ΔP:

$$\Delta P = \frac{dP}{dy}\Delta y \approx -nk_BT\left[\frac{mg}{k_BT}\right]h = -nmgh$$

Now that we know the pressure difference, we can calculate the y component of the net force:

$$F_{\text{net},y} = A\,\Delta P = -nmg(A\,h)$$

> **QUESTION** $A\,h$ is the volume V of the box, and $n = N/V$ is the number of molecules per m^3 in the box, so what does this equation reduce to?

We have the striking result that the air inside the box pushes down on the box with a force equal to the combined weight Mg of all N molecules in the box:

$$F_y = -Nmg = -Mg$$

We have shown that the difference in the time- and space-averaged momentum transfers by molecular collisions to the top and bottom of the box is equal to the weight of the gas in the box, as predicted by the Momentum Principle for a multiparticle system. The pressure difference is very slight, but then the weight of the gas is very small, for that matter. What is surprising is that at any particular instant, relatively few of the molecules are actually in contact with the box, yet the effects of these relatively few molecules is the same as though they were all sitting on the bottom of the box.

You could think of a box full of water in the same way. The water pressure is larger at the bottom than at the top, but with water this difference is quite large, corresponding to the much higher density of water. In fact, a column of water only 10 m high makes a pressure equal to that produced by the many kilometers of atmosphere.

Consider a column of water 10 m high with cross-sectional area A. The density of water is 1 g/cm^3, which is $1\times10^3\ \text{kg/m}^3$. The total mass of the column is the density (kg/m^3) times the volume $A(10\ \text{m})$, so the pressure on the bottom of the column is

$$\frac{(1\times10^3\ \text{kg/m}^3)A(10\ \text{m})(9.8\ \text{N/kg})}{A} \approx 1\times10^5\ \text{N/m}^2$$

This is the same result we found for atmospheric pressure at STP.

> **QUESTION** In the preceding discussion the box was in vacuum, but under normal conditions the box we were weighing would have been surrounded by air. Suppose that the box has thin walls and is initially open to the air. Then we close the lid, trapping air inside it. Consider all forces including buoyancy forces, and determine what the scales will read. Will it be the weight of the box alone or the box plus air?

The scales will measure the weight of the box alone, because the weight of the air is $M_{\text{air}}g$ and the buoyancy force is $M_{\text{air}}g$ upward.

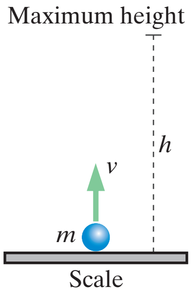


Figure S1.14 The ball has just hit the scale and has rebounded upward.

Application: Weight of a Bouncing Molecule

There is a related calculation that is amusing. You may have done a related homework problem earlier on collisions, in which case you already went through a similar calculation. Consider a single molecule (otherwise in vacuum) that bounces up and down on a scale without losing significant energy. Figure S1.14 shows a snapshot at the instant that the molecule is just bouncing up after hitting the scale.

What do the scales read? If the scales can respond quickly, we will see brief spikes each time the molecule strikes it (Figure S1.15). Let's determine what the time-averaged force is.

> **QUESTION** How long does it take for the molecule to reach the top of its trajectory, h, starting with a speed v? What then is the time Δt between impacts? How much momentum transfer is there to the scale on each impact?

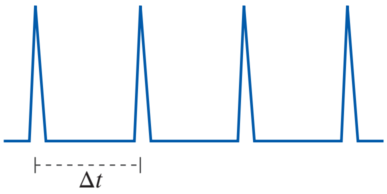


Figure S1.15 Impacts of the ball on the scale.

It takes a time interval v/g to go up (for the speed to decrease from v to 0 with acceleration $-g$) and another time interval v/g to come down, so the time between impacts is $\Delta t = 2v/g$. Each impact transfers an amount of momentum $\Delta P = 2mv$. Therefore the time-averaged force is

$$\frac{\Delta P}{\Delta t} = \frac{2mv}{2v/g} = mg$$

If the scale is sluggish, and can't respond in a time as short as $\Delta t = 2v/g$, the scale will simply register the value mg, just as though the molecule were sitting quietly on the scale.

S1.5 ENERGY TRANSFERS

In this section we offer an analysis of energy transfers between a gas and its surroundings. We will address such questions as these: How much energy transfer Q due to a temperature difference is required to raise the temperature of a gas by one degree (the heat capacity of a gas)? How does the temperature of a gas change when you compress it quickly? Do the answers to these questions depend on what kind of gas is involved?

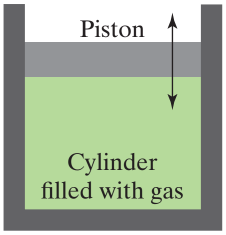


Figure S1.16 A cylinder with a piston that can move vertically.

We need a device that lets us control the flow of energy into and out of a gas, in the form of work W or energy transfer Q. We will use a system consisting of a cylindrical container containing gas that is enclosed by a piston that can move in and out of the cylinder with little friction but which fits tightly enough to keep the gas from leaking out (Figure S1.16). This is similar to a cylinder in an automobile engine, into which is sprayed a mixture of gasoline vapor and air. The mixture is ignited by a spark, and the chemical reactions raise the temperature and pressure very high very quickly. The piston is pushed outward, which turns a shaft that ultimately drives the wheels.

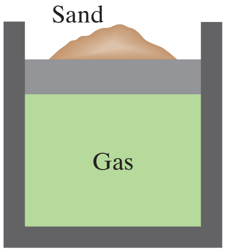


Figure S1.17 The piston can be loaded with varying amounts of sand.

Force and Pressure

Figure S1.17 shows a cylinder with a vertical-running piston on which we can load varying amounts of sand, in order to be able to control the pressure of the contained gas, and to be able to do controlled amounts of work on the gas. We will also put the cylinder in contact with hot or cold objects and allow energy transfer into or out of the cylinder.

> **QUESTION** Consider the piston plus sand as the system of interest for a moment and think about what forces act on this system.

A free-body diagram for the piston + sand system (Figure S1.18) includes the downward gravitational forces on the piston (Mg) and on the sand (mg), an upward time- and space-averaged force due to the pressure of the enclosed gas on the lower surface of the piston, and a downward time- and space-averaged force due to the pressure of the outside atmosphere on the upper surface of the system.

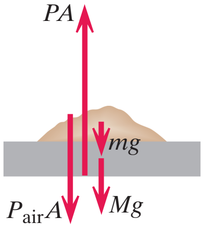


Figure S1.18 Forces on the piston.

Since pressure is force per unit area, the upward force is PA, where A is the surface area of the bottom of the piston. Similarly, the downward force contributed by the outside atmosphere is $P_{\text{air}}A$. These pressure-related forces are not actually continuous, since they are the result of collisions of individual gas molecules with the piston and sand. However, the rate of collisions is so extremely high over the area of the piston that the force seems essentially constant. For example, in Checkpoint 2 you found that on average, at STP (standard temperature and pressure) about 6×10^{21} helium atoms strike a tiny 1-mm-diameter section every second.

> **QUESTION** In mechanical equilibrium (velocity of piston not changing), solve for the gas pressure inside the cylinder.

The Momentum Principle tells us that in equilibrium the net force on the piston + sand system must be zero, from which we are able to deduce that the pressure of the gas inside the cylinder is

$$P = P_{\text{air}} + \frac{Mg + mg}{A}$$

A Sudden Change

By varying the amount of sand (m) we can vary the pressure of the gas under study.

> **QUESTION** If you suddenly add a lot of sand, what happens?

If you suddenly add a lot of sand to the piston, there is suddenly a sizable nonzero net downward force on the piston + sand system: $F_{\text{net}} = AP_{\text{air}} + Mg + mg - AP \neq 0$. The piston starts to pick up speed downward. As it does so, it runs into gas molecules and tends to increase their speeds.

> **QUESTION** What happens to the temperature of the gas in the cylinder?

Since higher average speed means higher temperature, the gas temperature starts to increase at the same time that the volume of the gas is decreasing. This is a double whammy: both increased temperature and decreased volume contribute to increased pressure, since $P = (N/V)k_B T$. Therefore the pressure in the gas quickly rises, and eventually there will be a new equilibrium with a lower piston (supporting more sand) and a higher gas pressure in the cylinder.

However, getting to that new equilibrium is pretty complicated. If there is no friction or other energy dissipation, the piston will oscillate down and up, with the gas pressure going up and down. It is even possible to determine an effective "spring stiffness" for the gas and calculate the frequency of the oscillation. However, in any real system there will be some friction, so we know that the system will eventually settle down to a new equilibrium configuration.

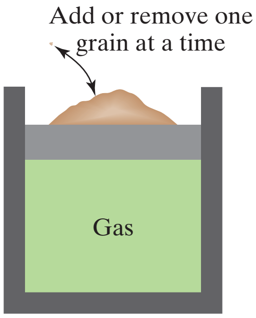


Figure S1.19 By adding or removing one grain of sand at a time we effect a "quasistatic" compression or expansion.

Quasistatic Processes

To avoid these complicated (though interesting) transient effects, we will study what happens when we add sand very carefully and very slowly, one grain at a time, and we assume that the new equilibrium is established almost immediately. This is called a "quasistatic compression" because the system is at all times very nearly in equilibrium (Figure S1.19). Similarly, if we slowly remove one grain at a time, we can carry out a "quasistatic expansion." Note in particular that at no time does the piston have any significant amount of kinetic energy, and macroscopic kinetic energy is essentially zero at all times. Of course there is plenty of microscopic kinetic energy in the gas molecules and the outside air molecules and in the thermal motion of atoms in the cylinder walls, piston, and sand.

Suppose we carry out a lengthy, time-consuming quasistatic compression by adding lots of sand, one grain at a time, very slowly. The piston goes down quite a ways, the pressure in the gas is a lot higher, and the volume of the gas is a lot smaller. If we know the pressure and volume, we can calculate the temperature by using the ideal gas law $P = (N/V)k_BT$ (assuming the gas density isn't too high to make this invalid).

Can we predict how low the piston will go for a given amount of added sand? Oddly enough, no—not without knowing something more about this device. There are two extreme cases that are both important in practice and calculable for an ideal gas. If the apparatus is made of metal (a very good thermal conductor) and is in good thermal contact with a large object at temperature T, the process will proceed at nearly constant temperature, with energy transfer from the gas into the surroundings. If the apparatus is made of glass (a very poor thermal conductor), the temperature of the gas inside the cylinder will rise in a predictable way, with negligible energy transfer to the surroundings in the form of energy transfer Q. We will analyze both kinds of processes: constant temperature processes and no-Q processes.

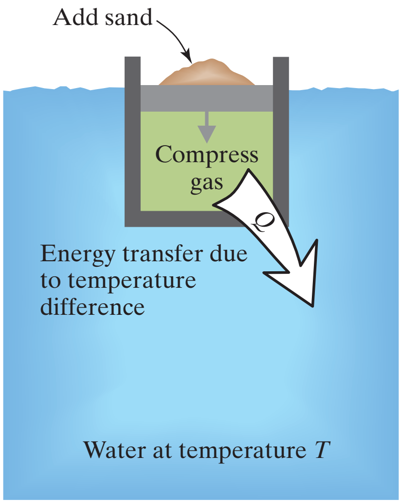


Figure S1.20 A cylinder of gas immersed in a large volume of water.

Constant-Temperature (Isothermal) Compression

Suppose that the cylinder is made of metal (which is a very good thermal conductor) and is sitting in a very big tub of water whose temperature is T, as shown in Figure S1.20.

As we compress the gas, the temperature in the gas starts to increase. However, this will lead to energy flowing out of the gas into the water, because whenever the temperatures differ in two objects that are in thermal contact with each other, we have seen that there is a transfer of energy from the hotter object into the colder object. In fact, for many materials the rate of energy transfer is proportional to the temperature difference—double the temperature difference, double the rate at which energy transfers from the hotter object into the colder one.

