1 Energy in Thermal Physics

1.1 Thermal Equilibrium

The most familiar concept in thermodynamics is **temperature**. It's also one of the trickiest concepts—I won't be ready to tell you what temperature *really* is until Chapter 3. For now, however, let's start with a very naive definition:

> **Temperature** is what you measure with a thermometer.

If you want to measure the temperature of a pot of soup, you stick a thermometer (such as a mercury thermometer) into the soup, wait a while, then look at the reading on the thermometer's scale. This definition of temperature is what's called an **operational definition**, because it tells you how to *measure* the quantity in question.

Ok, but why does this procedure work? Well, the mercury in the thermometer expands or contracts, as its temperature goes up or down. Eventually the temperature of the mercury equals the temperature of the soup, and the volume occupied by the mercury tells us what that temperature is.

Notice that our thermometer (and any other thermometer) relies on the following fundamental fact: When you put two objects in contact with each other, and wait long enough, they tend to come to the same temperature. This property is so fundamental that we can even take it as an alternative *definition* of temperature:

> **Temperature** is the thing that's the same for two objects, after they've been in contact long enough.

I'll refer to this as the **theoretical definition** of temperature. But this definition is extremely vague: What kind of "contact" are we talking about here? How long is "long enough"? How do we actually ascribe a numerical value to the temperature? And what if there is more than one quantity that ends up being the same for both objects?

Before answering these questions, let me introduce some more terminology:

After two objects have been in contact long enough, we say that they are in **thermal equilibrium**.

The time required for a system to come to thermal equilibrium is called the **relaxation time**.

So when you stick the mercury thermometer into the soup, you have to wait for the relaxation time before the mercury and the soup come to the same temperature (so you get a good reading). After that, the mercury is in thermal equilibrium with the soup.

Now then, what do I mean by "contact"? A good enough definition for now is that "contact," in this sense, requires some means for the two objects to exchange energy spontaneously, in the form that we call "heat." Intimate mechanical contact (i.e., touching) usually works fine, but even if the objects are separated by empty space, they can "radiate" energy to each other in the form of electromagnetic waves. If you want to *prevent* two objects from coming to thermal equilibrium, you need to put some kind of thermal insulation in between, like spun fiberglass or the double wall of a thermos bottle. And even then, they'll eventually come to equilibrium; all you're really doing is increasing the relaxation time.

The concept of relaxation time is usually clear enough in particular examples. When you pour cold cream into hot coffee, the relaxation time for the contents of the cup is only a few seconds. However, the relaxation time for the coffee to come to thermal equilibrium with the surrounding room is many minutes.*

The cream-and-coffee example brings up another issue: Here the two substances not only end up at the same temperature, they also end up blended with each other. The blending is not necessary for *thermal* equilibrium, but constitutes a second type of equilibrium—**diffusive equilibrium**—in which the molecules of each substance (cream molecules and coffee molecules, in this case) are free to move around but no longer have any tendency to move one way or another. There is also **mechanical equilibrium**, when large-scale motions (such as the expansion of a balloon—see Figure 1.1) can take place but no longer do. For each type of equilibrium between two systems, there is a quantity that can be exchanged between the systems:

Exchanged quantity	Type of equilibrium
energy	thermal
volume	mechanical
particles	diffusive

Notice that for thermal equilibrium I'm claiming that the exchanged quantity is *energy.* We'll see some evidence for this in the following section.

When two objects are able to exchange energy, and energy tends to move spontaneously from one to the other, we say that the object that gives up energy is at

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*Some authors define relaxation time more precisely as the time required for the temperature difference to decrease by a factor of $e \approx 2.7$. In this book all we'll need is a qualitative definition.

Figure 1.1. A hot-air balloon interacts thermally, mechanically, and diffusively with its environment—exchanging energy, volume, and particles. Not all of these interactions are at equilibrium, however.

a *higher* temperature, and the object that sucks in energy is at a *lower* temperature. With this convention in mind, let me now restate the theoretical definition of temperature:

> **Temperature** is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously *lose* energy is at the *higher* temperature.

In Chapter 3 I'll return to this theoretical definition and make it much more precise, explaining, in the most fundamental terms, what temperature really *is*.

Meanwhile, I still need to make the *operational* definition of temperature (what you measure with a thermometer) more precise. How do you make a properly calibrated thermometer, to get a numerical *value* for temperature?

Most thermometers operate on the principle of thermal expansion: Materials tend to occupy more volume (at a given pressure) when they're hot. A mercury thermometer is just a convenient device for measuring the volume of a fixed amount of mercury. To define actual *units* for temperature, we pick two convenient temperatures, such as the freezing and boiling points of water, and assign them arbitrary numbers, such as 0 and 100. We then mark these two points on our mercury thermometer, measure off a hundred equally spaced intervals in between, and declare that this thermometer now measures temperature on the Celsius (or centigrade) scale, by definition!

Of course it doesn't have to be a mercury thermometer; we could instead exploit the thermal expansion of some other substance, such as a strip of metal, or a gas at fixed pressure. Or we could use an electrical property, such as the resistance, of some standard object. A few practical thermometers for various purposes are shown

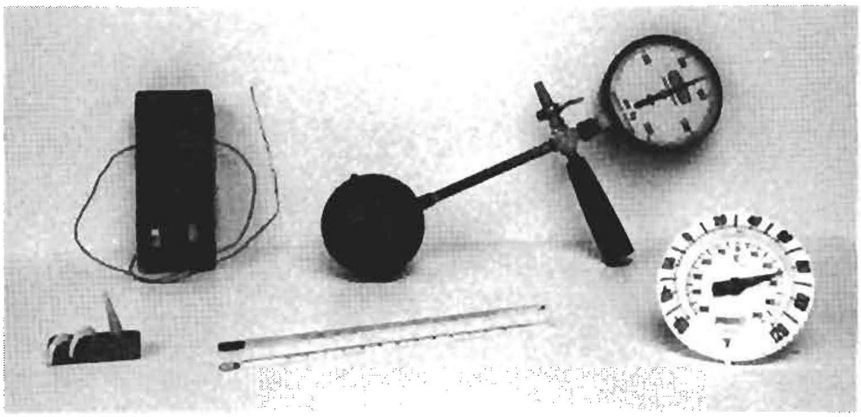

Figure 1.2. A selection of thermometers. In the center are two liquid-in-glass thermometers, which measure the expansion of mercury (for higher temperatures) and alcohol (for lower temperatures). The dial thermometer to the right measures the turning of a coil of metal, while the bulb apparatus behind it measures the pressure of a fixed volume of gas. The digital thermometer at left-rear uses a thermocouple—a junction of two metals—which generates a small temperature-dependent voltage. At left-front is a set of three potter's cones, which melt and droop at specified clay-firing temperatures.

in Figure 1.2. It's not obvious that the scales for various different thermometers would agree at all the intermediate temperatures between 0°C and 100°C. In fact, they generally won't, but in many cases the differences are quite small. If you ever have to measure temperatures with great precision you'll need to pay attention to these differences, but for our present purposes, there's no need to designate any one thermometer as the official standard.

A thermometer based on expansion of a gas is especially interesting, though, because if you extrapolate the scale down to very low temperatures, you are led to predict that for any low-density gas at constant pressure, the volume should go to *zero* at approximately −273°C. (In practice the gas will always liquefy first, but until then the trend is quite clear.) Alternatively, if you hold the volume of the gas fixed, then its *pressure* will approach zero as the temperature approaches −273°C (see Figure 1.3). This special temperature is called **absolute zero**, and defines the zero-point of the **absolute temperature scale**, first proposed by William Thomson in 1848. Thomson was later named Baron Kelvin of Largs, so the SI unit of absolute temperature is now called the **kelvin**.* A kelvin is the same size as a degree Celsius, but kelvin temperatures are measured up from absolute zero instead of from the freezing point of water. In round numbers, room temperature is approximately 300 K.

As we're about to see, many of the equations of thermodynamics are correct *only* when you measure temperature on the kelvin scale (or another absolute scale such as the Rankine scale defined in Problem 1.2). For this reason it's usually wise

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*The Unit Police have decreed that it is impermissible to say "degree kelvin"—the name is simply "kelvin"—and also that the names of all Official SI Units shall not be capitalized.

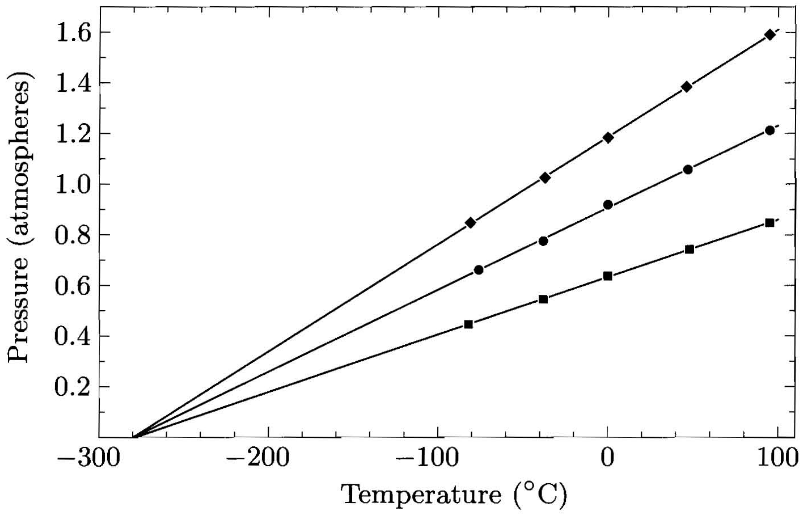

Figure 1.3. Data from a student experiment measuring the pressure of a fixed volume of gas at various temperatures (using the bulb apparatus shown in Figure 1.2). The three data sets are for three different amounts of gas (air) in the bulb. Regardless of the amount of gas, the pressure is a linear function of temperature that extrapolates to zero at approximately −280°C. (More precise measurements show that the zero-point does depend slightly on the amount of gas, but has a well-defined limit of −273.15°C as the density of the gas goes to zero.)

to convert temperatures to kelvins before plugging them into any formula. (Celsius is ok, though, when you're talking about the *difference* between two temperatures.)

Problem 1.1. The Fahrenheit temperature scale is defined so that ice melts at 32°F and water boils at 212°F.

(a) Derive the formulas for converting from Fahrenheit to Celsius and back.

(b) What is absolute zero on the Fahrenheit scale?

Problem 1.2. The Rankine temperature scale (abbreviated °R) uses the same size degrees as Fahrenheit, but measured up from absolute zero like kelvin (so Rankine is to Fahrenheit as kelvin is to Celsius). Find the conversion formula between Rankine and Fahrenheit, and also between Rankine and kelvin. What is room temperature on the Rankine scale?

Problem 1.3. Determine the kelvin temperature for each of the following:

(a) human body temperature;

(b) the boiling point of water (at the standard pressure of 1 atm);

(c) the coldest day you can remember;

(d) the boiling point of liquid nitrogen (−196°C);

(e) the melting point of lead (327°C).

Problem 1.4. Does it ever make sense to say that one object is "twice as hot" as another? Does it matter whether one is referring to Celsius or kelvin temperatures? Explain.

Problem 1.5. When you're sick with a fever and you take your temperature with a thermometer, approximately what is the relaxation time?

Problem 1.6. Give an example to illustrate why you *cannot* accurately judge the temperature of an object by how hot or cold it feels to the touch.