The mechanism for energy transfer due to a temperature difference is that atoms in the hotter object are on average moving faster than atoms in the colder object, so in collisions between atoms at the boundary between the two systems it is likely that energy will be gained by the colder object and lost by the hotter object.

Energy transfer out of the gas will lower the temperature of the gas, since the total energy of the gas is proportional to the temperature. Quickly the temperature of the gas will fall back to the temperature of the water. The temperature of the big tub of water on the other hand will hardly change as a result of the energy added to it from the gas, because there is such a large mass of water to warm up.

Therefore the entire quasistatic compression takes place essentially at the temperature of the water, and the final temperature of the gas is nearly the same as the initial temperature of the gas. This is a constant-temperature compression (also called an "isothermal" compression, which just means constant temperature). Similarly, we can slowly remove sand from the piston and carry out a quasistatic constant-temperature expansion.

QUESTION Suppose that the original gas pressure and volume were P_1 and V_1, and as the result of a constant-temperature process the final volume is V_2. What is the final pressure P_2?

Since the temperature hasn't changed, from the ideal gas law $P = (N/V)k_BT$ we can deduce that $P_1V_1 = P_2V_2$, and therefore $P_2 = P_1(V_1/V_2)$.

Energy in a Constant-Temperature Compression

A more difficult question we can ask (and answer!) is this: How much energy was added to the water in the constant-temperature compression?

> **QUESTION** What energy inputs and outputs were made to the gas? What energy change occurred in the gas?

The piston did work on the gas, and there was energy transfer Q out of the gas (and into the water). The Earth's gravitational force did work on the gas (since the center of mass of the gas went down), but this is negligibly small compared to the work done by the piston (the lowering of the heavy piston involves much more gravitational energy than the lowering of the low-mass gas).

> **QUESTION** Did the total energy of the gas change (ignoring the small gravitational energy change)?

Since the total energy of an ideal gas is proportional to temperature (including rotational and vibrational energy if the gas is not monatomic), and we made sure that we kept the temperature constant, the total energy of the gas did not change. Therefore we have this energy equation for the open system that is the gas:

$$\Delta(\text{energy of gas}) = (W \text{ by piston}) - (|Q| \text{ that flowed into water}) = 0$$

Symbolically, $\Delta E_{\text{gas}} = W + Q = 0$, where Q is negative (transfer out of system). In thermal processes of this kind, the energy equation is called "the first law of thermodynamics."

If we can calculate the work done by the piston, we can equate that result to the amount of energy transfer Q into the water. The piston exerts a (time- and space-averaged) force PA on the gas, where P is the pressure in the gas and A is the cross-sectional area of the piston (Figure S1.21).

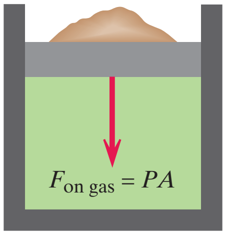


Figure S1.21 Force on the gas by the piston.

> **QUESTION** If the piston drops a distance h, is the work it does PAh?

As the piston drops, the pressure in the gas increases, so the force is not constant. We have to integrate the variable force through the distance h in order to determine the work. If we measure x downward from the initial piston position, at each step dx of the way the increment of work done is $PA\,dx$. However, $A\,dx$ is an increment of volume (base area A times altitude dx), and the change in the volume is negative. Putting this all together, we have this:

WORK DONE BY A PISTON ON A GAS

$$W = -\int_{V_1}^{V_2} P dV$$

Check the sign: If the volume decreases, the integral will be negative, and the minus sign in front of the integral makes the work done on the gas be positive, which is correct. Conversely, in an expansion of a gas, the integral is positive and the work is negative, because the gas is doing work on the piston rather than the other way round.

> **QUESTION** In a constant-temperature (isothermal) compression, work is done on the gas. Where does this energy flow go? How does the temperature stay constant?

As the piston moves down, it increases the average energy of the gas molecules that run into it. Therefore the input work starts to raise the temperature of the gas (higher speeds), but this higher temperature causes energy transfer Q out of the cylinder, into the (very slightly) lower-temperature water. The net effect is for energy to flow into the gas in the form of mechanical work, and out of the gas into the water in the form of energy transfer Q. There is no change in the total energy of the gas, because the temperature of the gas didn't change. The outward energy transfer brings the gas temperature back to what it was before the falling piston tried to increase the temperature.

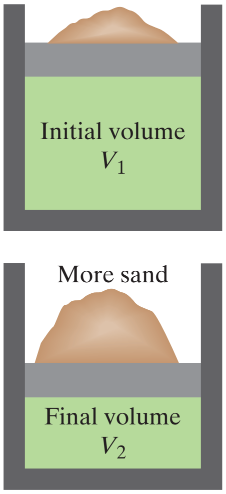


Figure S1.22 The gas is compressed at a constant temperature T (the cylinder is immersed in a large tub of water at temperature T).

Now we can calculate quantitatively the work done by the piston in the constant-temperature compression, which is equal to the energy transfer from the gas to the surrounding water. We add lots of sand, one grain at a time (to maintain quasistatic equilibrium), and we compress the gas from an initial volume V_1 to a final volume V_2 (Figure S1.22).

Replace P by Nk_BT/V, where T is a constant:

$$W = -\int_{V_1}^{V_2} P\,dV = -\int_{V_1}^{V_2} \frac{Nk_BT}{V}\,dV$$

$$W = -Nk_BT\int_{V_1}^{V_2} \frac{dV}{V} = -Nk_BT[\ln V]_{V_1}^{V_2} = -Nk_BT\ln\left(\frac{V_2}{V_1}\right)$$

Since the process was a compression, V_2 is smaller than V_1. Since $-\ln(V_2/V_1) = \ln(V_1/V_2)$, we have

$$W_{\text{by piston}} = |Q_{\text{into water}}| = Nk_BT\ln\left(\frac{V_1}{V_2}\right)$$

Just as the symbol W is normally used for "work," so the symbol Q is normally used for "energy transfer due to a temperature difference." Here Q is negative (energy output).

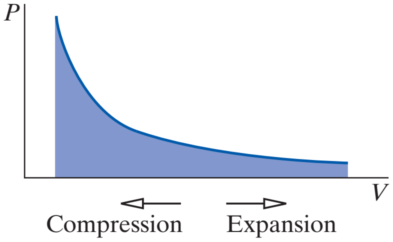


Figure S1.23 If T is kept constant, then the product PV is also constant.

Graphical Representation

There is a useful graphical representation of this constant-temperature process. We plot the pressure P vs. the volume V, as shown in Figure S1.23, and the process is represented by a curve of constant T (which is also a curve of constant PV, since $PV = Nk_BT$). The area under the process curve is the integral of $P\,dV$. In a compression the volume decreases, so we move to the left on the graph and the integral is negative; W is positive and Q is negative. In an expansion the volume increases, and we move to the right on the graph and the integral is positive; W is negative and Q is positive.

$$W = -\int_{V_1}^{V_2} P\,dV$$

The First Law of Thermodynamics

For historical reasons, in thermal processes the Energy Principle is called "the first law of thermodynamics."

THE FIRST LAW OF THERMODYNAMICS

$$\Delta E_{\text{sys}} = W + Q$$

In the particular case of constant-temperature (isothermal) compression of an ideal gas, we have

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

where E_{int} is the "internal" energy of the gas (the sum of the translational, rotational, vibrational, and other energy terms of all the molecules).

For historical reasons, many textbooks dealing with thermal physics define work W as the work done *by* a system rather than work done *on* a system, so the sign of W is changed. We define W as the work done on the system to be consistent with other, nonthermal uses of the Energy Principle.

Heat Capacity

We were able to calculate the important properties of a constant-temperature compression, where the apparatus was in good thermal contact with its surroundings. Before analyzing the opposite extreme, where the apparatus is thermally insulated from its surroundings and no energy transfer due to a temperature difference is involved, we will review the concept of heat capacity in this context.

Lock the piston in position so that the volume of the gas won't change (Figure S1.24), and so no work is done ($W = 0$). Put the apparatus in a big tub of water whose temperature is higher than the gas temperature, so that energy transfer will go from the water to the gas. Allow an amount of energy transfer Q due to the temperature difference to enter the gas and observe how much temperature rise ΔT has occurred in the gas. We define the "specific heat capacity C_V at constant volume" on a per-molecule basis in the following way, where N as usual is the total number of molecules in the gas:

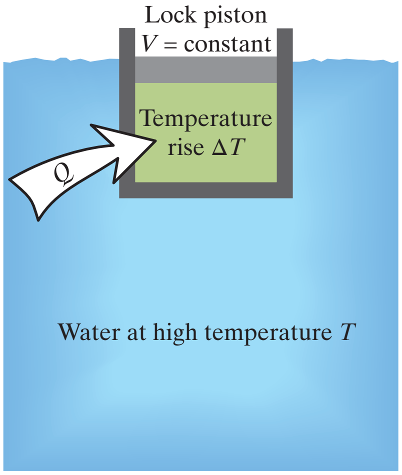


Figure S1.24 If the piston is locked so the volume of the gas cannot change, we can measure C_V of the gas.

$$\Delta E_{\text{thermal}} = NC_V\Delta T \quad \text{(constant volume)}$$

Since $W = 0$, this is also equal to Q. The larger the specific heat capacity, the smaller the temperature rise ΔT for a given energy input Q.

QUESTION What is C_V for a monatomic gas such as helium?

Since the total energy in a monatomic gas is $N\overline{K}_{\text{trans}} = \frac{3}{2}Nk_BT$, the energy transfer Q will increase the total energy of the gas by an amount $\frac{3}{2}Nk_B\Delta T$, so $C_V = \frac{3}{2}k_B$. Experimental measurements of the specific heat capacity of monatomic gases agree with this prediction.

For gases that are not monatomic, such as nitrogen (N_2), C_V can be larger than $\frac{3}{2}k_B$ because the total energy can be larger than $\frac{3}{2}Nk_BT$ due to rotational and vibrational energy relative to the center of mass of the molecule. Before quantum mechanics, theoretical predictions for the contribution of the rotational and vibrational energies to the specific heat capacity of gases did not agree with experimental measurements. This was one of the puzzles that was eventually resolved by quantum mechanics, as we found in Chapter 12.

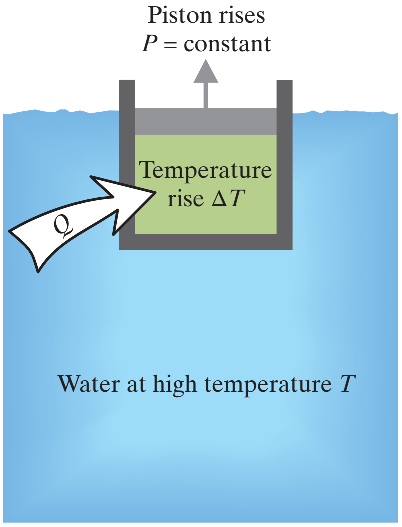


Figure S1.25 If the piston is free to move, the pressure inside the cylinder remains the same, and we can measure C_p of the gas.

SPECIFIC HEAT CAPACITY AT CONSTANT VOLUME ON A PER-MOLECULE BASIS

$$C_V = \frac{3}{2}k_B \quad \text{for a monatomic gas (He, etc.)}$$

$$C_V \geq \frac{3}{2}k_B \quad \text{for other gases (N}_2\text{, etc.)}$$

Heat Capacity at Constant Pressure

If we don't lock the piston but let the gas expand at constant pressure, the incoming energy transfer Q due to the temperature difference not only raises the energy of the gas by an amount $\Delta E_{\text{thermal}} = NC_V\Delta T$ but also raises the piston, which involves an amount of work W (Figure S1.25). We define the "specific heat capacity C_P at constant pressure" on a per-molecule basis as follows:

$$Q = NC_P\Delta T \quad \text{(constant pressure)}$$

Evidently C_P is bigger than C_V, because $NC_P\Delta T = NC_V\Delta T + W$. We can calculate the work done on the piston by the gas as the gas expands, which is the negative of the work done by the piston on the gas:

$$W = \int_{V_1}^{V_2} PdV = P\int_{V_1}^{V_2} dV = PV_2 - PV_1 = Nk_BT_2 - Nk_BT_1 = Nk_B\Delta T$$

Therefore for an ideal gas there is a simple relationship between C_V and C_P:

$$NC_P\Delta T = NC_V\Delta T + Nk_B\Delta T$$
$$C_P = C_V + k_B$$

Checkpoint 5 What is the specific heat capacity at constant pressure on a per-molecule basis C_P for helium?