Problem 1.7. When the temperature of liquid mercury increases by one degree Celsius (or one kelvin), its volume increases by one part in 550,000. The fractional increase in volume per unit change in temperature (when the pressure is held fixed) is called the **thermal expansion coefficient**, β:

$$\beta \equiv \frac{\Delta V/V}{\Delta T}$$

(where V is volume, T is temperature, and Δ signifies a change, which in this case should really be infinitesimal if β is to be well defined). So for mercury, $\beta = 1/550,000\ \mathrm{K}^{-1} = 1.81\times10^{-4}\ \mathrm{K}^{-1}$. (The exact value varies with temperature, but between 0°C and 200°C the variation is less than 1%.)

- **(a)** Get a mercury thermometer, estimate the size of the bulb at the bottom, and then estimate what the inside diameter of the tube has to be in order for the thermometer to work as required. Assume that the thermal expansion of the glass is negligible.
- **(b)** The thermal expansion coefficient of water varies significantly with temperature: It is $7.5 \times 10^{-4}\ \mathrm{K}^{-1}$ at 100°C, but decreases as the temperature is lowered until it becomes *zero* at 4°C. Below 4°C it is slightly *negative*, reaching a value of $-0.68 \times 10^{-4}\ \mathrm{K}^{-1}$ at 0°C. (This behavior is related to the fact that ice is less dense than water.) With this behavior in mind, imagine the process of a lake freezing over, and discuss in some detail how this process would be different if the thermal expansion coefficient of water were always positive.

Problem 1.8. For a solid, we also define the **linear thermal expansion coefficient**, α, as the fractional increase in length per degree:

$$\alpha \equiv \frac{\Delta L/L}{\Delta T}.$$

- **(a)** For steel, α is $1.1 \times 10^{-5}\ \mathrm{K}^{-1}$. Estimate the total variation in length of a 1-km steel bridge between a cold winter night and a hot summer day.
- **(b)** The dial thermometer in Figure 1.2 uses a coiled metal strip made of two different metals laminated together. Explain how this works.
- **(c)** Prove that the volume thermal expansion coefficient of a solid is equal to the sum of its linear expansion coefficients in the three directions: $\beta = \alpha_x + \alpha_y + \alpha_z$. (So for an isotropic solid, which expands the same in all directions, $\beta = 3\alpha$.)

1.2 The Ideal Gas

Many of the properties of a low-density gas can be summarized in the famous **ideal gas law**,

$$PV = nRT, \tag{1.1}$$

where P = pressure, V = volume, n = number of moles of gas, R is a universal constant, and T is the temperature *in kelvins.* (If you were to plug a Celsius temperature into this equation you would get nonsense—it would say that the volume or pressure of a gas goes to zero at the freezing temperature of water and becomes negative at still lower temperatures.)

The constant R in the ideal gas law has the empirical value

$$R = 8.31 \ \frac{\mathrm{J}}{\mathrm{mol \cdot K}} \tag{1.2}$$

in SI units, that is, when you measure pressure in $\mathrm{N/m^2} = \mathrm{Pa}$ (pascals) and volume in $\mathrm{m^3}$. Chemists often measure pressure in atmospheres ($1\ \mathrm{atm} = 1.013 \times 10^5\ \mathrm{Pa}$) or bars ($1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$ exactly) and volume in liters ($1\ \mathrm{liter} = (0.1\ \mathrm{m})^3$), so be careful.

A **mole** of molecules is Avogadro's number of them,

$$N_\mathrm{A} = 6.02 \times 10^{23}. \tag{1.3}$$

This is another "unit" that's more useful in chemistry than in physics. More often we will want to simply discuss the number of *molecules*, denoted by capital N:

$$N = n \times N_\mathrm{A}. \tag{1.4}$$

If you plug in N/N_A for n in the ideal gas law, then group together the combination R/N_A and call it a new constant k, you get

$$PV = NkT. \tag{1.5}$$

This is the form of the ideal gas law that we'll usually use. The constant k is called **Boltzmann's constant**, and is tiny when expressed in SI units (since Avogadro's number is so huge):

$$k = \frac{R}{N_\mathrm{A}} = 1.381 \times 10^{-23}\ \mathrm{J/K}. \tag{1.6}$$

In order to remember how all the constants are related, I recommend memorizing

$$nR = Nk. \tag{1.7}$$

Units aside, though, the ideal gas law summarizes a number of important physical facts. For a given amount of gas at a given temperature, doubling the pressure squeezes the gas into exactly half as much space. Or, at a given volume, doubling the temperature causes the pressure to double. And so on. The problems below explore just a few of the implications of the ideal gas law.

Like nearly all the laws of physics, the ideal gas law is an *approximation*, never exactly true for a real gas in the real world. It is valid in the limit of low density, when the average space between gas molecules is much larger than the size of a molecule. For air (and other common gases) at room temperature and atmospheric pressure, the average distance between molecules is roughly ten times the size of a molecule, so the ideal gas law is accurate enough for most purposes.

Problem 1.9. What is the volume of one mole of air, at room temperature and 1 atm pressure?

Problem 1.10. Estimate the number of air molecules in an average-sized room.

Problem 1.11. Rooms A and B are the same size, and are connected by an open door. Room A, however, is warmer (perhaps because its windows face the sun). Which room contains the greater mass of air? Explain carefully.

Problem 1.12. Calculate the average volume per molecule for an ideal gas at room temperature and atmospheric pressure. Then take the cube root to get an estimate of the average distance between molecules. How does this distance compare to the size of a small molecule like N_2 or H_2O?

Problem 1.13. A mole is approximately the number of protons in a gram of protons. The mass of a neutron is about the same as the mass of a proton, while the mass of an electron is usually negligible in comparison, so if you know the total number of protons and neutrons in a molecule (i.e., its "atomic mass"), you know the approximate mass (in grams) of a mole of these molecules.* Referring to the periodic table at the back of this book, find the mass of a mole of each of the following: water, nitrogen (N_2), lead, quartz (SiO_2).

Problem 1.14. Calculate the mass of a mole of dry air, which is a mixture of N_2 (78% by volume), O_2 (21%), and argon (1%).

Problem 1.15. Estimate the average temperature of the air inside a hot-air balloon (see Figure 1.1). Assume that the total mass of the unfilled balloon and payload is 500 kg. What is the mass of the air inside the balloon?

Problem 1.16. The exponential atmosphere.

(a) Consider a horizontal slab of air whose thickness (height) is dz. If this slab is at rest, the pressure holding it up from below must balance both the pressure from above and the weight of the slab. Use this fact to find an expression for dP/dz, the variation of pressure with altitude, in terms of the density of air.

(b) Use the ideal gas law to write the density of air in terms of pressure, temperature, and the average mass m of the air molecules. (The information needed to calculate m is given in Problem 1.14.) Show, then, that the pressure obeys the differential equation

$$\frac{dP}{dz} = -\frac{mg}{kT}P,$$

called the **barometric equation.**

(c) Assuming that the temperature of the atmosphere is independent of height (not a great assumption but not terrible either), solve the barometric equation to obtain the pressure as a function of height: $P(z) = P(0)e^{-mgz/kT}$. Show also that the density obeys a similar equation.

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*The precise definition of a mole is the number of carbon-12 atoms in 12 grams of carbon-12. The **atomic mass** of a substance is then the mass, in grams, of exactly one mole of that substance. Masses of *individual* atoms and molecules are often given in **atomic mass units**, abbreviated "u", where 1 u is defined as exactly 1/12 the mass of a carbon-12 atom. The mass of an isolated proton is actually slightly greater than 1 u, while the mass of an isolated neutron is slightly greater still. But in this problem, as in most thermal physics calculations, it's fine to round atomic masses to the nearest integer, which amounts to counting the total number of protons and neutrons.

(d) Estimate the pressure, in atmospheres, at the following locations: Ogden, Utah (4700 ft or 1430 m above sea level); Leadville, Colorado (10,150 ft, 3090 m); Mt. Whitney, California (14,500 ft, 4420 m); Mt. Everest, Nepal/Tibet (29,000 ft, 8840 m). (Assume that the pressure at sea level is 1 atm.)

Problem 1.17. Even at low density, real gases don't quite obey the ideal gas law. A systematic way to account for deviations from ideal behavior is the **virial expansion**,

$$PV = nRT\left(1 + \frac{B(T)}{(V/n)} + \frac{C(T)}{(V/n)^2} + \cdots\right),$$

where the functions $B(T)$, $C(T)$, and so on are called the **virial coefficients**. When the density of the gas is fairly low, so that the volume per mole is large, each term in the series is much smaller than the one before. In many situations it's sufficient to omit the third term and concentrate on the second, whose coefficient $B(T)$ is called the second virial coefficient (the first coefficient being 1). Here are some measured values of the second virial coefficient for nitrogen (N_2):

T (K)	B (cm^3/mol)
100	−160
200	−35
300	−4.2
400	9.0
500	16.9
600	21.3

(a) For each temperature in the table, compute the second term in the virial equation, $B(T)/(V/n)$, for nitrogen at atmospheric pressure. Discuss the validity of the ideal gas law under these conditions.

(b) Think about the forces between molecules, and explain why we might expect $B(T)$ to be negative at low temperatures but positive at high temperatures.

(c) Any proposed relation between P, V, and T, like the ideal gas law or the virial equation, is called an **equation of state**. Another famous equation of state, which is qualitatively accurate even for dense fluids, is the **van der Waals equation**,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT,$$

where a and b are constants that depend on the type of gas. Calculate the second and third virial coefficients (B and C) for a gas obeying the van der Waals equation, in terms of a and b. (Hint: The binomial expansion says that $(1+x)^p \approx 1 + px + \frac{1}{2}p(p-1)x^2$, provided that $|px| \ll 1$. Apply this approximation to the quantity $[1 - (nb/V)]^{-1}$.)

(d) Plot a graph of the van der Waals prediction for $B(T)$, choosing a and b so as to approximately match the data given above for nitrogen. Discuss the accuracy of the van der Waals equation over this range of conditions. (The van der Waals equation is discussed much further in Section 5.3.)

Microscopic Model of an Ideal Gas

In Section 1.1 I defined the concepts of "temperature" and "thermal equilibrium," and briefly noted that thermal equilibrium arises through the exchange of *energy* between two systems. But how, exactly, is temperature related to energy? The answer to this question is not simple in general, but it *is* simple for an ideal gas, as I'll now attempt to demonstrate.

I'm going to construct a mental "model" of a container full of gas.* The model will not be accurate in all respects, but I hope to preserve some of the most important aspects of the behavior of real low-density gases. To start with, I'll make the model as simple as possible: Imagine a cylinder containing just *one* gas molecule, as shown in Figure 1.4. The length of the cylinder is L, the area of the piston is A, and therefore the volume inside is $V = LA$. At the moment, the molecule has a velocity vector $\vec{v}$, with horizontal component v_x. As time passes, the molecule bounces off the walls of the cylinder, so its velocity changes. I'll assume, however, that these collisions are always elastic, so the molecule doesn't lose any kinetic energy; its *speed* never changes. I'll also assume that the surfaces of the cylinder and piston are perfectly smooth, so the molecule's path as it bounces is symmetrical about a line normal to the surface, just like light bouncing off a mirror.†

Here's my plan. I want to know how the *temperature* of a gas is related to the kinetic *energy* of the molecules it contains. But the only thing I know about temperature so far is the ideal gas law,

$$PV = NkT \tag{1.8}$$

(where P is pressure). So what I'll first try to do is figure out how the *pressure* is related to the kinetic energy; then I'll invoke the ideal gas law to relate pressure to temperature.