Molar Specific Heat Capacity

Specific heat capacity is often given on a per-mole basis rather than a per-molecule basis. The molar specific heat capacity at constant volume for an ideal gas is $C_V = \frac{3}{2}R$, where R is the molar gas constant (8.3 J/K), which is $6 \times 10^{23} k_B$. The molar specific heat capacity at constant pressure is $C_P = C_V + R$ for an ideal gas.

No-*Q* (Adiabatic) Compression

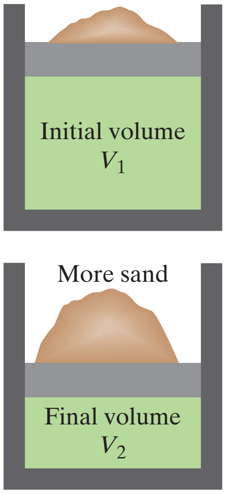


Figure S1.26 If the cylinder and piston are made of insulating material, no energy transfer Q can occur between the gas and its surroundings. This is called an adiabatic compression.

With the apparatus made of metal and sitting in a big tub of water, the temperature during the compression didn't change. Now we analyze the opposite extreme. We make the cylinder and piston out of glass or ceramic (which are poor conductors for energy transfer due to a temperature difference) to minimize energy transfer out of the gas as the gas gets hotter during the compression. In fact, we make the approximation that there is no energy transfer at all (Figure S1.26). Such a no-Q process is also called "adiabatic" (which means "no energy transfer due to a temperature difference").

How realistic is such a no-Q approximation? For many real situations this can be a rather good approximation if the compression or expansion is fast, so that there isn't enough time for significant energy transfer due to a temperature difference. Such a flow of energy from one object to another is a rather slow process. For example, a cup of coffee sitting on a table may stay quite hot for ten minutes or more.

However, didn't we say that we were going to carry out compressions and expansions very slowly, "quasistatically"? Yes, so there is a contradiction. However, it is often the case that motion may be slow enough to be a good approximation to a quasistatic process and nevertheless may also be fast compared to the time required for significant energy transfer due to a temperature difference. Again, think of how long it takes a cup of coffee to cool off.

We again consider the gas in the cylinder as the system of interest, and the work done by the piston is equal to the increase in energy of the gas:

$$W = -\int_{V_1}^{V_2} PdV = NC_V\Delta T$$

QUESTION Why did we use C_V in this equation? The volume isn't constant in this compression!

An ideal gas is unique among materials in that its total energy is entirely determined by the temperature, independent of volume or pressure. So the change of energy of the gas itself is just $NC_V\Delta T$, even when the volume is not constant. As a practical matter, real gases behave this way as long as the density is not too high. At high densities the energy of the gas includes a significant term associated with the interatomic forces.

We can work through the integration, starting from a "differential" form of the equation shown above:

$$-PdV = NC_V dT$$

Use the gas law $P = (N/V)k_B T$ to substitute for the pressure:

$$-Nk_B T\frac{dV}{V} = NC_V dT$$

Divide through by $k_B T$ and rearrange:

$$\left(\frac{C_V}{k_B}\right)\frac{dT}{T} + \frac{dV}{V} = 0$$

$$\left(\frac{C_V}{k_B}\right)\int\frac{dT}{T} + \int\frac{dV}{V} = 0$$

Now integrate:

$$\left(\frac{C_V}{k_B}\right)\ln T + \ln V = \text{constant}$$

Rewrite, using the properties of logarithms:

$$\ln T^{(C_V/k_B)} + \ln V = \ln\left(T^{(C_V/k_B)}V\right) = \text{constant}$$

Therefore we have

$$T^{(C_V/k_B)}V = \text{constant}$$

Checkpoint 6 Use the ideal gas law to eliminate T from this expression, and show that $PV^\gamma = \text{constant}$ in a no-Q process, where the parameter γ is defined as the ratio of the constant-pressure specific heat capacity to the constant-volume specific heat capacity, $\gamma \equiv C_P/C_V$. (Since C_P is greater than C_V, γ is greater than 1.) In particular, if the initial pressure and volume are P_1 and V_1, and the final pressure and volume are P_2 and V_2, then $P_2V_2^\gamma = P_1V_1^\gamma$. Alternatively, we also have $T_2^{(C_V/k_B)}V_2 = T_1^{(C_V/k_B)}V_1$.

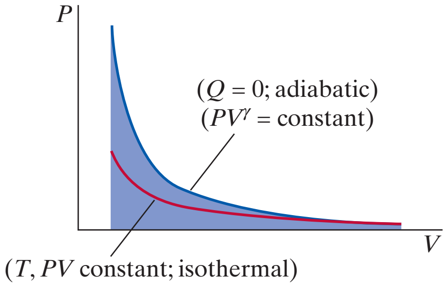


Figure S1.27 *PV* curves for a no-*Q* (adiabatic) process and a constant temperature (isothermal) process.

Graphical Representation

Again, there is a useful graphical representation of this no-Q process. In Figure S1.27 we plot the pressure P vs. the volume V, and the process is represented by a curve along which $PV^\gamma = \text{constant}$. The area under the process curve represents the work W. For comparison we also show the curve for a constant-temperature process (T and PV constant). The no-Q curve is much steeper than the constant-temperature curve.

Work vs. *Q*

We have studied the response of a gas to energy inputs and outputs, both mechanical W (work) and thermal Q (energy transfer due to a temperature difference). Work represents organized, orderly, macroscopic energy input.

Energy transfer due to a temperature difference represents disorganized, disorderly, microscopic energy input. There is randomness at the atomic level in the collisions of atoms, which is the basic mechanism for energy transfer due to a temperature difference. In Chapter 12 we saw deep consequences of the distinction between work W and energy transfer Q.

S1.6 FUNDAMENTAL LIMITATIONS ON EFFICIENCY

An important technology involves the conversion of energy transfer Q due to a temperature difference into useful work done by an engine on some object in the surroundings (Figure S1.28). Such an engine is called a "heat engine." For example, in a steam-powered electricity generating plant, coal is burned to warm up water that drives a steam engine to turn a generator, which converts the work done by the steam engine into electric energy. Energy conservation of course puts limits on how much useful work you can get from the burning of the coal—but there is a further limitation due to the second law of thermodynamics. It turns out that in a practical generating plant only about one-third of the energy of the coal can be turned into useful work! The fundamental problem is that energy transfer due to a temperature difference is a disorderly energy transfer, and the second law of thermodynamics takes that into account.

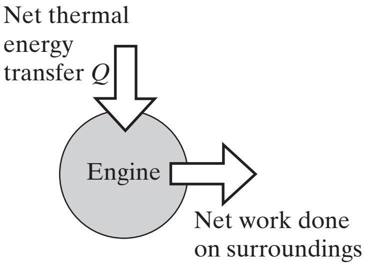


Figure S1.28 An engine converts net energy transfer Q into useful work done by the engine on the surroundings.

We will find that the most efficient processes are "reversible" processes—that is, processes that produce no change in the entropy of the Universe (a reversed movie of such a process looks possible). In the next sections we discuss two processes, mechanical friction and finite-temperature-difference energy transfer, which are major contributors to entropy production and whose effects must be minimized in order to obtain the most efficient performance in a mechanical system. Where we are headed is to establish limits on how efficiently thermal energy can be turned into mechanical energy in a heat engine, as a consequence of the second law of thermodynamics. This is a revealing example of the power of the second law of thermodynamics to set limits on possible phenomena.

Friction and Entropy Production

The second law of thermodynamics says that the entropy of the Universe never decreases. Portions of the Universe may experience a decrease of entropy, but only if the entropy of other portions increases at least as much (and typically more). An example of a process that increases the total entropy of the Universe is sliding friction. A block sliding across a table slows down as kinetic energy associated with the overall motion of the block is dissipated into random (thermal) energy inside the block and table, with an increase in entropy.

This friction process is irreversible. We would be astonished if after coming to rest the block suddenly started picking up speed back toward its starting position, although this would not violate conservation of energy. However, the probability is vanishingly small that the dissipated energy in the block and table could concentrate back into an orderly motion of the block.

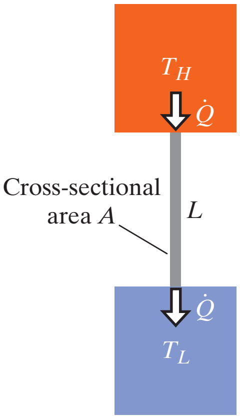


Figure S1.29 Energy flows at a rate $\dot{Q}$ from high temperature to low.

Energy Transfer and Entropy Production

Mechanical friction contributes to increasing the entropy of the Universe. We will show that energy transfer between two objects that have different temperatures also makes the total entropy of the Universe increase. This is then a process to avoid, if possible, in an efficient heat engine.

Connect a metal bar between a large block at a high temperature T_H and another large block at a low temperature T_L (Figure S1.29). We write the rate of energy transfer from the high-temperature block (the "source") to the lower-temperature block (the "sink") as $\dot{Q}$. The dot over the letter Q means "rate" or "amount per second." Since Q has units of joules, $\dot{Q}$ has units of joules/second, or watts. This energy transfer rate is

- proportional to the "thermal conductivity" σ of the bar (metals have higher thermal conductivity than glass or plastic),
- proportional to the temperature difference (twice the temperature difference, twice the rate of energy transfer),
- proportional to the cross-sectional area A of the bar (twice the cross-sectional area is like having two bars), and
- inversely proportional to the length L of the bar (twice the length of the bar, half the energy transfer rate):

RATE OF ENERGY TRANSFER DUE TO A TEMPERATURE DIFFERENCE

$$\dot{Q} = \sigma A \frac{(T_H - T_L)}{L}$$

Units are J/s, or W. $\dot{Q}$ is a positive quantity and is the absolute value of the rate of energy flow into or out of a system due to a temperature difference.

The quantity $(T_H - T_L)/L$ is called the "temperature gradient." The larger the gradient (the more rapidly the temperature changes with distance along the bar), the larger the number of joules per second of energy transfer.

We want to show you that energy transfer between different temperatures increases the total entropy of the Universe. Suppose that the source and sink are so large that small energy transfers don't change their temperatures much. Since $1/T = \partial S/\partial E$ at constant V, it follows that an energy input $(\Delta E = Q)$ into a system whose temperature and volume hardly change leads to the following entropy change of that reservoir:

$$\Delta S = \frac{Q}{T}$$

Suppose that the energy transfer *rate* is $\dot{Q}$. In a short time interval Δt, the high-temperature source at temperature T_H loses an amount of energy $\dot{Q}\Delta t$.

QUESTION In this short time interval Δt, does the entropy of the source increase or decrease? By how much?

Since $\Delta S_H = (\Delta E)/T_H$, and the high-temperature source loses energy, we have $\Delta S_H = -(\dot{Q}\Delta t)/T_H$.

In this same time interval, the low-temperature sink at temperature T_L gains the same amount of energy, $\dot{Q}\Delta t$.

QUESTION In this short time interval Δt, does the entropy of the sink increase or decrease? By how much?

Since the low-temperature sink gains energy, we have $\Delta S_L = +(\dot{Q}\Delta t)/T_L$.

There is a crucial and perhaps not entirely obvious point: Does the entropy of the *bar* change during this time interval? No. The blocks are so large that their temperatures don't change much in a short time interval, so the temperatures at the ends of the bar, and all along the bar, are not changing. Every second, energy enters the bar, but the same amount of energy leaves the bar, so the energy of the bar isn't changing. Nothing about the bar is changing. It is merely a conduit for the energy transfer, but its state is not changing.

Therefore the change in the total entropy of the Universe in a time interval Δt is

$$\Delta S_{\text{source}} + \Delta S_{\text{sink}} + \Delta S_{\text{bar}} = -\frac{\dot{Q}\Delta t}{T_H} + \frac{\dot{Q}\Delta t}{T_L} + 0 = \dot{Q}\Delta t\left(\frac{1}{T_L} - \frac{1}{T_H}\right)$$

> **QUESTION** Is this quantity positive or negative? Is this consistent with the second law of thermodynamics?

Since $T_L < T_H$, $1/T_L > 1/T_H$, and the entropy change of the Universe in this process is positive. This is consistent with the second law of thermodynamics, which states that the entropy of the Universe should never decrease.

Reversible and Irreversible Processes

An increase in the total entropy of the Universe is associated with an irreversible process, because to return to the earlier state would require that the total entropy of the Universe actually decrease, which won't happen with macroscopic systems. We would be astonished if the energy transfer suddenly reversed and ran from the colder block thermally back "uphill" to the hotter block!

There is only one way to carry out energy transfer due to a temperature difference reversibly or nearly so (that is, with little or no change in the total entropy of the Universe)—do it between systems whose temperatures are very nearly equal to each other ($T_H \approx T_L$). There's a practical problem, however.

> **QUESTION** If the two temperatures are nearly equal (to avoid increasing the entropy of the Universe), at what rate is energy transferred from the (slightly) hotter source to the (slightly) cooler sink?

Energy transfer will flow extremely slowly, because $\dot{Q}$ is proportional to the temperature difference (or more specifically to the temperature gradient). If there is hardly any temperature difference, the energy transfer rate will be very small. So we can carry out such energy transfers nearly reversibly, hardly changing the entropy of the Universe, but only if we do it so slowly as to be of little practical use in driving some kind of mechanical heat engine that converts thermal energy into work.

S1.7 A MAXIMALLY EFFICIENT PROCESS

Despite the serious practical problem that reversible energy transfer due to a nearly zero difference in temperature proceeds infinitesimally slowly, we will analyze reversible "heat engines" in which (nearly) reversible energy input with tiny temperature differences is used (very slowly!) to do something mechanically useful, such as lift a weight or turn an electric generator. We will also assume that we can nearly eliminate sliding friction. The idea that we will pursue is to see how efficiently we can convert disorderly thermal energy into orderly mechanical energy (a lifted weight). We expect that reversible processes, which don't increase the total entropy of the Universe, should be the most efficient processes, though we recognize that these most efficient processes must proceed excruciatingly slowly.

Since we will use nearly reversible processes to do work, we could run the heat engine backward. Such a backward-running engine turns out to be a refrigerator—an engine in which work input to the engine can lead to extracting thermal energy from something to make it colder or to keep it cold.

The conception of a theoretically most efficient possible heat engine, and the recognition that this ideal engine would have to be reversible and not increase what we now call the total entropy of the Universe, was due to a young French engineer, Sadi Carnot, in 1824. His achievement is all the more remarkable because it came before the principle of energy conservation was established!

After using the second law of thermodynamics to determine the maximum possible efficiency of infinitely slow heat engines, in the last part of the supplement we will analyze engines that run at useful speeds. We will find as expected that they are even less efficient than the infinitely slow engines.

A Cyclic Process of a Reversible Engine

Some of the first practical heat engines drove pumps to pump water out of deep mines in England, repeatedly lifting large amounts of water large distances. The energy came from burning coal, which boiled water to make steam in a cylinder that pushed up on a piston and operated the pump. People started wondering how efficient such an engine could be. What limits the amount of useful work you can get from burning a ton of coal?

We describe a scheme for running a heat engine in a reversible way, which ought to be as efficient as possible. For concreteness, our engine is a device consisting of a cylinder containing an ideal gas, with a piston and some sand on the piston to adjust the pressure on the gas (Figure S1.30). This is a simple device that permits energy exchanges in the form of work and energy transfer due to a temperature difference. As we'll see, the actual construction details of the engine don't matter for the theoretical question regarding the maximum possible efficiency, though they matter very much in the actual construction of a useful engine.

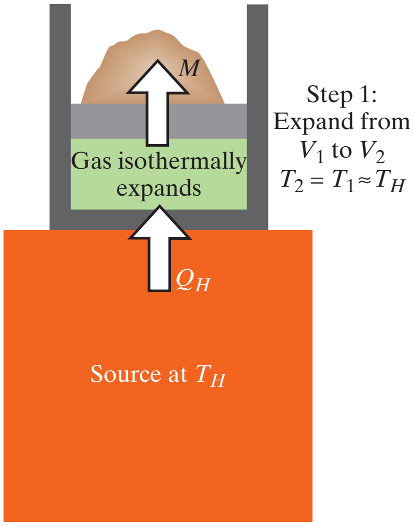


Figure S1.30 Constant-temperature expansion; gas temperature just slightly lower than T_H. The quantity M is the absolute value of the work done on the system, where W is negative in this situation, since the system does work on the surroundings.

During the rest of this supplement we'll be dealing with work done on the piston by the surroundings (a positive quantity in the Energy Principle) and work done on the surroundings by the piston (a negative quantity in the Energy Principle). To simplify the diagrams and the discussion, we'll use the name M for the absolute value of the mechanical energy transfer ($|W|$) between system and surroundings, and on diagrams we'll indicate with an arrow the direction of the energy transfer, as in Figure S1.30.

In many textbooks dealing with thermal physics, work W is defined as positive when the energy transfer is from the system to the surroundings, which is opposite to the definition in mechanics, where work W is defined to be positive when the energy transfer is from the surroundings to the system. For consistency between mechanics and thermal physics, we always say that W is positive when work is done on the system, and we use M for the absolute magnitude of W. In Figure S1.30 there is mechanical energy transfer from the system to the surroundings, so W is negative, but its absolute value M is a positive quantity.

A Constant-Temperature (Isothermal) Expansion

In addition to the engine itself, we need a large high-temperature source, large enough that extracting some energy from it will cause only a negligible decrease in its temperature. Start by arranging that the engine (the gas cylinder with its piston) has a temperature very slightly lower than the temperature T_H of the high-temperature source. We connect the engine to the high-temperature source and perform a reversible constant-temperature (isothermal) expansion of the engine, doing some work on the surroundings in the process (Figure S1.30). We lift the piston by slowly shifting some sand sideways from the piston onto nearby shelves. This requires almost no work on our part but results in the lifting of some weight. We make sure that the temperature of the gas doesn't change during this process. There is energy transfer into the engine because it is very slightly cooler, but the temperature difference is so slight that there is negligible change in the entropy of the Universe.

Entropy and Energy in Lifting the Piston

Remember that the entropy change of a system when there is energy transfer Q is $\Delta S = Q/T$. In lifting the piston the entropy of the high-temperature source has changed by an amount $\Delta S_H = -Q_H/T_H$, where Q_H is a positive quantity. The entropy of the gas has changed by an amount $\Delta S_{\text{gas}} = +Q_H/T_H$. The entropy of the Universe hasn't changed at all. (The increased entropy of the gas is associated with the fact that there are more ways to arrange the molecules in a large volume than in a small volume.)

Because the temperature hasn't changed, there is no change in the energy of the ideal gas. Recall that the energy of an ideal gas, or a low-density real gas, is a function solely of the temperature, not the volume. (A dense real gas is more complicated, because the electric potential energy for pairs of molecules depends on distance, and therefore the energy of the gas depends on volume as well as temperature.)

We have succeeded in converting all of the energy transfer from the high temperature source into useful work (lifting the piston), because none of the input energy went into changing the energy of the gas. This is 100% efficiency in converting thermal energy into useful work on the surroundings. What's the problem?

The Need for a Cycle

The problem is this: We need to be able to do this again, and again, and again. For example, we want to keep pumping water out of the deep mine, over and over. However, to repeat the lifting process, we have to return to the original state, with the gas compressed. We could simply reverse the process, doing work on the gas (constant-temperature compression), with energy transfer from the gas into the high-temperature source. The net effect, though, would be that there was zero net energy transfer to the gas, and zero net work done on the surroundings.

We need to run our heat engine in a nontrivial repetitive cycle, where we can lift the piston repeatedly. Each time we lift the piston and do useful work, we need to get the piston back down again without having to do the same amount of work to push it down. If we can get the gas back to its original state with net work done on the surroundings, we will have a useful device.

One possibility for bringing the piston down would be to let the gas cool down. However, to lower the temperature we would have to place the gas cylinder in contact with a large object at some low temperature T_L, called the "sink" because, as we'll see, we will dump some energy into it. We can't place the gas cylinder in contact with the sink immediately, because the gas is at a high temperature T_H, and placing the hot gas in contact with the cold sink would mean that there would be a large temperature difference, and there would be a large increase in the entropy of the Universe associated with the energy transfer from the hot gas to the cold sink.

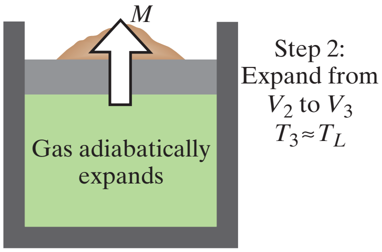


Figure S1.31 No-Q expansion; the gas temperature drops to T_L.

A No-Q (Adiabatic) Expansion

To avoid this large production of entropy, we need to bring the temperature of the gas down almost to T_L *before* making contact with the sink. To do this, we disconnect the gas cylinder from the high-temperature source and perform a reversible no-Q (adiabatic) expansion, which does some more work on the surroundings and lowers the temperature of the engine (Figure S1.31). This is accomplished by slowly removing some weight from the piston, allowing the gas to expand and the temperature to fall. We stop the expansion when the temperature of the gas is just slightly higher than the low temperature T_L of the sink.

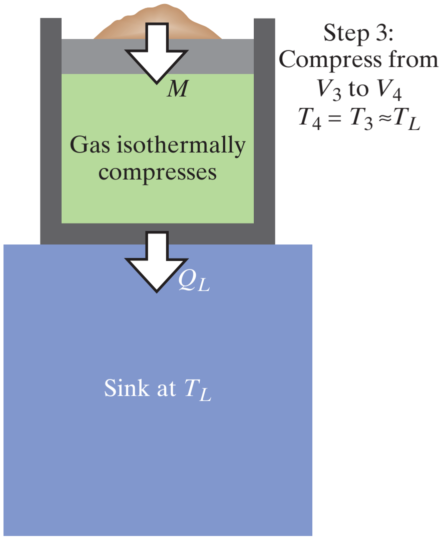


Figure S1.32 Constant-temperature compression; the gas temperature is just slightly higher than T_L.

A Constant-Temperature (Isothermal) Compression

We can now safely place the gas cylinder in contact with the low-temperature sink. This is okay as far as entropy production is concerned, because we made sure that the temperature of the gas is only very slightly higher than the sink temperature T_L. The piston is now quite high, and we need to bring it down. We do this by slowly adding some weight to the piston, performing a constant-temperature (isothermal) compression (Figure S1.32). There is energy transfer into the sink. Because the temperature of the ideal gas is nearly T_L at all times, there is no energy change in the gas. Therefore the work that we do is equal to the energy transfer Q_L into the sink.

There is an increase in the entropy of the sink $\Delta S_L = +Q_L/T_L$, and there is an entropy decrease in the entropy of the gas $\Delta S_{\text{gas}} = -Q_L/T_L$. The entropy of the Universe doesn't change. The decreased entropy of the gas is associated with the fact that there are fewer ways to arrange the molecules in a small volume than in a large volume.

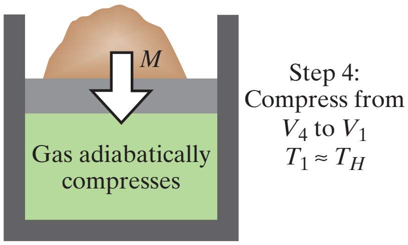


Figure S1.33 No-Q compression; gas temperature rises to T_H. The engine is now back to its original state, ready to begin another cycle.