Well, what is the pressure of my simplified gas? Pressure means force per unit area, exerted in this case on the piston (and the other walls of the cylinder). What

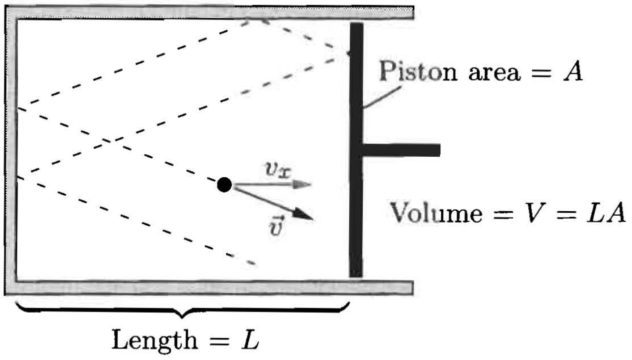

Figure 1.4. A greatly simplified model of an ideal gas, with just one molecule bouncing around elastically.

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*This model dates back to a 1738 treatise by Daniel Bernoulli, although many of its implications were not worked out until the 1840s.

†These assumptions are actually valid only for the *average* behavior of molecules bouncing off surfaces; in any *particular* collision a molecule might gain or lose energy, and can leave the surface at almost any angle.

is the pressure exerted on the piston by the molecule? Usually it's zero, since the molecule isn't even touching the piston. But periodically the molecule crashes into the piston and bounces off, exerting a relatively large force on the piston for a brief moment. What I really want to know is the *average* pressure exerted on the piston over long time periods. I'll use an overbar to denote an average taken over some long time period, like this: $\overline{P}$. I can calculate the average pressure as follows:

$$\overline{P} = \frac{\overline{F}_{x,\text{ on piston}}}{A} = \frac{-\overline{F}_{x,\text{ on molecule}}}{A} = -\frac{m\overline{\left(\frac{\Delta v_x}{\Delta t}\right)}}{A}. \tag{1.9}$$

In the first step I've written the pressure in terms of the x component of the force exerted by the molecule on the piston. In the second step I've used Newton's third law to write this in terms of the force exerted by the piston on the molecule. Finally, in the third step, I've used Newton's second law to replace this force by the mass m of the molecule times its acceleration, $\Delta v_x/\Delta t$. I'm still supposed to average over some long time period; I can do this simply by taking Δt to be fairly large. However, I should include only those accelerations that are caused by the piston, not those caused by the wall on the opposite side. The best way to accomplish this is to take Δt to be exactly the time it takes for the molecule to undergo one round-trip from the left to the right and back again:

$$\Delta t = 2L/v_x. \tag{1.10}$$

(Collisions with the perpendicular walls will not affect the molecule's motion in the x direction.) During this time interval, the molecule undergoes exactly one collision with the piston, and the change in its x velocity is

$$\Delta v_x = (v_{x,\text{ final}}) - (v_{x,\text{ initial}}) = (-v_x) - (v_x) = -2v_x. \tag{1.11}$$

Putting these expressions into equation 1.9, I find for the average pressure on the piston

$$\overline{P} = -\frac{m}{A}\frac{(-2v_x)}{(2L/v_x)} = \frac{mv_x^2}{AL} = \frac{mv_x^2}{V}. \tag{1.12}$$

It's interesting to think about why there are *two* factors of v_x in this equation. One of them came from Δv_x: If the molecule is moving faster, each collision is more violent and exerts more pressure. The other one came from Δt: If the molecule is moving faster, collisions occur more frequently.

Now imagine that the cylinder contains not just one molecule, but some large number, N, of identical molecules, with random* positions and directions of motion. I'll pretend that the molecules don't collide or interact with each other—just with

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*What, exactly, does the word *random* mean? Philosophers have filled thousands of pages with attempts to answer this question. Fortunately, we won't be needing much more than an everyday understanding of the word. Here I simply mean that the distribution of molecular positions and velocity vectors is more or less uniform; there's no obvious tendency toward any particular direction.

the walls. Since each molecule periodically collides with the piston, the average pressure is now given by a sum of terms of the form of equation 1.12:

$$\overline{P}V = mv_{1x}^2 + mv_{2x}^2 + mv_{3x}^2 + \cdots. \tag{1.13}$$

If the number of molecules is large, the collisions will be so frequent that the pressure is essentially continuous, and we can forget the overbar on the P. On the other hand, the sum of v_x^2 for all N molecules is just N times the *average* of their v_x^2 values. Using the same overbar to denote this average over all molecules, equation 1.13 then becomes

$$PV = Nm\overline{v_x^2}. \tag{1.14}$$

So far I've just been exploring the consequences of my model, without bringing in any facts about the real world (other than Newton's laws). But now let me invoke the ideal gas law (1.8), treating it as an experimental fact. This allows me to substitute NkT for PV on the left-hand side of equation 1.14. Canceling the N's, we're left with

$$kT = m\overline{v_x^2} \qquad \text{or} \qquad \overline{\tfrac{1}{2}mv_x^2} = \tfrac{1}{2}kT. \tag{1.15}$$

I wrote this equation the second way because the left-hand side is almost equal to the average translational **kinetic energy** of the molecules. The only problem is the x subscript, which we can get rid of by realizing that the same equation must also hold for y and z:

$$\overline{\tfrac{1}{2}mv_y^2} = \overline{\tfrac{1}{2}mv_z^2} = \tfrac{1}{2}kT. \tag{1.16}$$

The average translational kinetic energy is then

$$\overline{K}_{\text{trans}} = \overline{\tfrac{1}{2}mv^2} = \tfrac{1}{2}m\overline{(v_x^2 + v_y^2 + v_z^2)} = \tfrac{1}{2}kT + \tfrac{1}{2}kT + \tfrac{1}{2}kT = \tfrac{3}{2}kT. \tag{1.17}$$

(Note that the average of a sum is the sum of the averages.)

This is a good place to pause and think about what just happened. I started with a naive model of a gas as a bunch of molecules bouncing around inside a cylinder. I also invoked the ideal gas law as an experimental fact. Conclusion: The average translational kinetic energy of the molecules in a gas is given by a simple constant times the temperature. So if this model is accurate, the temperature of a gas is a direct measure of the average translational kinetic energy of its molecules.

This result gives us a nice interpretation of Boltzmann's constant, k. Recall that k has just the right units, J/K, to convert a temperature into an energy. Indeed, we now see that k is essentially a *conversion factor* between temperature and molecular energy, at least for this simple system. Think about the numbers, though: For an air molecule at room temperature (300 K), the quantity kT is

$$(1.38 \times 10^{-23}\ \text{J/K})(300\ \text{K}) = 4.14 \times 10^{-21}\ \text{J}, \tag{1.18}$$

and the average translational energy is 3/2 times as much. Of course, since molecules are so small, we would expect their kinetic energies to be tiny. The joule, though, is not a very convenient unit for dealing with such small energies. Instead we often use the **electron-volt** (eV), which is the kinetic energy of an electron that has been accelerated through a voltage difference of one volt: 1 eV $= 1.6\times10^{-19}$ J. Boltzmann's constant is 8.62×10^{-5} eV/K, so at room temperature,

$$kT = (8.62\times10^{-5}\ \text{eV/K})(300\ \text{K}) = 0.026\ \text{eV} \approx \frac{1}{40}\ \text{eV}. \tag{1.19}$$

Even in electron-volts, molecular energies at room temperature are rather small.

If you want to know the average *speed* of the molecules in a gas, you can *almost* get it from equation 1.17, but not quite. Solving for $\overline{v^2}$ gives

$$\overline{v^2} = \frac{3kT}{m}, \tag{1.20}$$

but if you take the square root of both sides, you get not the average speed, but rather the square root of the average of the squares of the speeds (root-mean-square, or rms for short):

$$v_{\text{rms}} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}. \tag{1.21}$$

We'll see in Section 6.4 that v_{rms} is only slightly larger than $\overline{v}$, so if you're not too concerned about accuracy, v_{rms} is a fine estimate of the average speed. According to equation 1.21, light molecules tend to move faster than heavy ones, at a given temperature. If you plug in some numbers, you'll find that small molecules at ordinary temperatures are bouncing around at *hundreds* of meters per second.

Getting back to our main result, equation 1.17, you may be wondering whether it's really true for real gases, given all the simplifying assumptions I made in deriving it. Strictly speaking, my derivation breaks down if molecules exert forces on each other, or if collisions with the walls are inelastic, or if the ideal gas law itself fails. Brief interactions between molecules are generally no big deal, since such collisions won't change the average velocities of the molecules. The only serious problem is when the gas becomes so dense that the space occupied by the molecules themselves becomes a substantial fraction of the total volume of the container. Then the basic picture of molecules flying in straight lines through empty space no longer applies. In this case, however, the ideal gas law also breaks down, in such a way as to precisely preserve equation 1.17. Consequently, this equation is still true, not only for dense gases but also for most liquids and sometimes even solids! I'll prove it in Section 6.3.

Problem 1.18. Calculate the rms speed of a nitrogen molecule at room temperature.

Problem 1.19. Suppose you have a gas containing hydrogen molecules and oxygen molecules, in thermal equilibrium. Which molecules are moving faster, on average? By what factor?

Problem 1.20. Uranium has two common isotopes, with atomic masses of 238 and 235. One way to separate these isotopes is to combine the uranium with fluorine to make uranium hexafluoride gas, UF_6, then exploit the difference in the average thermal speeds of molecules containing the different isotopes. Calculate the rms speed of each type of molecule at room temperature, and compare them.

Problem 1.21. During a hailstorm, hailstones with an average mass of 2 g and a speed of 15 m/s strike a window pane at a 45° angle. The area of the window is 0.5 m^2 and the hailstones hit it at a rate of 30 per second. What average pressure do they exert on the window? How does this compare to the pressure of the atmosphere?

Problem 1.22. If you poke a hole in a container full of gas, the gas will start leaking out. In this problem you will make a rough estimate of the rate at which gas escapes through a hole. (This process is called **effusion**, at least when the hole is sufficiently small.)

(a) Consider a small portion (area = A) of the inside wall of a container full of gas. Show that the number of molecules colliding with this surface in a time interval Δt is $PA\,\Delta t/(2m\overline{v_x})$, where P is the pressure, m is the average molecular mass, and $\overline{v_x}$ is the average x velocity of those molecules that collide with the wall.

(b) It's not easy to calculate $\overline{v_x}$, but a good enough approximation is $(\overline{v_x^2})^{1/2}$, where the bar now represents an average over all molecules in the gas. Show that $(\overline{v_x^2})^{1/2} = \sqrt{kT/m}$.

(c) If we now take away this small part of the wall of the container, the molecules that *would* have collided with it will instead escape through the hole. Assuming that nothing *enters* through the hole, show that the number N of molecules inside the container as a function of time is governed by the differential equation

$$\frac{dN}{dt} = -\frac{A}{2V}\sqrt{\frac{kT}{m}}\,N.$$

Solve this equation (assuming constant temperature) to obtain a formula of the form $N(t) = N(0)e^{-t/\tau}$, where τ is the "characteristic time" for N (and P) to drop by a factor of e.

(d) Calculate the characteristic time for a gas to escape from a 1-liter container punctured by a 1-mm^2 hole.

(e) Your bicycle tire has a slow leak, so that it goes flat within about an hour after being inflated. Roughly how big is the hole? (Use any reasonable estimate for the volume of the tire.)

(f) In Jules Verne's *Round the Moon*, the space travelers dispose of a dog's corpse by quickly opening a window, tossing it out, and closing the window. Do you think they can do this quickly enough to prevent a significant amount of air from escaping? Justify your answer with some rough estimates and calculations.