A No-Q (Adiabatic) Compression

We stop the compression at a particular state of the gas chosen with care so that we can do the following: We disconnect the engine from the low-temperature sink and perform a no-Q compression that raises the temperature of the gas to a temperature just barely less than T_H, the temperature of the high-temperature source. We do some work to perform this compression (Figure S1.33).

This compression brings the system back to its original state (density, pressure, temperature), so we can repeat the cycle of four processes all over again. The possible usefulness of this engine is that we can run it repeatedly, over and over. What remains to be analyzed is how much work is done on the surroundings in one cycle, and how much energy input we need to supply. Of course if we find that the net work is zero, the engine won't be useful. However, explicit calculations for an ideal gas show that at least in that case there is net work done on the surroundings. We will find that this is true for any reversible engine run in such a cycle.

This reversible cycle of two constant-temperature (isothermal) processes and two no-Q (adiabatic) processes running between a high-temperature source and a low-temperature sink is called a "Carnot cycle."

Summary of the Cycle

Figures S1.34 and S1.35 summarize the four processes of the engine cycle.

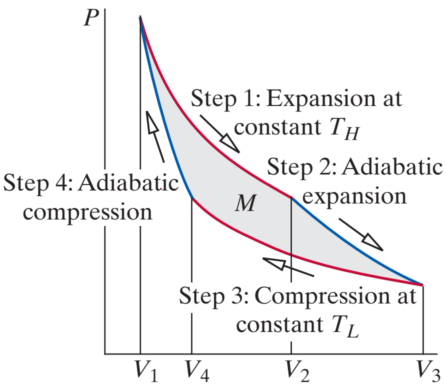


Figure S1.34 P vs. V for the engine cycle. The shaded area represents the net work done by the engine on the surroundings.

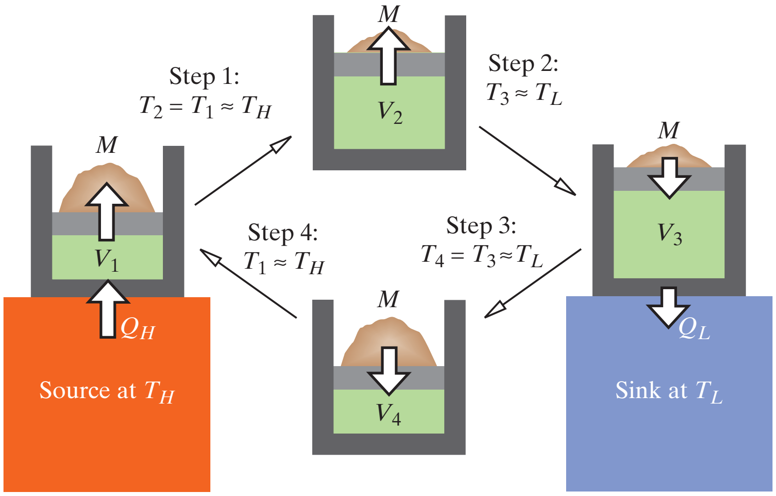


Figure S1.35 The heat engine cycle.

Step 1: Isothermal expansion in contact with T_H

Step 2: Adiabatic expansion (no contact); temperature falls to T_L

Step 3: Isothermal compression in contact with T_L

Step 4: Adiabatic compression (no contact); temperature rises to T_H

The four processes return the gas to its original temperature and volume. The question is, did we get any net work out of this cycle? Figure S1.34 shows the pressure vs. volume during the cycle. Earlier in this supplement we saw that the work done on the gas is $-\int_{V_1}^{V_2} PdV$, so the work done by the gas on the surroundings is $+\int_{V_1}^{V_2} PdV$, which is the area under one of these curves. Because V increases during steps 1 and 2, the work done on the surroundings is positive, but this work is negative in steps 3 and 4 because V decreases. The net work done on the surroundings is therefore represented by the shaded area shown in Figure S1.34. There is net energy output M, related to the fact that the PV curves for the adiabatic processes (shown in blue and given by $PV^\gamma = \text{constant}$) are steeper than the PV curves for the isothermal processes (shown in red and given by $PV = \text{constant}$).

Entropy in a Cycle of a Reversible Engine

Let Q_H be the (absolute value of the) energy extracted from the source at temperature T_H during the constant-temperature expansion, and let Q_L be the (absolute value of the) energy dumped into the sink at temperature T_L during the constant-temperature compression. Remember that the entropy change of a system when there is energy transfer Q is $\Delta S = Q/T$.

$$\text{The entropy change of the high-temperature source in one cycle} = -\frac{Q_H}{T_H}$$

$$\text{The entropy change of the low-temperature sink in one cycle} = +\frac{Q_L}{T_L}$$

QUESTION Is there any entropy change *in the engine* in one cycle?

The entropy change of the engine in one cycle is zero, because the gas is brought back to its original state.

QUESTION Therefore, in one cycle, how much entropy change is there in the surroundings as a result of the work done on and by the surroundings?

Only the energy transfer due to a temperature difference affects the entropy during one cycle (work doesn't contribute), and we calculated these through the equation $\Delta S = Q/T$. We were careful to run the engine in a reversible way, avoiding making any increase in the total entropy of the Universe, so in one cycle we have

$$-\frac{Q_H}{T_H} + \frac{Q_L}{T_L} + 0 = 0$$

Therefore we can write this important relationship for one cycle of the engine:

ONE CYCLE OF A REVERSIBLE ENGINE

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

This is a surprisingly simple result for such a complicated process. What does this simple result depend on? It depends solely on the second law of thermodynamics, that statistically the total entropy of the Universe will essentially never decrease.

We illustrated the processes in the cycle with a cylinder filled with an ideal gas, but the result above doesn't actually depend at all on the details of how the engine is constructed. In particular, it doesn't matter whether the engine contains helium gas, or a solid block of rubber, or a liter of liquid alcohol. There would be an easily visible difference between using a solid or liquid rather than a gas in the engine, because the distance through which the piston would move would be much smaller than with a gas. However, the simple result shown above would remain the same.

Energy in a Cycle of a Reversible Engine

Let's review the energy changes in the engine in one cycle. The source inputs an amount of energy Q_H. The sink removes an amount of energy Q_L. The working substance returns to its original state, so it undergoes no change of energy. Is there anything else? Yes, it may be that there has been net work done on the surroundings. How can we tell? We can use the fact that the internal energy of the engine does not change in one complete cycle:

$$\Delta E_{\text{engine}} = Q_H - Q_L + W = 0$$

QUESTION Use the result that $Q_H/T_H = Q_L/T_L$ (because the total entropy of the Universe doesn't change), to determine whether W is positive or negative.

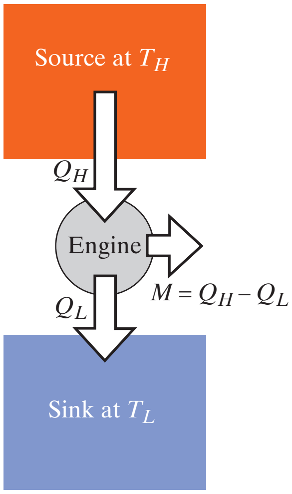


Figure S1.36 Conservation of energy lets us determine the net mechanical energy output from the engine to the surroundings.

Because $Q_H = (T_H/T_L)Q_L > Q_L$, we have $W = Q_L - Q_H < 0$. The fact that W is negative means that our heat engine does net work on the surroundings in one cycle. Figure S1.36 outlines the basic scheme. In one cycle the net effect is that the engine takes in energy Q_H from a hot source, does some work on something (for example, turns an electric generator), and exhausts the remaining energy Q_L into a cold sink. The magnitude of the work done on the surroundings is $M = |W| = Q_H - Q_L$.

The crucial issue is that the heat engine will not run in repeatable cycles without exhausting some energy to the low-temperature sink. You *cannot* convert all of the energy Q_H into useful energy output; a portion of Q_H goes into the low-temperature sink (Q_L). We need the low-temperature block to allow us to begin the constant-temperature compression phase of the cycle in a way that avoids any energy transfer with significant temperature difference, which would increase the total entropy of the Universe.

We have to pay for the high-temperature energy Q_H that we use, and the loss of some of the input energy in the form of Q_L is an unfortunate fact of life. We pay for coal or fuel oil or electricity to warm something up to the high temperature T_H, from which we can draw energy to do work for us.

For example, in an old railroad steam engine a fire maintained water at a high temperature to constitute the high-temperature source. In an automobile engine we burn gasoline to create a high temperature and push the pistons. In an electricity generating station we burn coal or fuel oil, or use nuclear fission reactions, to create a high-temperature source from which to drive the generators. We'd like to get our full money's worth (Q_H), but we don't. We only get $M = |W| = Q_H - Q_L$, having "lost" some of the energy to a low-temperature sink, which typically is our ordinary surroundings at around 20 °C (293 K).

Efficiency

This leads to the question, what fraction of the energy Q_H that we pay for turns into useful energy output M? This fraction is called the "efficiency" of the heat engine:

$$\text{efficiency} \equiv \frac{M}{Q_H}$$

QUESTION Given this definition of efficiency, prove the following result:

THE EFFICIENCY OF A REVERSIBLE ENGINE

$$\text{Efficiency} = 1 - \frac{T_L}{T_H}$$

We have $M/Q_H = (Q_H - Q_L)/Q_H = 1 - Q_L/Q_H = 1 - T_L/T_H$. This may seem surprising. The efficiency of a reversible engine depends solely on the ratio of the absolute temperatures of the source and sink. We emphasize that it doesn't matter how the engine is designed or what kind of materials it is made of. This is the highest efficiency we can ever achieve for converting thermal energy into useful work in a heat engine.

Checkpoint 7 An actual electricity generating plant is powered by a nuclear reactor, with a high temperature of 300 °C and low temperature of 25 °C (near room temperature). What would be the efficiency, if we can treat the processes as being reversible?

No Other Engine Can Be More Efficient

We can show that no heat engine running between temperatures T_H and T_L can be more efficient than a reversible engine.

The proof is a "proof by contradiction." Suppose that an inventor claims to have invented some cleverly designed new kind of (cyclic) engine, with a higher efficiency than $(1 - T_L/T_H)$ when run between these same two temperatures. In that case, for a given Q_H the new engine would exhaust less Q_L than is exhausted from a reversible engine, and the entropy change of the Universe with this new engine would be negative instead of zero:

$$-\frac{Q_H}{T_H} + \frac{Q_L}{T_L} < 0 \quad \text{(Impossible!)}$$

This would be a violation of the second law of thermodynamics, so it is impossible. We can be quite sure that the inventor's claims are not valid. Note carefully that the inventor's claims don't violate energy conservation. Nothing about energy conservation forbids converting 100% of the input energy Q_H into useful energy output M in a cycle. The impossibility lies, rather, in the massive improbability of seeing the total entropy of the Universe decrease.

We took great pains to make a reversible heat engine, for which the total entropy change of the Universe was zero. No other engine can be more efficient. In fact, any real engine will have some friction and some energy transfer across differing temperatures, in which case the entropy change of the Universe will be positive. So the second law of thermodynamics leads to the following, where "$= 0$" applies only to ideal, reversible engines, and "> 0" applies to real engines:

ENTROPY CHANGE OF THE UNIVERSE FOR REAL HEAT ENGINES

$$\Delta S_{\text{Universe}} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \geq 0$$

We should not underestimate the need for the ingenuity of inventors, however. The reversible heat engine made with an ideal gas cylinder is pretty useless for practical purposes. The challenge to ingenuity is to design engines that are practical, and this involves many kinds of engineering design decisions and trade-offs. However, no matter how ingenious the design, the second law of thermodynamics puts a rigid limitation on how efficient *any* heat engine can be.

There are non-heat engines that have high efficiency. Almost all of the electric energy flowing into an electric motor is converted into mechanical energy. Fuel cells convert chemical energy into mechanical energy with high efficiency. The limitation we have found applies only to heat engines, in which a high-temperature source drives the engine and necessarily exhausts energy to a low-temperature sink.

> **QUESTION** If $\Delta S_{\text{Universe}} > 0$ in one cycle of a heat engine, show that the efficiency is less than the ideal efficiency $(1 - T_L/T_H)$ obtained with a reversible engine.
>
> $$\Delta S_{\text{Universe}} > 0$$
>
> $$\frac{Q_L}{T_L} > \frac{Q_H}{T_H}$$
>
> $$\frac{Q_L}{Q_H} > \frac{T_L}{T_H}$$
>
> $$M = Q_H - Q_L = Q_H\left(1 - \frac{Q_L}{Q_H}\right) < Q_H\left(1 - \frac{T_L}{T_H}\right)$$
>
> $$\text{efficiency} = \frac{M}{Q_H} < \left(1 - \frac{T_L}{T_H}\right)$$

Running the Engine Backward: A Refrigerator or Heat Pump

We could run our engine backward, since we took care to make all aspects of the cycle reversible. Starting from our original starting point, we would disconnect from the hot block, perform a no-Q expansion to lower the temperature to that of the cold block, connect to the cold block, do a constant-temperature expansion, then disconnect from the cold block. Next we do a no-Q compression to raise the temperature to that of the hot block, connect to the hot block, and do a constant-temperature compression back to the original state.

The net effect in one cycle is that the low-temperature block gives some energy Q_L to the engine, the high-temperature block absorbs some energy Q_H from the engine, and we do some (positive) work on the system (instead of the engine doing work on the surroundings). Here is the Energy Principle when we run this reversed engine:

$$\Delta E_{\text{engine}} = Q_L - Q_H + W = 0$$

> **QUESTION** Use the result that $Q_H/T_H = Q_L/T_L$ (which is still valid for our reversed engine, as you can convince yourself) to determine whether W is positive or negative.

Since $Q_H = (T_H/T_L)Q_L > Q_L$, we have $W = Q_H - Q_L > 0$. This seems an odd kind of "engine": it doesn't do any work for us—we have to do work on it. Is that of any use? Yes! At the cost of doing some work, we extract energy from a low-temperature block and exhaust it into a high-temperature block. This is a refrigerator (Figure S1.37).

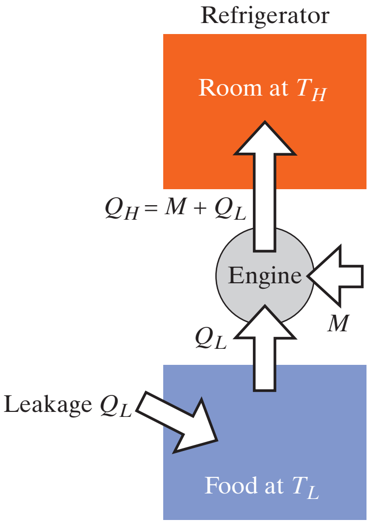


Figure S1.37 Run the engine backward and you have a refrigerator.

Consider how we keep food cold in an ordinary home refrigerator. A reversed engine maintains the inside of the refrigerator at a low temperature T_L, while the room is at a higher temperature T_H. Although the door and walls are heavily insulated, some energy does leak through from the room, and this energy, Q_L, must be removed to keep the food at a constant low temperature T_L. We exhaust an amount of energy Q_H into the room at temperature T_H. It takes an amount of mechanical energy input M to achieve this effect of moving energy out of the cold region and into the warm region.

In the most favorable case (no increase in total entropy) we have the following two conditions stemming from entropy and energy considerations (the high-temperature exhaust energy must equal the sum of the low-temperature energy plus the work we put in to drive the cycle):

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L} \quad \text{and} \quad Q_H = Q_L + M$$

Here our view of "efficiency" shifts a bit. What we care about is how much mechanical energy input M we have to do to remove an amount of leakage energy Q_L from the inside of the refrigerator.

> **QUESTION** Show that the energy removal we get per amount of work done is as follows:

$$\frac{Q_L}{M} = \frac{1}{(T_H/T_L)-1} > 1$$

Isn't this result somewhat surprising? Are we getting something for nothing when Q_L is bigger than the work M that we do? No, there's no violation of energy conservation. It's just that Q_L plus M equals the output energy Q_H, and we only have to add a modest amount of work to drive the energy "uphill."

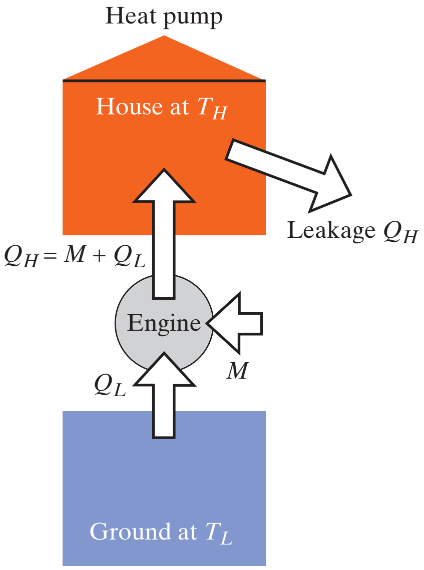


Figure S1.38 Run the engine backward and you have a heat pump.

Heat Pump

A related device is the "heat pump" used in some areas to warm homes by driving low-temperature energy "uphill" into a higher-temperature house. Figure S1.38 shows a house whose interior is maintained at a temperature T_H despite continual leakage Q_H into the outside air. Energy Q_L at low temperature T_L is pumped out of the ground into the house, by the addition of some work M that we do in an engine called a heat pump. This is somewhat similar to the refrigerator situation, except that now what we care about is how much high-temperature energy Q_H we get per amount of work W done by the heat pump.

> **QUESTION** Show that this ratio is given by the following equation for the heat pump:

$$\frac{Q_H}{M} = \frac{1}{1-(T_L/T_H)} > 1$$

Again, this feels like we're getting something for nothing, since Q_H is greater than the work W that we do. After all, if you warm the house directly with gas or oil or electric energy, you have to pay for every joule of leakage, not some small fraction of the leakage. So why aren't heat pumps much more commonly used than they are? Basically because we've been calculating the best deal we can possibly obtain (the case of the reversible engine—that is, one whose operation leads to no increase in the total entropy of the Universe). Real engines running either forward or reversed don't attain the theoretical maximum performance, as we will see in the next sections.

S1.8 *WHY DON'T WE ATTAIN THE THEORETICAL EFFICIENCY?

In Checkpoint 7 you calculated the reversible-engine efficiency of an actual nuclear-powered electricity generating plant to be 48%, but the observed efficiency of this plant is only 30%. Real heat engines do not attain the efficiency predicted by the second law of thermodynamics for ideal reversible engines. In fact, the real efficiency is often only about half of the theoretical efficiency. The reason for less than optimum performance in real engines is partly due to mechanical friction, but this effect can be minimized by good design and proper lubrication. The main limitation on performance comes from the practical necessity of incorporating energy transfers between parts of the system that are at significantly different temperatures, which leads to sizable increases in the total entropy of the Universe, and to much reduced efficiency.

The problem is speed. As we saw earlier in the supplement, the rate of energy transfer $\dot{Q}$ in joules per second between two objects (such as the hot or cold block and the engine) at temperatures T_H and T_L connected by some conducting material of length L and cross-sectional area A, with thermal conductivity σ is this:

$$\dot{Q} = \sigma A \frac{(T_H - T_L)}{L}$$

QUESTION What is the rate of energy transfer in a reversible engine when in contact with the hot block or the cold block?

Alas, a reversible heat engine is totally impractical when it comes to getting anything done in a finite amount of time, because the rate of energy transfer is zero. If an engine is perfectly reversible, a cycle takes an infinite amount of time!

Consider the portion of a heat engine's cycle where the working substance is in thermal contact with the high-temperature source. In order to carry out the expansion quickly, there must be a high rate of energy transfer from the source into the working substance. That means we need a large contact area A, a short distance L, and a high thermal conductivity σ. Most significant of all, the temperature of the source (T_H) must be considerably higher than the temperature of the engine, leading to irreversibility and increase of the entropy of the Universe.

The Efficiency of a Nonreversible Engine

Suppose that when the engine is in contact with the high-temperature block at temperature T_H, the engine is at a lower temperature T_1, so that there is a finite energy transfer rate into the engine of $\dot{Q}_H = b(T_H - T_1)$ joules per second, where b is a constant that lumps together the factors of thermal conductivity, cross-sectional area, and length ($\sigma A/L$). Similarly, assume that when the engine is in contact with the low-temperature block at temperature T_L, the engine is at a higher temperature T_2, so that there is a finite energy transfer rate into the working substance of $\dot{Q}_L = b(T_2 - T_L)$ joules per second.

Now the energy flow diagram looks like Figure S1.39, with an ideal reversible engine running between the temperatures T_1 and T_2, but with irreversible finite-rate energy transfer between this reversible engine and the source and sink at temperatures T_H and T_L.

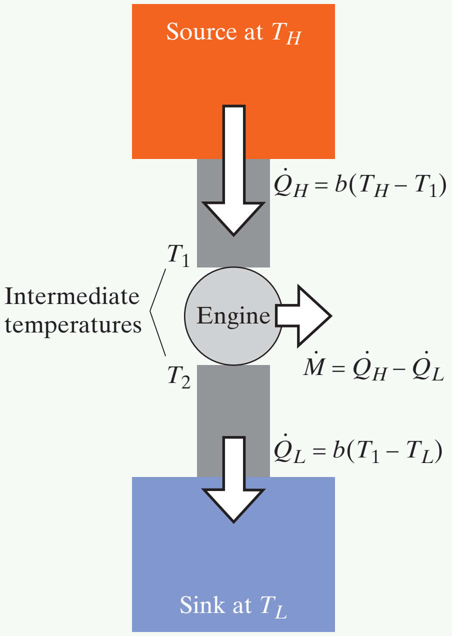


Figure S1.39 A heat engine that runs at a nonzero rate.

Energy enters the engine from the high-temperature source at a rate $\dot{Q}_H$, work is done on the surroundings at a rate $\dot{M}$, and energy is dumped into the low-temperature sink at a rate $\dot{Q}_L$. All of these quantities are measured in watts (joules per second). From energy conservation we have

$$\dot{Q}_H = \dot{M} + \dot{Q}_L$$

This engine will necessarily be less efficient than a reversible engine due to the irreversible energy transfers, as can be seen by noting that the engine is effectively operating between a high temperature that is lower than T_H and a low temperature that is higher than T_L.

Refrigerators and Heat Pumps

Similar issues of efficiency apply to refrigerators and heat pumps. Energy leaks into a refrigerator at some rate (joules per second) and must be removed by "pushing it thermally uphill" to a higher temperature, the temperature of the room. However, in order to have a nonzero rate of energy flow from the food to the engine, the engine must reach an even lower temperature than the food, with entropy-producing energy transfer from the food into the engine. Also, in order for there to be a nonzero rate of energy flow from the engine to the room air, the engine must reach an even higher temperature than the air, with entropy-producing energy transfer from the engine into the air. Schematically the situation looks like Figure S1.40.

Often a refrigerator or freezer has exposed coils (a "heat exchanger") where the energy transfer occurs between the working substance circulating in the coils and the air. If you touch the coils, you find that they are indeed much hotter than room temperature, in order to drive a sufficiently high rate of energy transfer into the air. Notice not only that the heat exchanger must be hotter than the air, but also that it is a rather large and costly device because it has to have a large surface area to get a large rate of energy transfer.

In the case of heat pumps, where the heat pump picks up low-temperature energy underground, the heat pump must reach an even lower temperature in order to get a nonzero rate of energy flow from the ground into the engine. Also, in order for there to be a nonzero rate of energy flow into the house, the engine must reach an even higher temperature than the air, with entropy-producing energy transfer from the engine into the air. The radiators (heat exchangers) in the house must be considerably hotter than the air. There is considerable expense in all the metal in the ground and in the house that enables adequate energy transfer rate. Schematically the situation looks like Figure S1.41.

So although a heat pump does have a theoretical advantage in warming a house in part from energy in the cold ground, the expense of the heat exchangers and the problems of going to rather low temperatures in the ground are practical limitations, especially in very cold climates. Heat pumps are more useful in climates where the winters are not too severe.