1.3 Equipartition of Energy

Equation 1.17 is a special case of a much more general result, called the **equipartition theorem**. This theorem concerns not just translational kinetic energy but *all* forms of energy for which the formula is a quadratic function of a coordinate or velocity component. Each such form of energy is called a **degree of freedom**. So far, the only degrees of freedom I've talked about are translational motion in the x, y, and z directions. Other degrees of freedom might include rotational motion, vibrational motion, and elastic potential energy (as stored in a spring). Look at the similarities of the formulas for all these types of energy:

$$\tfrac{1}{2}mv_x^2, \quad \tfrac{1}{2}mv_y^2, \quad \tfrac{1}{2}mv_z^2, \quad \tfrac{1}{2}I\omega_x^2, \quad \tfrac{1}{2}I\omega_y^2, \quad \tfrac{1}{2}k_sx^2, \quad \text{etc.} \tag{1.22}$$

The fourth and fifth expressions are for rotational kinetic energy, a function of the moment of inertia I and the angular velocity ω. The sixth expression is for elastic potential energy, a function of the spring constant k_s and the amount of displacement from equilibrium, x. The equipartition theorem simply says that for each degree of freedom, the average energy will be $\frac{1}{2}kT$:

> **Equipartition theorem:** At temperature T, the average energy of any quadratic degree of freedom is $\frac{1}{2}kT$.

If a system contains N molecules, each with f degrees of freedom, and there are no other (non-quadratic) temperature-dependent forms of energy, then its *total* thermal energy is

$$U_{\text{thermal}} = N \cdot f \cdot \tfrac{1}{2}kT. \tag{1.23}$$

Technically this is just the *average* total thermal energy, but if N is large, fluctuations away from the average will be negligible.

I'll prove the equipartition theorem in Section 6.3. For now, though, it's important to understand exactly what it says. First of all, the quantity U_{thermal} is almost never the *total* energy of a system; there's also "static" energy that doesn't change as you change the temperature, such as energy stored in chemical bonds or the rest energies (mc^2) of all the particles in the system. So it's safest to apply the equipartition theorem only to *changes* in energy when the temperature is raised or lowered, and to avoid phase transformations and other reactions in which bonds between particles may be broken.

Another difficulty with the equipartition theorem is in counting how many degrees of freedom a system has. This is a skill best learned through examples. In a gas of monatomic molecules like helium or argon, only translational motion counts, so each molecule has three degrees of freedom, that is, $f = 3$. In a diatomic gas like oxygen (O_2) or nitrogen (N_2), each molecule can also *rotate* about two different axes (see Figure 1.5). Rotation about the axis running down the length of the molecule doesn't count, for reasons having to do with quantum mechanics. The

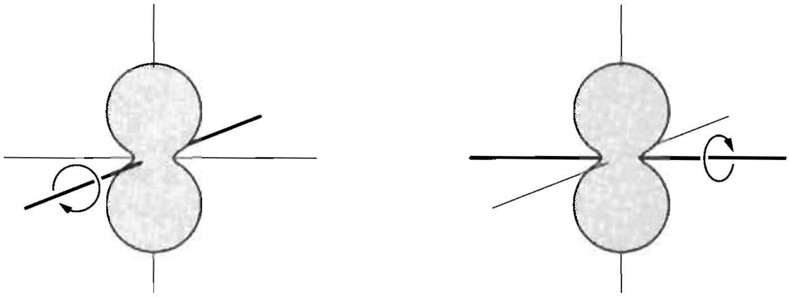

Figure 1.5. A diatomic molecule can rotate about two independent axes, perpendicular to each other. Rotation about the third axis, down the length of the molecule, is not allowed.

same is true for carbon dioxide (CO_2), since it also has an axis of symmetry down its length. However, most polyatomic molecules can rotate about all three axes.

It's not obvious why a rotational degree of freedom should have exactly the same average energy as a translational degree of freedom. However, if you imagine gas molecules knocking around inside a container, colliding with each other and with the walls, you can see how the average rotational energy should eventually reach some equilibrium value that is larger if the molecules are moving fast (high temperature) and smaller if the molecules are moving slow (low temperature). In any particular collision, rotational energy might be converted to translational energy or vice versa, but on average these processes should balance out.

A diatomic molecule can also *vibrate*, as if the two atoms were held together by a spring. This vibration should count as *two* degrees of freedom, one for the vibrational kinetic energy and one for the potential energy. (You may recall from classical mechanics that the average kinetic and potential energies of a simple harmonic oscillator are equal—a result that is consistent with the equipartition theorem.) More complicated molecules can vibrate in a variety of ways: stretching, flexing, twisting. Each "mode" of vibration counts as two degrees of freedom.

However, at room temperature many vibrational degrees of freedom do *not* contribute to a molecule's thermal energy. Again, the explanation lies in quantum mechanics, as we will see in Chapter 3. So air molecules (N_2 and O_2), for instance, have only five degrees of freedom, not seven, at room temperature. At higher temperatures, the vibrational modes *do* eventually contribute. We say that these modes are "frozen out" at room temperature; evidently, collisions with other molecules are sufficiently violent to make an air molecule rotate, but hardly ever violent enough to make it vibrate.

In a solid, each atom can vibrate in three perpendicular directions, so for each atom there are six degrees of freedom (three for kinetic energy and three for potential energy). A simple model of a crystalline solid is shown in Figure 1.6. If we let N stand for the number of *atoms* and f stand for the number of degrees of freedom *per atom*, then we can use equation 1.23 with $f = 6$ for a solid. Again, however, some of the degrees of freedom may be "frozen out" at room temperature.

Liquids are more complicated than either gases or solids. You can generally use the formula $\frac{3}{2}kT$ to find the average translational kinetic energy of molecules in a

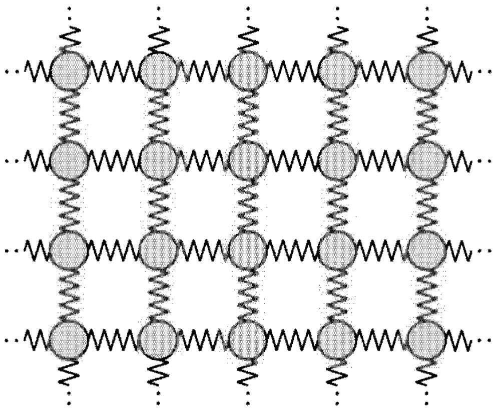

Figure 1.6. The "bed-spring" model of a crystalline solid. Each atom is like a ball, joined to its neighbors by springs. In three dimensions, there are six degrees of freedom per atom: three from kinetic energy and three from potential energy stored in the springs.

liquid, but the equipartition theorem doesn't work for the rest of the thermal energy, because the intermolecular potential energies are not nice quadratic functions.

You might be wondering what practical consequences the equipartition theorem has: How can we *test* it, experimentally? In brief, we would have to add some energy to a system, measure how much its temperature changes, and compare to equation 1.23. I'll discuss this procedure in more detail, and show some experimental results, in Section 1.6.

Problem 1.23. Calculate the total thermal energy in a liter of helium at room temperature and atmospheric pressure. Then repeat the calculation for a liter of air.

Problem 1.24. Calculate the total thermal energy in a gram of lead at room temperature, assuming that none of the degrees of freedom are "frozen out" (this happens to be a good assumption in this case).

Problem 1.25. List all the degrees of freedom, or as many as you can, for a molecule of water vapor. (Think carefully about the various ways in which the molecule can vibrate.)

1.4 Heat and Work

Much of thermodynamics deals with three closely related concepts: **temperature**, **energy**, and **heat**. Much of students' difficulty with thermodynamics comes from confusing these three concepts with each other. Let me remind you that temperature, fundamentally, is a measure of an object's tendency to spontaneously give up energy. We have just seen that in many cases, when the energy content of a system increases, so does its temperature. But please don't think of this as the *definition* of temperature—it's merely a statement *about* temperature that happens to be true.

To further clarify matters, I really should give you a precise definition of **energy**. Unfortunately, I can't do this. Energy is the most fundamental dynamical concept in all of physics, and for this reason, I can't tell you what it is in terms of something more fundamental. I can, however, list the various *forms* of energy—kinetic, electrostatic, gravitational, chemical, nuclear—and add the statement that, while energy can often be converted from one form to another, the *total* amount of energy in the universe never changes. This is the famous law of **conservation of energy**. I sometimes picture energy as a perfectly indestructible (and unmakable) fluid, which moves about from place to place but whose total amount never changes. (This image is convenient but *wrong*—there simply isn't any such fluid.)

Suppose, for instance, that you have a container full of gas or some other thermodynamic system. If you notice that the energy of the system increases, you can conclude that some energy came in from outside; it can't have been manufactured on the spot, since this would violate the law of conservation of energy. Similarly, if the energy of your system decreases, then some energy must have escaped and gone elsewhere. There are all sorts of mechanisms by which energy can be put into or taken out of a system. However, in thermodynamics, we usually classify these mechanisms under two categories: **heat** and **work**.

Heat is defined as any spontaneous flow of energy from one object to another, caused by a difference in temperature between the objects. We say that "heat" flows from a warm radiator into a cold room, from hot water into a cold ice cube, and from the hot sun to the cool earth. The *mechanism* may be different in each case, but in each of these processes the energy transferred is called "heat."

Work, in thermodynamics, is defined as any other transfer of energy into or out of a system. You do work on a system whenever you push on a piston, stir a cup of coffee, or run current through a resistor. In each case, the system's energy will increase, and usually its temperature will too. But we don't say that the system is being "heated," because the flow of energy is not a spontaneous one caused by a difference in temperature. Usually, with work, we can identify some "agent" (possibly an inanimate object) that is "actively" putting energy into the system; it wouldn't happen "automatically."

The definitions of heat and work are not easy to internalize, because both of these words have very different meanings in everyday language. It is strange to think that there is no "heat" entering your hands when you rub them together to warm them up, or entering a cup of tea that you are warming in the microwave. Nevertheless, both of these processes are classified as work, not heat.

Notice that both heat and work refer to energy *in transit*. You can talk about the total *energy* inside a system, but it would be meaningless to ask how much heat, or how much work, is *in* a system. We can only discuss how much heat *entered* a system, or how much work *was done on* a system.

I'll use the symbol U for the total energy inside a system. The symbols Q and W will represent the amounts of energy that enter a system as heat and work, respectively, during any time period of interest. (Either one could be negative, if energy *leaves* the system.) The sum $Q + W$ is then the total energy that enters the system, and, by conservation of energy, this is the amount by which the system's energy changes (see Figure 1.7). Written as an equation, this statement is

$$\Delta U = Q + W, \tag{1.24}$$

the change in energy equals the heat added plus the work done.* This equation is

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*Many physics and engineering texts define W to be positive when work-energy *leaves* the system rather than enters. Then equation 1.24 instead reads $\Delta U = Q - W$. This sign convention is convenient when dealing with heat engines, but I find it confusing in other situations. My sign convention is consistently followed by chemists, and seems to be catching on among physicists.

Another notational issue concerns the fact that we'll often want ΔU, Q, and W to be infinitesimal. In such cases I'll usually write dU instead of ΔU, but I'll leave the symbols Q and W alone. Elsewhere you may see "dQ" and "dW" used to represent infinitesimal amounts of heat and work. Whatever you do, *don't* read these as the "changes" in Q and W—that would be meaningless. To caution you not to commit this crime, many authors put a little bar through the d, writing $đQ$ and $đW$. To me, though, that $đ$ still looks like it should be pronounced "change." So I prefer to do away with the d entirely and just remember when Q and W are infinitesimal and when they're not.