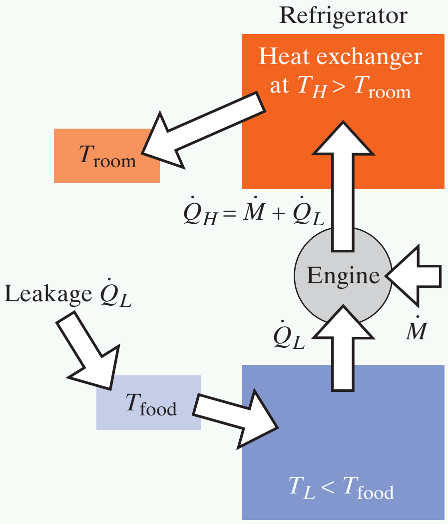


Figure S1.40 A refrigerator with nonzero cooling rate.

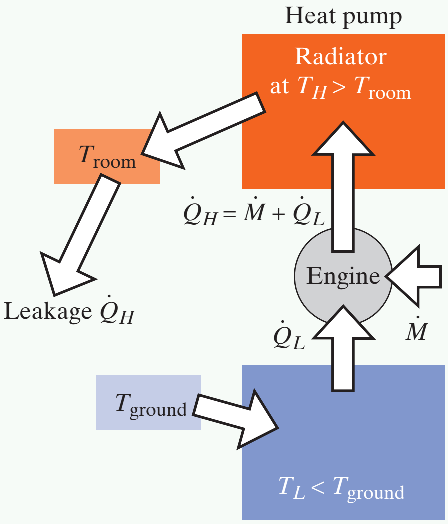


Figure S1.41 A heat pump with nonzero energy transfer rate due to a temperature difference.

S1.9 *APPLICATION: A RANDOM WALK

If you would find it useful to study one more application of the basic statistical concepts underlying our analysis of a gas, here is an interesting one. If we could watch one special molecule wandering around in the air, colliding frequently with air molecules, its path would look something like Figure S1.42. This kind of motion is called a "random walk." It is somewhat surprising to find that despite the random nature of this motion we can calculate something significant about the motion, using simple statistical reasoning.

One Dimension

For simplicity, first we'll consider just the x component of the motion. Pick the origin of the x axis to be at the original position of the special molecule. The first thing that happens is that the special molecule moves until it collides with an air molecule. We call this first x component of the displacement Δx_1.

This component of the displacement may be to the right ($+x$ direction) or to the left ($-x$ direction). As a result of the collision, the special molecule may change direction, and change speed. The next displacement before another collision we call Δx_2, and so on. After N collisions, the net displacement Δx away from the origin is

$$\Delta x = \Delta x_1 + \Delta x_2 + \Delta x_3 + \Delta x_4 + \cdots + \Delta x_N$$

After N collisions, what is the average (most probable) position of the special molecule? On average, it is just as likely that it has moved to the right as moved to the left, so the average x component of displacement ought to be zero. It is easy to see that this will be the case, by taking the average value:

$$\overline{\Delta x} = \overline{\Delta x_1} + \overline{\Delta x_2} + \overline{\Delta x_3} + \cdots + \overline{\Delta x_N}$$

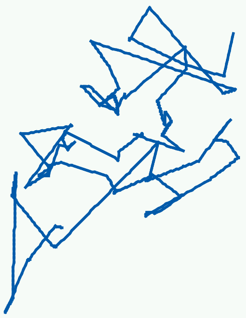


Figure S1.42 A 2-D random walk, generated by a computer program, using random numbers and many steps.

Each of the individual x displacements are equally likely to be to the left or the right, so the average value of the nth x displacement (for $n = 1, 2, 3, \ldots N$) is zero. Therefore the average value of the net x component of displacement is also zero.

On average, after N collisions the special molecule ends up to the left of the origin as often as it ends up to the right. However, we can ask the question, “On average, how far away from the origin (along the x axis) does the special molecule get, no matter whether it ends up to the left or the right?” A good indicator of this distance is the average value of the square of the net x displacement, $(\Delta x)^2$, because that’s always a positive number. We can calculate this average.

Since $\Delta x = \Delta x_1 + \Delta x_2 + \Delta x_3 + \Delta x_4 + \cdots + \Delta x_N$, we have

$$(\Delta x)^2 = (\Delta x_1)^2 + (\Delta x_2)^2 + \cdots + (\Delta x_N)^2 + 2\Delta x_1 \Delta x_2 + 2\Delta x_1 \Delta x_3 + 2\Delta x_1 \Delta x_4 + \cdots$$

In this square of the net x displacement, there are two kinds of terms: squares of individual x displacements such as $(\Delta x_2)^2$ and “cross terms” like $2\Delta x_1 \Delta x_3$. Given the random nature of the process, we expect that one-fourth of the time both Δx_1 and Δx_3 are positive (product is positive), one-fourth of the time they’re both negative (product is positive), one-fourth of the time Δx_1 is positive with Δx_3 negative (product is negative), and one-fourth of the time Δx_1 is negative with Δx_3 positive (product is negative). Therefore, the average value of each cross term $\overline{2\Delta x_i \Delta x_j}$ $(i \neq j)$ is zero.

As for the other terms, the squares of individual x displacements such as $(\Delta x_2)^2$, the average value of each of these terms is some number $d_x{}^2$, related to d^2, the square of the mean free path that we discussed in Section S1.3.

QUESTION Count up how many of these square terms there are for N collisions and calculate the average value of the square of the net displacement:

$$\overline{(\Delta x)^2} = ?$$

There are N of these terms, and the square root of this quantity is the “root-mean-square” or “rms” value of the net displacement:

$$\Delta x_{\text{rms}} = \sqrt{\overline{(\Delta x)^2}} = (\sqrt{N})d_x$$

We can also write this equation in terms of time. If we let v be the average speed of the special molecule between collisions and we let T be the average time between collisions, we have $v = d/T$. Also, the total time t for the N collisions is $t = NT$.

QUESTION Rewrite the equation for the rms displacement in terms of just d_x, v, and t (that is, eliminate N and T): $\Delta x_{\text{rms}} = ?$

We find that $\Delta x_{\text{rms}} = \sqrt{N d_x d_x} = \sqrt{N(vT)d_x} = \sqrt{v d_x}\sqrt{t}$. This is a somewhat curious result. For ordinary motion at constant speed, displacement increases proportional to time: double the time, double the displacement. In contrast, the rms displacement in a random walk grows with the square root of the time: on average, the rms displacement doubles when the time quadruples.

This calculation was done for the x component of the motion, but we can generalize our result to real three-dimensional motion in a gas. Figure S1.43 shows a three-dimensional displacement involving Δx, Δy, and Δz.

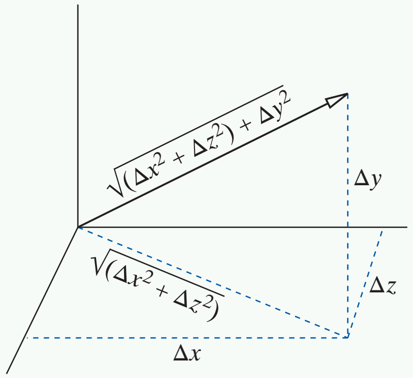


Figure S1.43 Pythagorean theorem in three dimensions.

You can see in Figure S1.43 a three-dimensional version of the Pythagorean theorem for triangles. We can assume that the motion in each dimension is independent of the motions in the other two dimensions, and we have the following result:

$$\Delta r_{\text{rms}} = \sqrt{\overline{(\Delta x)^2}+\overline{(\Delta y)^2}+\overline{(\Delta z)^2}} = \sqrt{Nd_x^2+Nd_y^2+Nd_z^2} = (\sqrt{N})d$$

(Here, d_x is the component in the x direction of the three-dimensional mean free path d.)

Writing the rms displacement in terms of the average speed v, the time t, and the mean free path d, we have

$$\Delta r_{\text{rms}} = \sqrt{vd}\sqrt{t}$$

This result is somewhat unusual, because it predicts (correctly, it turns out) that for this random process the displacement from the starting location is proportional to the square root of the time rather than to the time.

SUMMARY

KEY IDEAS

- We can model a gas as tiny balls in rapid random motion.
- Applying statistical ideas to this microscopic model allows us to predict macroscopic relationships among pressure, volume, and temperature, including the ideal gas law.
- The definition of temperature in terms of entropy is consistent with the everyday temperature scale.
- Both work and energy transfer due to a temperature difference can change the temperature and/or volume of a gas in a chamber with a movable piston.
- The attainable efficiency of engines that convert thermal energy into useful work is constrained by the second law of thermodynamics.

Mean free path d: $n[\pi(R+r)^2(d)] \approx 1$

Root-mean-square speed: $v_{\text{rms}} \equiv \sqrt{\overline{v^2}}$

Work done on a gas: $W = -\int_{V_1}^{V_2} P\,dV$

First law of thermodynamics: $\Delta E_{\text{sys}} = W + Q$

Molecular specific heat capacity at constant volume C_V: $Q = NC_V\Delta T$

Molecular specific heat capacity at constant pressure C_P: $Q = NC_P\Delta T$

Number of gas molecules hitting an area A per second = $\frac{1}{4}nA\bar{v}$ (3-D; various speeds)

$$P = \frac{2}{3}n\left(\frac{\overline{p^2}}{2m}\right) = nk_BT$$

where $n = N/V$ (number of molecules per cubic meter)

For a multiatom gas molecule,

$$\Delta\overline{E}_{\text{tot}} = \Delta\left(\frac{3}{2}k_BT + \overline{E}_{\text{rot}} + \overline{E}_{\text{vib}}\right)$$

$C_V = \frac{3}{2}k_B$ for a monatomic gas (He, etc.)
$C_V \geq \frac{3}{2}k_B$ for other gases (N_2, etc.)
$C_P = C_V + k_B$ (molecular specific heat capacity)
$C_P = C_V + R$ (molar specific heat capacity)
In a constant-temperature (isothermal) compression,

$$W_{\text{by piston}} = Q_{\text{into surroundings}} = Nk_BT\ln\left(\frac{V_1}{V_2}\right)$$

In a no-Q (adiabatic) compression,
$PV^{\gamma} = \text{constant}$, where $\gamma = C_P/C_V$, and also

$$T^{(C_V/k_B)}V = \text{constant}$$

$k_B = 1.38 \times 10^{-23}\,\text{J/K}$
$R = (6.02 \times 10^{23})k_B = 8.3\,\text{J/K}$

At "standard temperature and pressure" (STP, which means a temperature of 0 °Celsius or 273 K, and a pressure of 1 atm), one mole of a gas occupies 22.4 L (a liter is 1000 cubic centimeters).

Sea-level pressure (1 atm) is $1 \times 10^5\,\text{N/m}^2$.

Rate of energy transfer due to a temperature difference:

$$\dot{Q} = \sigma A\frac{(T_H - T_L)}{L}\ (\text{J/s})$$

For a cyclic engine running between high temperature T_H and low temperature T_L we have:

Entropy change of the universe for real heat engines:

$$\Delta S_{\text{Universe}} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \geq 0$$

The efficiency of a real heat engine:

$$\text{Efficiency} = \frac{W}{Q_H} \leq 1 - \frac{T_L}{T_H}$$

The = sign applies only if the heat engine is reversible (extremely slow processes, no friction). A heat engine run in reverse is a refrigerator (or a heat pump).

QUESTION

Q1 How does the mean free path of an atom in a gas change if the temperature is increased, with the volume kept constant? Explain briefly.

PROBLEMS

Section S1.2

••P2 Gas leaks at a rate L (in molecules per second) through a small circular hole. If the density of the gas is doubled, the Kelvin temperature is doubled, and the radius of the hole is doubled, what is the new leak rate?

••P3 Suppose that we make a circular hole 4 mm in diameter in a balloon. Calculate the initial rate at which chlorine escapes through the hole (at 0 °C), in number of chlorine atoms leaving the balloon per second.