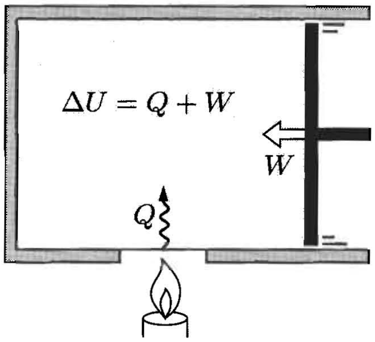

Figure 1.7. The total change in the energy of a system is the sum of the heat added to it and the work done on it.

really just a statement of the law of conservation of energy. However, it dates from a time when this law was just being discovered, and the relation between energy and heat was still controversial. So the equation was given a more mysterious name, which is still in use: the **first law of thermodynamics.**

The official SI unit of energy is the **joule**, defined as 1 kg·m^2/s^2. (So a 1-kg object traveling at 1 m/s has $\frac{1}{2}$ J of kinetic energy, $\frac{1}{2}mv^2$.) Traditionally, however, heat has been measured in **calories**, where 1 cal was defined as the amount of heat needed to raise the temperature of a gram of water by 1°C (while no work is being done on it). It was James Joule (among others*) who demonstrated that the same temperature increase could be accomplished by doing mechanical work (for instance, by vigorously stirring the water) instead of adding heat. In modern units, Joule showed that 1 cal equals approximately 4.2 J. Today the calorie is *defined* to equal exactly 4.186 J, and many people still use this unit when dealing with thermal or chemical energy. The well-known food calorie (sometimes spelled with a capital C) is actually a *kilo*calorie, or 4186 J.

Processes of heat transfer are further classified into three categories, according to the mechanism involved. **Conduction** is the transfer of heat by molecular contact: Fast-moving molecules bump into slow-moving molecules, giving up some of their energy in the process. **Convection** is the bulk motion of a gas or liquid, usually driven by the tendency of warmer material to expand and rise in a gravitational field. **Radiation** is the emission of electromagnetic waves, mostly infrared for objects at room temperature but including visible light for hotter objects like the filament of a lightbulb or the surface of the sun.

Problem 1.26. A battery is connected in series to a resistor, which is immersed in water (to prepare a nice hot cup of tea). Would you classify the flow of energy from the battery to the resistor as "heat" or "work"? What about the flow of energy from the resistor to the water?

Problem 1.27. Give an example of a process in which no heat is added to a system, but its temperature increases. Then give an example of the opposite: a process in which heat is added to a system but its temperature does not change.

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*Among the many others who helped establish the first law were Benjamin Thompson (Count Rumford), Robert Mayer, William Thomson, and Hermann von Helmholtz.

Problem 1.28. Estimate how long it should take to bring a cup of water to boiling temperature in a typical 600-watt microwave oven, assuming that all the energy ends up in the water. (Assume any reasonable initial temperature for the water.) Explain why no heat is involved in this process.

Problem 1.29. A cup containing 200 g of water is sitting on your dining room table. After carefully measuring its temperature to be 20°C, you leave the room. Returning ten minutes later, you measure its temperature again and find that it is now 25°C. What can you conclude about the amount of heat added to the water? (Hint: This is a trick question.)

Problem 1.30. Put a few spoonfuls of water into a bottle with a tight lid. Make sure everything is at room temperature, measuring the temperature of the water with a thermometer to make sure. Now close the bottle and shake it as hard as you can for several minutes. When you're exhausted and ready to drop, shake it for several minutes more. Then measure the temperature again. Make a rough calculation of the expected temperature change, and compare.

1.5 Compression Work

We'll deal with more than one type of work in this book, but the most important type is work done on a system (often a gas) by *compressing* it, as when you push on a piston. You may recall from classical mechanics that in such a case the amount of work done is equal to the force you exert dotted into the displacement:

$$W = \vec{F} \cdot d\vec{r}. \tag{1.25}$$

(There is some ambiguity in this formula when the system is more complicated than a point particle: Does $d\vec{r}$ refer to the displacement of the center of mass, or the point of contact (if any), or what? In thermodynamics, it is always the point of contact, and we won't deal with work done by long-range forces such as gravity. In this case the work-energy theorem tells us that the total energy of the system increases by W.*)

For a gas, though, it's much more convenient to express the work done in terms of the pressure and volume. For definiteness, consider the typical cylinder-piston arrangement shown in Figure 1.8. The force is parallel to the displacement, so we can forget about dot products and just write

$$W = F\,\Delta x. \tag{1.26}$$

(I'm taking Δx to be positive when the piston moves inward.)

What I want to do next is replace F by PA, the pressure of the gas times the area of the piston. But in order to make this replacement, I need to assume that as the gas is compressed it always remains in internal equilibrium, so that its pressure is uniform from place to place (and hence well defined). For this to be the case, the

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*For a detailed discussion of different definitions of "work," see A. John Mallinckrodt and Harvey S. Leff, "All About Work," *American Journal of Physics* **60**, 356–365 (1992).

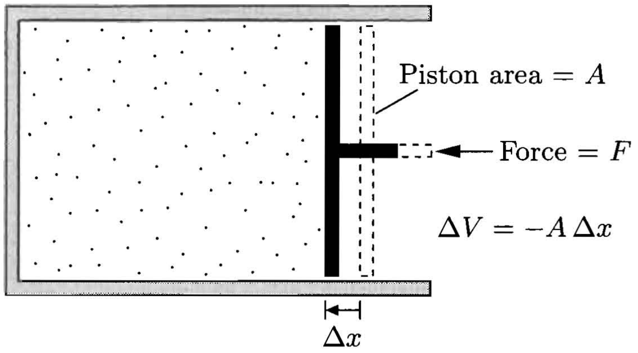

Figure 1.8. When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$.

piston's motion must be reasonably slow, so that the gas has time to continually equilibrate to the changing conditions. The technical term for a volume change that is slow in this sense is **quasistatic**. Although perfectly quasistatic compression is an idealization, it is usually a good approximation in practice. To compress the gas non-quasistatically you would have to slam the piston very hard, so it moves faster than the gas can "respond" (the speed must be at least comparable to the speed of sound in the gas).

For quasistatic compression, then, the force exerted on the gas equals the pressure of the gas times the area of the piston.* Thus,

$$W = PA\,\Delta x \qquad \text{(for quasistatic compression).} \tag{1.27}$$

But the product $A\,\Delta x$ is just minus the change in the volume of the gas (minus because the volume *decreases* when the piston moves in), so

$$W = -P\,\Delta V \qquad \text{(quasistatic).} \tag{1.28}$$

For example, if you have a tank of air at atmospheric pressure (10^5 N/m^2) and you wish to reduce its volume by one liter (10^{-3} m^3), you must perform 100 J of work. You can easily convince yourself that the same formula holds if the gas *expands*; then ΔV is positive, so the work done on the gas is negative, as required.

There is one possible flaw in the derivation of this formula. Usually the pressure will *change* during the compression. In that case, what pressure should you use—initial, final, average, or what? There's no difficulty for very small ("infinitesimal") changes in volume, since then any change in the pressure will be negligible. Ah—but we can always think of a large change as a bunch of small changes, one after another. So when the pressure *does* change significantly during the compression, we need to mentally divide the process into many tiny steps, apply equation 1.28 to each step, and add up all the little works to get the total work.

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*Even for quasistatic compression, friction between the piston and the cylinder walls could upset the balance between the force exerted from outside and the backward force exerted on the piston by the gas. If W represents the work done on the gas by the piston, this isn't a problem. But if it represents the work *you* do when pushing on the piston, then I'll need to assume that friction is negligible in what follows.

will escape as the gas is compressed and its temperature won't rise very much.* The difference between fast compression and slow compression is therefore very important in thermodynamics.

In this section I'll consider two idealized ways of compressing an ideal gas: **isothermal compression**, which is so slow that the temperature of the gas doesn't rise at all; and **adiabatic compression**, which is so fast that no heat escapes from the gas during the process. Most *real* compression processes will be somewhere between these extremes, usually closer to the adiabatic approximation. I'll start with the isothermal case, though, since it's simpler.

Suppose, then, that you compress an ideal gas isothermally, that is, without changing its temperature. This almost certainly implies that the process is quasistatic, so I can use formula 1.29 to calculate the work done, with P determined by the ideal gas law. On a PV diagram, the formula $P = NkT/V$, for constant T, is a concave-up hyperbola (called an **isotherm**), as shown in Figure 1.11. The work done is minus the area under the graph:

$$\begin{aligned} W &= -\int_{V_i}^{V_f} P\,dV = -NkT\int_{V_i}^{V_f}\frac{1}{V}\,dV \\ &= -NkT\left(\ln V_f - \ln V_i\right) = NkT\,\ln\frac{V_i}{V_f}. \end{aligned} \tag{1.30}$$

Notice that the work done is positive if $V_i > V_f$, that is, if the gas is being *compressed*. If the gas *expands* isothermally, the same equation applies but with $V_i < V_f$, that is, the work done *on* the gas is negative.

As the gas is compressed isothermally, heat must be flowing out, into the environment. To calculate how much, we can use the first law of thermodynamics and the fact that for and ideal gas U is proportional to T:

$$Q = \Delta U - W = \Delta(\tfrac{1}{2}NfkT) - W = 0 - W = NkT\,\ln\frac{V_f}{V_i}. \tag{1.31}$$

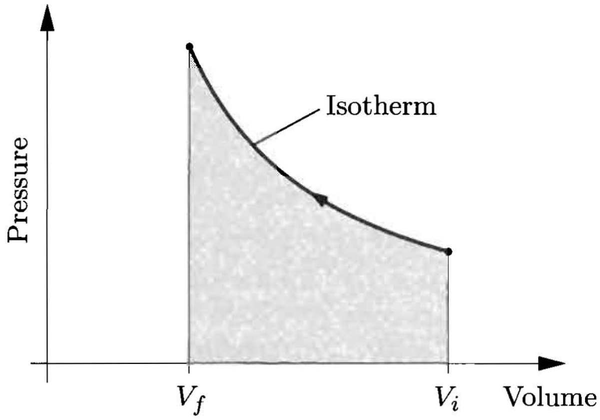

Figure 1.11. For isothermal compression of an ideal gas, the PV graph is a concave-up hyperbola, called an **isotherm**. As always, the work done is minus the area under the graph.

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*Scuba tanks are usually held under water as they are filled, to prevent the compressed air inside from getting too hot.

Thus the heat input is just minus the work done. For compression, Q is negative because heat *leaves* the gas; for isothermal expansion, heat must *enter* the gas so Q is positive.

Now let's consider adiabatic compression, which is so fast that *no* heat flows out of (or into) the gas. I'll still assume, however, that the compression is quasistatic. In practice this usually isn't a bad approximation.

If you do work on a gas but don't let any heat escape, the internal energy of the gas will increase:

$$\Delta U = Q + W = W. \tag{1.32}$$

If it's an *ideal* gas, U is proportional to T so the temperature increases as well. The curve describing this process on a PV diagram must connect a low-temperature isotherm to a high-temperature isotherm, and therefore must be steeper than either of the isotherms (see Figure 1.12).