••P4 What is the approximate time between collisions for one particular air molecule?

••P5 In an example problem in Section S1.2 we considered leakage from a flexible party balloon. If the leakage is from a rigid container (a metal storage tank, for example), the number of atoms per cubic meter, n, will decrease with time t. If the total volume of the tank is V, there are $N = nV$ atoms in the tank at any instant, so we can write the following “differential” equation (that is, an equation that involves derivatives):

$$\frac{d}{dt}(nV) = -\frac{1}{4}nA\bar{v}$$

This says, “the rate of change of the number of atoms in the tank is equal to the (negative) of the rate at which atoms are leaving the tank.” **(a)** Show that the differential equation is satisfied if the number density

$$n = n_{\text{initial}}e^{-(A\bar{v}/4V)t}$$

where t is the time elapsed since the hole was made. Just plug this function of n, and its derivative, into the equation and show that the two sides of the equation are equal for all values of the time t. Also show that the initial particle density n is equal to n_{initial}. **(b)** Despite the fancy math, this solution is really only approximate, because the average speed isn’t a constant but is decreasing. Suppose, however, that we use a heater to keep the container and the gas at a nearly constant temperature, so that the average speed does remain nearly constant. Suppose that the (rigid) container is again a sphere 30 cm in diameter, with a circular hole 1 mm in diameter. About how long would it take for most of the helium to leak out? Explain your choice of what you mean by “most.”

••P6 Natural uranium ore consists mostly of the isotope U-238 (92 protons and 146 neutrons), but 0.7% of the ore consists of the isotope U-235 (92 protons and 143 neutrons). Because only U-235 fissions in a reactor, industrial processes are used to enrich the uranium by enhancing the U-235 content.

One of the enrichment methods is “gaseous diffusion.” The gas UF_6, uranium hexafluoride, is manufactured from supplies of natural uranium and fluorine (each of the 6 fluorine atoms has 9 protons and 10 neutrons). A container is filled with UF_6 gas. There are tiny holes in the container, and gas molecules leak through these holes into an adjoining container, where pumps sweep out the leaked gas. **(a)** Explain why the gas that initially leaks into the second container has a slightly higher fraction of U-235 than is found in natural uranium. **(b)** Estimate roughly the practical change in the concentration of U-235 that can be achieved in this single-stage separation process. Explain what approximations or simplifying assumptions you have made to obtain your estimate. **(c)** A typical nuclear reactor requires uranium that has been enriched to the point where about 3% of the uranium is U-235. Estimate roughly the number of stages of gaseous diffusion required (that is, the number of times the gas must be allowed to leak from one container into another). Note that the effects are multiplicative.

This is why a practical gaseous diffusion plant has a large number of stages, each operating at high pressure, which makes this an expensive process. The first large gaseous diffusion plant was constructed during World War II at Oak Ridge, Tennessee, and used inexpensive Tennessee Valley Authority electricity.

••P7 You are on a spacecraft measuring 8 m by 3 m by 3 m when it is struck by a piece of space junk, leaving a circular hole of radius 4 mm, unfortunately in a place that can be reached only by making a time-consuming spacewalk. About how much time do you have to patch the leak? Explain what approximations you make in assessing the seriousness of the situation.

Section S1.4

••P8 A roughly spherical meteor made mainly of iron (density about 8 g/cm^3) is hurtling downward through the air at low altitude. At an instant when its speed is 1×10^4 m/s, calculate the approximate rate of change of the meteor’s speed. Do the analysis for two different meteors—one with a radius of 10 m and one with a radius of 100 m.

Start from fundamental principles. Do not try to use some existing equation that applies to a very different situation. Follow the kind of *reasoning* used in this supplement, applied to the new situation, rather than trying to use the *results* of this supplement.

A major difference from our earlier analyses is that the meteor is traveling much faster than the average thermal speed of the air molecules, so it is a good approximation to consider the air molecules below the meteor to be essentially at rest, and to assume that no air molecules manage to catch up with the meteor and hit it from behind. The meteor drills a temporary hole in the atmosphere, a vacuum, that gets filled explosively by air rushing in after the meteor has passed.

There is good evidence that a very large meteor, perhaps 10 km in diameter, hit the Earth near the Yucatan Peninsula in southern Mexico 65 million years ago and caused so much damage that the dinosaurs became extinct. See the excellent account in *T. rex and the Crater of Doom*, by Walter Alvarez (Princeton University Press, 1997). Alvarez is the geologist who made the first discoveries leading to our current understanding of this cataclysmic event.

••P9 A rigid, thermally insulated container with a volume of 22.4 L is filled with one mole of helium gas (4 g per mole) at a temperature of 0 C (273 K). The container is sitting in a room, surrounded by air at STP. **(a)** Calculate the pressure inside the container in $\mathrm{N/m^2}$. **(b)** Calculate the root-mean-square average speed of the helium atoms. **(c)** Now open a tiny square hole in the container, with area $1 \times 10^{-8}\ \mathrm{m^2}$ (the hole is 0.1 mm on a side). After 5 s, how many helium atoms have left the container? **(d)** Air molecules from the room enter the container through the hole during these 5 s. Which is greater, the number of air molecules that enter the container or the number of helium atoms that leave the container? Explain briefly. **(e)** Does the pressure inside the container increase slightly, stay the same, or decrease slightly during these 5 s? Explain briefly. If you have to make any simplifying assumptions, state them clearly.

Section S1.5

•P10 If you expand the volume of a gas containing N molecules to twice its original volume, while maintaining a constant temperature, how much energy transfer due to a temperature difference is there from the surroundings?

•P11 If you compress a volume of helium containing N atoms to half the original volume in a well-insulated cylinder, what is the ratio of the final pressure to the original pressure?

••P12 A mole of nitrogen is compressed (by piling lots of sand on the piston) to a volume of 12 L at room temperature (293 K). The cylinder is placed on an electric heating element whose temperature is maintained at 293.001 K. A quasistatic expansion is carried out at constant temperature by very slowly removing grains of sand from the top of the piston, with the temperature of the gas staying constant at 293 K. When the volume is 18 L, how much energy transfer Q has gone from the heating element into the gas? How much work W has been done on the piston by the gas? How much has the energy of the gas changed?

(You must assume that there is no energy transfer from the gas to the surrounding air, and no friction in the motion of the piston, all of which is pretty unrealistic in the real world! Nevertheless there are processes that can be approximated by a constant-temperature expansion. This problem is an idealization of a real process.)

••P13 Two moles of nitrogen is compressed (by piling lots of sand on the piston) to a volume of 11 L at room temperature (293 K). The cylinder is placed on an electric heating element whose temperature is maintained at 293.001 K. A quasistatic expansion is carried out at constant temperature by very slowly removing grains of sand from the top of the piston, with the temperature of the gas staying constant at 293 K. (You must assume that there is no energy transfer due to a temperature difference from the gas to the surrounding air, and no friction in the motion of the piston, all of which is pretty unrealistic in the real world! Nevertheless there are processes that can be approximated by a constant-temperature expansion. This problem is an idealization of a real process.) **(a)** When the volume is 20 L, how much energy transfer Q has gone from the heating element into the gas? **(b)** How much work W has been done on the piston by the gas? **(c)** How much has the energy of the gas changed?

••P14 Atmospheric pressure at sea level is about $1 \times 10^5\ \mathrm{N/m^2}$, which is about 15 pounds per square inch (psi). A bicycle tire typically is pumped up to 50 psi above atmospheric pressure (psi "gauge"), for an actual pressure of about 65 psi. In rapidly pumping up a bicycle tire, starting from atmospheric pressure, about how high does the temperature of the air rise? Explain what approximations and simplifying assumptions you make.

••P15 A horizontal cylinder 10 cm in diameter contains helium gas at room temperature and atmospheric pressure. A piston keeps the gas inside a region of the cylinder 20 cm long. **(a)** If you *quickly* pull the piston outward a distance of 12 cm, what is the approximate temperature of the helium immediately afterward? What approximations did you make? **(b)** How much work did you do, including sign? (Note that you need to consider the outside air as well as the inside helium in calculating the amount of work *you* do.) **(c)** Immediately after the pull, what force must you exert on the piston to hold it in position (with the helium enclosed in a volume that is $20 + 12 = 32$ cm long)? **(d)** You wait while the helium slowly returns to room temperature, maintaining the piston at its current location. After this wait, what force must you exert to hold the piston in position? **(e)** Next, you very *slowly* allow the piston to move back into the cylinder, stopping when the region of helium gas is 25 cm long. What force must you exert to hold the piston at this position? What approximations did you make?

Section S1.6

••P16 An aluminum bar 30 cm long and 3 cm by 4 cm on its sides is connected between two large metal blocks at temperatures of 135 °C and 20 °C, and energy is transferred from the hotter block to the cooler block at a rate $\dot{Q}_1$. If instead the two blocks were connected by an aluminum bar that is 20 cm long and 3 cm by 2 cm on its sides, what would be the energy transfer rate?

••P17 The thermal conductivity of copper (a good thermal conductor) is 400 W/K/m (for comparison, the thermal conductivity of iron is about 70 W/K/m, and that of glass is only about 1 W/K/m). One end of a copper bar 1 cm on a side and 30 cm long is immersed in a large pot of boiling water (100 °C), and the other end is embedded in a large block of ice (0 °C). It takes about 335 J to melt 1 g of ice. How long does it take to melt 1 g of ice? Does the entropy of the Universe increase, decrease, or stay the same?

Section S1.7

•P18 What is the efficiency of a reversible engine if the source is a large container of boiling water and the sink is a large block of melting ice?

•P19 Suppose that the temperature underground from where we draw low-temperature energy for a heat pump is about 5 °C, and we want to keep the house at a temperature of 20 °C. How many joules of work must our heat pump supply for every joule of leakage of energy there is out of the house?

••P20 A (nearly) reversible engine is used to melt ice as well as do some useful work. If the engine does 1000 J of work and dumps 400 J into the ice, what is the temperature of the high-temperature source?

••P21 In one cycle of a reversible engine running between a high-temperature source and a low-temperature sink, a consequence of the second law of thermodynamics is that $Q_H/T_H = Q_L/T_L$. This result is independent of what kind of material the engine contains. It is instructive to check this general result for a specific model where we can calculate everything explicitly. Consider a reversible cycle of an ideal gas of N molecules, starting at high temperature T_H and volume V_1. **(a)** Perform a constant-temperature (isothermal) expansion to volume V_2, and calculate the associated energy transfer Q_H into the gas. **(b)** Next perform a no-Q (adiabatic) expansion to volume V_3 and temperature T_L. **(c)** Next perform a constant-temperature (isothermal) compression to volume V_4, and calculate the associated energy transfer Q_L out of the gas. **(d)** Finally perform a no-Q (adiabatic) compression back to the starting state, temperature T_H and volume V_1.

••P22 Suppose that there is a leakage rate of 50 W through the insulation into a refrigerator, which we maintain at 3 °C. What is the minimum electric power required to continually remove this leakage energy, to maintain the low temperature? In that case, what is the rate at which energy is exhausted into the room? Room temperature is about 20 °C.

Section S1.9

••P23 As you have calculated, the average speed of an air molecule at room temperature is about 500 m/s, and we saw in Section S1.3 that the mean free path is about 7×10^{-8} m. What is Δr_{rms} for an air molecule after 1 s?

ANSWERS TO CHECKPOINTS

1 T decreases because average v decreases.

2 1×10^{22} molecules per second

3 $L \approx 3 \times 10^{-9}$ m

4 $1 \times 10^{5}\ \text{N/m}^2$

5 $\frac{3}{2}k_B + k_B = \frac{5}{2}k_B$

6 $\left(\frac{PV}{Nk_B}\right)^{c_v/k_B} V = \text{constant}$

$P^{C_V/k_B}V^{C_V/k_B+1} = \text{new constant}$

Take (C_V/k_B) root :

$PV^{1+k_B/C_V} = PV^{(C_V+k_B)/C_V} = PV^{C_P/C_V}$

7 0.48