To find an equation describing the exact shape of this curve, let me first use the equipartition theorem to write

$$U = \frac{f}{2}NkT, \tag{1.33}$$

where f is the number of degrees of freedom per molecule—3 for a monatomic gas, 5 for a diatomic gas near room temperature, etc. Then the energy change along any infinitesimal segment of the curve is

$$dU = \frac{f}{2}Nk\,dT. \tag{1.34}$$

Meanwhile, the work done during quasistatic compression is $-P\,dV$, so equation 1.32, applied to an infinitesimal part of the process, becomes

$$\frac{f}{2}Nk\,dT = -P\,dV. \tag{1.35}$$

This differential equation relates the changes in temperature and volume during the compression process. To solve the equation, however, we need to write the pressure P in terms of the variables T and V. The needed relation is just the ideal gas law; plugging in NkT/V for P and canceling the Nk gives

$$\frac{f}{2}\frac{dT}{T} = -\frac{dV}{V}. \tag{1.36}$$

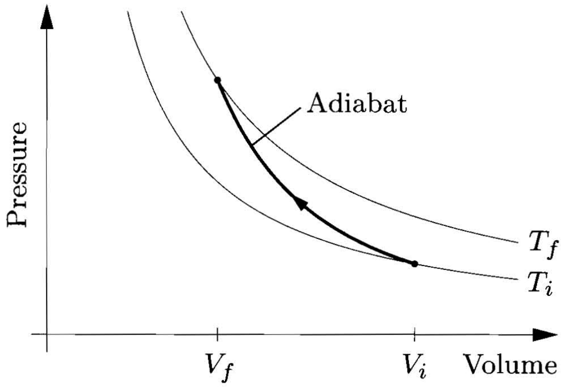

Figure 1.12. The PV curve for adiabatic compression (called an **adiabat**) begins on a lower-temperature isotherm and ends on a higher-temperature isotherm.

Now we can integrate both sides from the initial values (V_i and T_i) to the final values (V_f and T_f):

$$\frac{f}{2}\ln\frac{T_f}{T_i} = -\ln\frac{V_f}{V_i}. \tag{1.37}$$

To simplify this equation, exponentiate both sides and gather the i's and f's. After a couple of lines of algebra you'll find

$$V_f\, T_f^{f/2} = V_i\, T_i^{f/2}, \tag{1.38}$$

or more compactly,

$$VT^{f/2} = \text{constant}. \tag{1.39}$$

Given any starting point and any final volume, you can now calculate the final temperature. To find the final pressure you can use the ideal gas law to eliminate T on both sides of equation 1.38. The result can be written

$$V^{\gamma}P = \text{constant}, \tag{1.40}$$

where γ, called the **adiabatic exponent**, is an abbreviation for $(f+2)/f$.

Problem 1.35. Derive equation 1.40 from equation 1.39.

Problem 1.36. In the course of pumping up a bicycle tire, a liter of air at atmospheric pressure is compressed adiabatically to a pressure of 7 atm. (Air is mostly diatomic nitrogen and oxygen.)

- **(a)** What is the final volume of this air after compression?
- **(b)** How much work is done in compressing the air?
- **(c)** If the temperature of the air is initially 300 K, what is the temperature after compression?

Problem 1.37. In a Diesel engine, atmospheric air is quickly compressed to about 1/20 of its original volume. Estimate the temperature of the air after compression, and explain why a Diesel engine does not require spark plugs.

Problem 1.38. Two identical bubbles of gas form at the bottom of a lake, then rise to the surface. Because the pressure is much lower at the surface than at the bottom, both bubbles expand as they rise. However, bubble A rises very quickly, so that no heat is exchanged between it and the water. Meanwhile, bubble B rises slowly (impeded by a tangle of seaweed), so that it always remains in thermal equilibrium with the water (which has the same temperature everywhere). Which of the two bubbles is larger by the time they reach the surface? Explain your reasoning fully.

Problem 1.39. By applying Newton's laws to the oscillations of a continuous medium, one can show that the speed of a sound wave is given by

$$c_s = \sqrt{\frac{B}{\rho}},$$

where ρ is the density of the medium (mass per unit volume) and B is the **bulk modulus**, a measure of the medium's stiffness. More precisely, if we imagine applying an increase in pressure ΔP to a chunk of the material, and this increase results in a (negative) change in volume ΔV, then B is defined as the change in pressure divided by the magnitude of the fractional change in volume:

$$B \equiv \frac{\Delta P}{-\Delta V/V}.$$

This definition is *still* ambiguous, however, because I haven't said whether the compression is to take place isothermally or adiabatically (or in some other way).

(a) Compute the bulk modulus of an ideal gas, in terms of its pressure P, for both isothermal and adiabatic compressions.

(b) Argue that for purposes of computing the speed of a sound wave, the *adiabatic* B is the one we should use.

(c) Derive an expression for the speed of sound in an ideal gas, in terms of its temperature and average molecular mass. Compare your result to the formula for the rms speed of the molecules in the gas. Evaluate the speed of sound numerically for air at room temperature.

(d) When Scotland's Battlefield Band played in Utah, one musician remarked that the high altitude threw their bagpipes out of tune. Would you expect altitude to affect the speed of sound (and hence the frequencies of the standing waves in the pipes)? If so, in which direction? If not, why not?

Problem 1.40. In Problem 1.16 you calculated the pressure of earth's atmosphere as a function of altitude, assuming constant temperature. Ordinarily, however, the temperature of the bottommost 10–15 km of the atmosphere (called the **troposphere**) decreases with increasing altitude, due to heating from the ground (which is warmed by sunlight). If the temperature gradient $|dT/dz|$ exceeds a certain critical value, convection will occur: Warm, low-density air will rise, while cool, high-density air sinks. The decrease of pressure with altitude causes a rising air mass to expand adiabatically and thus to cool. The condition for convection to occur is that the rising air mass must *remain* warmer than the surrounding air despite this adiabatic cooling.

(a) Show that when an ideal gas expands adiabatically, the temperature and pressure are related by the differential equation

$$\frac{dT}{dP} = \frac{2}{f+2}\frac{T}{P}.$$

(b) Assume that dT/dz is just at the critical value for convection to begin, so that the vertical forces on a convecting air mass are always approximately in balance. Use the result of Problem 1.16(b) to find a formula for dT/dz in this case. The result should be a constant, independent of temperature and pressure, which evaluates to approximately $-10°\text{C/km}$. This fundamental meteorological quantity is known as the **dry adiabatic lapse rate**.

1.6 Heat Capacities

The **heat capacity** of an object is the amount of heat needed to raise its temperature, per degree temperature increase:

$$C \equiv \frac{Q}{\Delta T}. \tag{1.41}$$

(The symbol for heat capacity is a capital C.) Of course, the more of a substance you have, the larger its heat capacity will be. A more fundamental quantity is the **specific heat capacity**, defined as the heat capacity per unit mass:

$$c \equiv \frac{C}{m}. \tag{1.42}$$

(The symbol for specific heat capacity is a lowercase c.)

The most important thing to know about the definition (1.41) of heat capacity is that it is *ambiguous.* The amount of heat needed to raise an object's temperature by one degree *depends on the circumstances*, specifically, on whether you are also doing *work* on the object (and if so, how much). To see this, just plug the first law of thermodynamics into equation 1.41:

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}. \tag{1.43}$$

Even if the energy of an object is a well-defined function of its temperature alone (which is sometimes but not always the case), the work W done on the object can be anything, so C can be anything, too.

In practice, there are two types of circumstances (and choices for W) that are most likely to occur. Perhaps the most obvious choice is $W = 0$, when there is *no* work being done on the system. Usually this means that the system's volume isn't changing, since if it were, there would be compression work equal to $-P\Delta V$. So the heat capacity, for the particular case where $W = 0$ and V is constant, is called the **heat capacity at constant volume**, denoted C_V. From equation 1.43,

$$C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{1.44}$$

(The subscript V indicates that the changes are understood to occur with the volume held fixed. The symbol ∂ indicates a *partial* derivative, in this case treating U as a function of T and V, with only T, not V, varying as the derivative is taken.) A better name for this quantity would be "energy capacity," since it is the *energy* needed to raise the object's temperature, per degree, regardless of whether the energy actually enters as heat. For a gram of water, C_V is 1 cal/°C or about 4.2 J/°C.

In everyday life, however, objects often *expand* as they are heated. In this case they do work on their surroundings, so W is negative, so C is *larger* than C_V: you need to add additional heat to compensate for the energy lost as work. If the *pressure* surrounding your object happens to be constant, then the total heat needed is unambiguous, and we refer to the heat needed per degree as C_P, the **heat capacity at constant pressure**. Plugging the formula for compression-expansion work into equation 1.43 gives

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{1.45}$$

The last term on the right is the additional heat needed to compensate for the energy lost as work. Notice that the more the volume increases, the larger this term is. For solids and liquids, $\partial V/\partial T$ is usually small and can often be neglected. For gases, however, the second term is quite significant. (The first term, $(\partial U/\partial T)_P$, is not quite the same as C_V, since it is P, not V, that is held fixed in the partial derivative.)

Equations 1.41 through 1.45 are essentially definitions, so they apply to any object whatsoever. To determine the heat capacity of some *particular* object, you generally have three choices: measure it (see Problem 1.41); look it up in a reference work where measured values are tabulated; or try to predict it theoretically. The last is the most fun, as we'll see repeatedly throughout this book. For some objects we already know enough to predict the heat capacity.

Suppose that our system stores thermal energy only in quadratic "degrees of freedom," as described in Section 1.3. Then the equipartition theorem says $U = \frac{1}{2}NfkT$ (neglecting any "static" energy, which doesn't depend on temperature), so

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\frac{NfkT}{2}\right) = \frac{Nfk}{2}, \tag{1.46}$$

assuming that f is independent of temperature. (Note that in this case it doesn't matter whether V or P is held fixed in the derivative $\partial U/\partial T$.) This result gives us a direct method of measuring the number of degrees of freedom in an object, or, if we know this number, of testing the equipartition theorem. For instance, in a monatomic gas like helium, $f = 3$, so we expect $C_V = \frac{3}{2}Nk = \frac{3}{2}nR$; that is, the heat capacity *per mole* should be $\frac{3}{2}R = 12.5$ J/K. For diatomic and polyatomic molecules the heat capacity should be larger, in proportion to the number of degrees of freedom per molecule. Figure 1.13 (see the following page) shows a graph of C_V vs. temperature for a mole of hydrogen (H_2) gas, showing how the vibrational and rotational degrees of freedom freeze out at low temperatures. For a solid, there are six degrees of freedom per atom, so the heat capacity per mole should be $\frac{6}{2}R = 3R$; this general result is called the **rule of Dulong and Petit**. In this case, though, *all* of the degrees of freedom freeze out at low temperature, so the heat capacity approaches zero as $T \to 0$. What qualifies as "low" temperature depends on the material, as shown in Figure 1.14.

What about heat capacities of gases at constant pressure? For an *ideal* gas, the derivative $\partial U/\partial T$ is the same with P fixed as with V fixed, and we can compute the second term in equation 1.45 using the ideal gas law. At constant pressure,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\frac{NkT}{P}\right) = \frac{Nk}{P} \qquad \text{(ideal gas).} \tag{1.47}$$

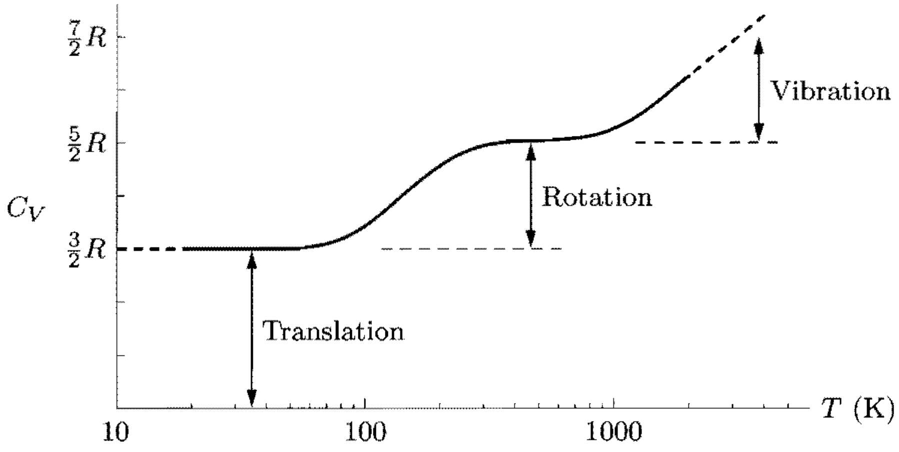

Figure 1.13. Heat capacity at constant volume of one mole of hydrogen (H_2) gas. Note that the temperature scale is logarithmic. Below about 100 K only the three translational degrees of freedom are active. Around room temperature the two rotational degrees of freedom are active as well. Above 1000 K the two vibrational degrees of freedom also become active. At atmospheric pressure, hydrogen liquefies at 20 K and begins to dissociate at about 2000 K. Data from Woolley et al. (1948).

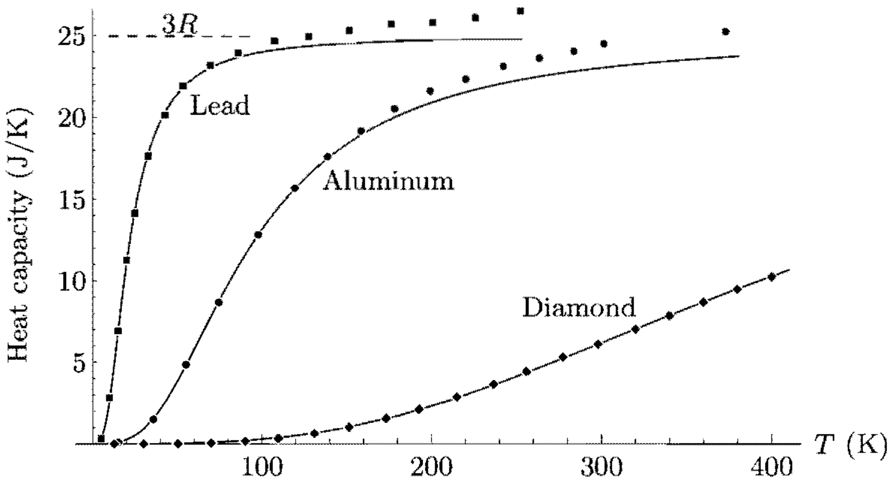

Figure 1.14. Measured heat capacities at constant pressure (data points) for one mole each of three different elemental solids. The solid curves show the heat capacity at constant *volume* predicted by the model used in Section 7.5, with the horizontal scale chosen to best fit the data for each substance. At sufficiently high temperatures, C_V for each material approaches the value $3R$ predicted by the equipartition theorem. The discrepancies between the data and the solid curves at high T are mostly due to the differences between C_P and C_V. At $T = 0$ all degrees of freedom are frozen out, so both C_P and C_V go to zero. Data from Y. S. Touloukian, ed., *Thermophysical Properties of Matter* (Plenum, New York, 1970).

Therefore,

$$C_P = C_V + Nk = C_V + nR \qquad \text{(ideal gas)}. \tag{1.48}$$

In other words, for each mole of an ideal gas, the heat capacity at constant pressure exceeds the heat capacity at constant volume by R, the gas constant. Oddly, the additional term in the heat capacity doesn't depend on *what* the pressure is, so long as it is constant. Apparently, if the pressure is high the gas expands less, in such a way that the work done on the environment is independent of P.

Problem 1.41. To measure the heat capacity of an object, all you usually have to do is put it in thermal contact with another object whose heat capacity you know. As an example, suppose that a chunk of metal is immersed in boiling water (100°C), then is quickly transferred into a Styrofoam cup containing 250 g of water at 20°C. After a minute or so, the temperature of the contents of the cup is 24°C. Assume that during this time no significant energy is transferred between the contents of the cup and the surroundings. The heat capacity of the cup itself is negligible.

- **(a)** How much heat is lost by the water?
- **(b)** How much heat is gained by the metal?
- **(c)** What is the heat capacity of this chunk of metal?
- **(d)** If the mass of the chunk of metal is 100 g, what is its specific heat capacity?

Problem 1.42. The specific heat capacity of Albertson's *Rotini Tricolore* is approximately 1.8 J/g·°C. Suppose you toss 340 g of this pasta (at 25°C) into 1.5 liters of boiling water. What effect does this have on the temperature of the water (before there is time for the stove to provide more heat)?

Problem 1.43. Calculate the heat capacity of liquid water *per molecule*, in terms of k. Suppose (incorrectly) that all the thermal energy of water is stored in quadratic degrees of freedom. How many degrees of freedom would each molecule have to have?

Problem 1.44. At the back of this book is a table of thermodynamic data for selected substances at room temperature. Browse through the C_P values in this table, and check that you can account for most of them (approximately) using the equipartition theorem. Which values seem anomalous?

Problem 1.45. As an illustration of why it matters which variables you hold fixed when taking partial derivatives, consider the following mathematical example. Let $w = xy$ and $x = yz$.

- **(a)** Write w purely in terms of x and z, and then purely in terms of y and z.
- **(b)** Compute the partial derivatives

$$\left(\frac{\partial w}{\partial x}\right)_y \quad \text{and} \quad \left(\frac{\partial w}{\partial x}\right)_z,$$

  and show that they are not equal. (Hint: To compute $(\partial w/\partial x)_y$, use a formula for w in terms of x and y, not z. Similarly, compute $(\partial w/\partial x)_z$ from a formula for w in terms of only x and z.)

- **(c)** Compute the other four partial derivatives of w (two each with respect to y and z), and show that it matters which variable is held fixed.

Problem 1.46. Measured heat capacities of solids and liquids are almost always at constant pressure, not constant volume. To see why, estimate the pressure needed to keep V fixed as T increases, as follows.

(a) First imagine slightly increasing the temperature of a material at constant pressure. Write the change in volume, dV_1, in terms of dT and the thermal expansion coefficient β introduced in Problem 1.7.

(b) Now imagine slightly compressing the material, holding its temperature fixed. Write the change in volume for *this* process, dV_2, in terms of dP and the **isothermal compressibility** κ_T, defined as

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

(This is the reciprocal of the isothermal bulk modulus defined in Problem 1.39.)

(c) Finally, imagine that you compress the material just enough in part (b) to offset the expansion in part (a). Then the ratio of dP to dT is equal to $(\partial P/\partial T)_V$, since there is no net change in volume. Express this partial derivative in terms of β and κ_T. Then express it more abstractly in terms of the partial derivatives used to define β and κ_T. For the second expression you should obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}.$$

This result is actually a purely mathematical relation, true for any three quantities that are related in such a way that any two determine the third.

(d) Compute β, κ_T, and $(\partial P/\partial T)_V$ for an ideal gas, and check that the three expressions satisfy the identity you found in part (c).

(e) For water at 25°C, $\beta = 2.57 \times 10^{-4}\ \mathrm{K}^{-1}$ and $\kappa_T = 4.52 \times 10^{-10}\ \mathrm{Pa}^{-1}$. Suppose you increase the temperature of some water from 20°C to 30°C. How much pressure must you apply to prevent it from expanding? Repeat the calculation for mercury, for which (at 25°C) $\beta = 1.81 \times 10^{-4}\ \mathrm{K}^{-1}$ and $\kappa_T = 4.04 \times 10^{-11}\ \mathrm{Pa}^{-1}$. Given the choice, would you rather measure the heat capacities of these substances at constant V or at constant P?

Latent Heat

In some situations you can put heat into a system without increasing its temperature at *all.* This normally happens at a **phase transformation**, such as melting ice or boiling water. Technically, the heat capacity is then *infinite*:

$$C = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty \qquad \text{(during a phase transformation).} \tag{1.49}$$

However, you still might want to know how much heat is required to melt or boil the substance completely. This amount, divided by the mass of the substance, is called the **latent heat** of the transformation, and denoted L:

$$L \equiv \frac{Q}{m} \qquad \text{to accomplish the transformation.} \tag{1.50}$$

Like the definition of heat capacity, this definition is ambiguous, since any amount of work could also be done during the process. By convention, however, we assume that the pressure is constant (usually 1 atm), and that no other work is done besides the usual constant-pressure expansion or compression. The latent heat for melting ice is 333 J/g, or 80 cal/g. The latent heat for boiling water is 2260 J/g, or 540 cal/g. (To get a feel for these numbers, recall that raising the temperature of water from 0°C to 100°C requires 100 cal/g.)

Problem 1.47. Your 200-g cup of tea is boiling-hot. About how much ice should you add to bring it down to a comfortable sipping temperature of 65°C? (Assume that the ice is initially at $-15°$C. The specific heat capacity of ice is 0.5 cal/g·°C.)

Problem 1.48. When spring finally arrives in the mountains, the snow pack may be two meters deep, composed of 50% ice and 50% air. Direct sunlight provides about 1000 watts/m^2 to earth's surface, but the snow might reflect 90% of this energy. Estimate how many weeks the snow pack should last, if direct solar radiation is the only source of energy.

Enthalpy

Constant-pressure processes occur quite often, both in the natural world and in the laboratory. Keeping track of the compression-expansion work done during these processes gets to be a pain after a while, but there is a convenient trick that makes it a bit easier. Instead of always talking about the *energy* content of a system, we can agree to always add in the work needed to make room for it (under a constant pressure, usually 1 atm). This work is PV, the pressure of the environment times the total volume of the system (that is, the total space you would need to clear out to make room for it). Adding PV onto the energy gives a quantity called the **enthalpy**, denoted H:

$$H \equiv U + PV. \tag{1.51}$$

This is the *total* energy you would have to come up with, to create the system out of nothing and put it into this environment (see Figure 1.15). Or, put another way, if you could somehow annihilate the system, the energy you could extract is not just U, but also the work (PV) done by the atmosphere as it collapses to fill the vacuum left behind.

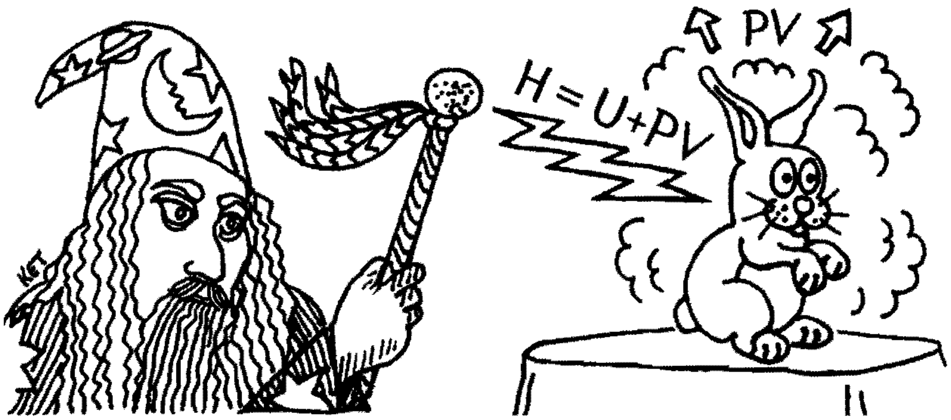

Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

To see the usefulness of enthalpy, suppose that some change takes place in the system—you add some heat, or chemicals react, or whatever—while the pressure is always held constant. The energy, volume, and enthalpy can all change, by amounts that I'll call ΔV, ΔU, and ΔH. The new enthalpy is

$$\begin{aligned} H + \Delta H &= (U + \Delta U) + P(V + \Delta V) \\ &= (U + PV) + (\Delta U + P\,\Delta V) \\ &= H + (\Delta U + P\,\Delta V), \end{aligned} \tag{1.52}$$

so the change in enthalpy during a constant-pressure process is

$$\Delta H = \Delta U + P\,\Delta V \qquad (\text{constant } P). \tag{1.53}$$

This says that enthalpy can increase for two reasons: either because the energy increases, or because the system expands and work is done on the atmosphere to make room for it.

Now recall the first law of thermodynamics: The change in energy equals the heat added to the system, plus the compression-expansion work done on it, plus any other work (e.g., electrical) done on it:

$$\Delta U = Q + (-P\,\Delta V) + W_{\text{other}}. \tag{1.54}$$

Combining this law with equation 1.53, we obtain

$$\Delta H = Q + W_{\text{other}} \qquad (\text{constant } P), \tag{1.55}$$

that is, the change in enthalpy is caused *only* by heat and other forms of work, *not* by compression-expansion work (during constant-pressure processes). In other words, you can forget all about compression-expansion work if you deal with enthalpy instead of energy. If no "other" types of work are being done, the change in enthalpy tells you *directly* how much heat has been added to the system. (That's why we use the symbol H.)

For the simple case of raising an object's temperature, the change in enthalpy per degree, at constant pressure, is the same as the heat capacity at constant pressure, C_P:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P. \tag{1.56}$$

This formula is really the best way to define C_P, though you can easily see that it is equivalent to equation 1.45. Just as C_V should really be called "energy capacity," C_P should really be called "enthalpy capacity." And as with C_V, there doesn't have to be any heat involved at all, since the enthalpy could just as well enter as "other" work, as in a microwave oven.

Chemistry books are full of tables of ΔH values for more dramatic processes: phase transformations, chemical reactions, ionization, dissolution in solvents, and so on. For instance, standard tables say that the change in enthalpy when you boil one mole of water at 1 atm is 40,660 J. Since a mole of water is about 18 grams

(16 for the oxygen and 2 for the hydrogen), this means that the change in enthalpy when you boil one *gram* of water should be (40,660 J)/18 = 2260 J, precisely the number I quoted earlier for the latent heat. However, not all of this energy ends up in the vaporized water. The volume of one mole of water vapor, according to the ideal gas law, is RT/P (while the initial volume of the liquid is negligible), so the work needed to push the atmosphere away is

$$PV = RT = (8.31\ \text{J/K})(373\ \text{K}) = 3100\ \text{J}. \tag{1.57}$$

This is only 8% of the 40,660 J of energy put in, but sometimes it's necessary to keep track of such things.

As another example, consider the chemical reaction in which hydrogen and oxygen gas combine to form liquid water:

$$\text{H}_2 + \tfrac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}. \tag{1.58}$$

For each mole of water produced, ΔH for this reaction is −286 kJ; in tables this quantity is referred to as the **enthalpy of formation** of water, because it's being "formed" out of elemental constituents in their most stable states. (The numerical value assumes that both the reactants and the product are at room temperature and atmospheric pressure. This number and others like it are tabulated in the data section at the back of this book.) If you simply burn a mole of hydrogen, then 286 kJ is the amount of heat you get out. Nearly all of this energy comes from the thermal and chemical energy of the molecules themselves, but a small amount comes from work done by the atmosphere as it collapses to fill the space left behind by the consumed gases.

You might wonder, though, whether some of the 286 kJ can't be extracted as *work* (perhaps electrical work) rather than as heat. Certainly this would be a good thing, since electricity is so much more useful and versatile than heat. In general the answer is that much of the energy from a chemical reaction *can* be extracted as work, but there are limits, as we'll see in Chapter 5.

Problem 1.49. Consider the combustion of one mole of H_2 with 1/2 mole of O_2 under standard conditions, as discussed in the text. How much of the heat energy produced comes from a decrease in the internal energy of the system, and how much comes from work done by the collapsing atmosphere? (Treat the volume of the liquid water as negligible.)

Problem 1.50. Consider the combustion of one mole of methane gas:

$$\text{CH}_4(\text{gas}) + 2\text{O}_2(\text{gas}) \longrightarrow \text{CO}_2(\text{gas}) + 2\text{H}_2\text{O}(\text{gas}).$$

The system is at standard temperature (298 K) and pressure (10^5 Pa) both before and after the reaction.

(a) First imagine the process of converting a mole of methane into its elemental consituents (graphite and hydrogen gas). Use the data at the back of this book to find ΔH for this process.

(b) Now imagine forming a mole of CO_2 and two moles of water vapor from their elemental constituents. Determine ΔH for this process.

(c) What is ΔH for the actual reaction in which methane and oxygen form carbon dioxide and water vapor directly? Explain.

(d) How much heat is given off during this reaction, assuming that no "other" forms of work are done?

(e) What is the change in the system's *energy* during this reaction? How would your answer differ if the H_2O ended up as liquid water instead of vapor?

(f) The sun has a mass of 2×10^{30} kg and gives off energy at a rate of 3.9×10^{26} watts. If the source of the sun's energy were ordinary combustion of a chemical fuel such as methane, about how long could it last?

Problem 1.51. Use the data at the back of this book to determine ΔH for the combustion of a mole of glucose,

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O.$$

This is the (net) reaction that provides most of the energy needs in our bodies.

Problem 1.52. The enthalpy of combustion of a gallon (3.8 liters) of gasoline is about 31,000 kcal. The enthalpy of combustion of an ounce (28 g) of corn flakes is about 100 kcal. Compare the cost of gasoline to the cost of corn flakes, per calorie.

Problem 1.53. Look up the enthalpy of formation of atomic hydrogen in the back of this book. This is the enthalpy change when a mole of atomic hydrogen is formed by dissociating 1/2 mole of molecular hydrogen (the more stable state of the element). From this number, determine the energy needed to dissociate a single H_2 molecule, in electron-volts.

Problem 1.54. A 60-kg hiker wishes to climb to the summit of Mt. Ogden, an ascent of 5000 vertical feet (1500 m).

(a) Assuming that she is 25% efficient at converting chemical energy from food into mechanical work, and that essentially all the mechanical work is used to climb vertically, roughly how many bowls of corn flakes (standard serving size 1 ounce, 100 kilocalories) should the hiker eat before setting out?

(b) As the hiker climbs the mountain, three-quarters of the energy from the corn flakes is converted to thermal energy. If there were no way to dissipate this energy, by how many degrees would her body temperature increase?

(c) In fact, the extra energy does not warm the hiker's body significantly; instead, it goes (mostly) into evaporating water from her skin. How many liters of water should she drink during the hike to replace the lost fluids? (At 25°C, a reasonable temperature to assume, the latent heat of vaporization of water is 580 cal/g, 8% more than at 100°C.)

Problem 1.55. Heat capacities are normally positive, but there is an important class of exceptions: systems of particles held together by gravity, such as stars and star clusters.

(a) Consider a system of just two particles, with identical masses, orbiting in circles about their center of mass. Show that the gravitational potential energy of this system is -2 times the total kinetic energy.

(b) The conclusion of part (a) turns out to be true, at least on average, for *any* system of particles held together by mutual gravitational attraction:

$$\overline{U}_{\text{potential}} = -2\overline{U}_{\text{kinetic}}.$$

Here each $\overline{U}$ refers to the total energy (of that type) for the entire system, averaged over some sufficiently long time period. This result is known as the **virial theorem**. (For a proof, see Carroll and Ostlie (1996), Section 2.4.) Suppose, then, that you add some energy to such a system and then wait for the system to equilibrate. Does the average total kinetic energy increase or decrease? Explain.

(c) A star can be modeled as a gas of particles that interact with each other only gravitationally. According to the equipartition theorem, the average kinetic energy of the particles in such a star should be $\frac{3}{2}kT$, where T is the average temperature. Express the total energy of a star in terms of its average temperature, and calculate the heat capacity. Note the sign.

(d) Use dimensional analysis to argue that a star of mass M and radius R should have a total potential energy of $-GM^2/R$, times some constant of order 1.

(e) Estimate the average temperature of the sun, whose mass is 2×10^{30} kg and whose radius is 7×10^8 m. Assume, for simplicity, that the sun is made entirely of protons and electrons.

1.7 Rates of Processes

Usually, to determine *what* the equilibrium state of a system is, we need not worry about *how long* the system takes to reach equilibrium. Thermodynamics, by many people's definitions, includes only the study of equilibrium states themselves. Questions about time and rates of processes are then considered a separate (though related) subject, sometimes called **transport theory** or **kinetics**.

In this book I won't say much about rates of processes, because these kinds of questions are often quite difficult and require somewhat different tools. But transport theory is important enough that I should say *something* about it, at least the simpler aspects. That is the purpose of this section.*

Heat Conduction

At what rate does heat flow from a hot object to a cold object? The answer depends on many factors, particularly on what *mechanisms* of heat transfer are possible under the circumstances.

If the objects are separated by empty space (like the sun and the earth, or the inner and outer walls of a thermos bottle) then the only possible heat transfer mechanism is radiation. I'll derive a formula for the rate of radiation in Chapter 7.

If a fluid (gas or liquid) can mediate the heat transfer, then convection—bulk motion of the fluid—is often the dominant mechanism. Convection rates depend on all sorts of factors, including the heat capacity of the fluid and the many possible forces acting on it. I won't try to calculate any convection rates in this book.

That leaves conduction: heat transfer by direct contact at the molecular level. Conduction can happen through a solid, liquid, or gas. In a liquid or a gas the

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*This section is somewhat outside the main development of the book. No other sections depend on it, so you may omit or postpone it if you wish.

energy is transferred through molecular collisions: When a fast molecule hits a slow molecule, energy is usually transferred from the former to the latter. In solids, heat is conducted via lattice vibrations and, in metals, via conduction electrons. Good electrical conductors tend to be good heat conductors as well, because the same conduction electrons can carry both electric current and energy, while lattice vibrations are much less efficient than electrons at conducting heat.

Regardless of these details, the rate of heat conduction obeys a mathematical law that is not hard to guess. For definiteness, imagine a glass window separating the warm interior of a building from the cold outdoors (see Figure 1.16). We would expect the amount of heat Q that passes through the window to be directly proportional to the window's total area A, and to the amount of time that passes, Δt. We would probably expect Q to be *inversely* proportional to the thickness of the window, Δx. Finally, we would expect Q to depend on the indoor and outdoor temperatures, in such a way that $Q = 0$ if these temperatures are the same. The simplest guess is that Q is directly proportional to the temperature difference, $\Delta T = T_2 - T_1$; this guess turns out to be correct for any heat transfer by conduction (though not for radiation). Summarizing these proportionalities, we can write

$$Q \propto \frac{A\,\Delta T\,\Delta t}{\Delta x}, \qquad \text{or} \qquad \frac{Q}{\Delta t} \propto A\,\frac{dT}{dx}. \tag{1.59}$$

The constant of proportionality depends on the material through which the heat is being conducted (in this case, glass). This constant is called the **thermal conductivity** of the material. The usual symbol for thermal conductivity is k, but to distinguish it from Boltzmann's constant I'll called it k_t. I'll also put a minus sign into the equation to remind us that if T increases from left to right, Q flows from right to left. The law of heat conduction is then

$$\frac{Q}{\Delta t} = -k_t A\,\frac{dT}{dx}. \tag{1.60}$$

This equation is known as the **Fourier heat conduction law**, after the same J. B. J. Fourier who invented Fourier analysis.

To *derive* the Fourier heat conduction law, and to predict the value of k_t for a particular material, we would have to invoke a detailed molecular model of what happens during heat conduction. I'll do this for the easiest case, an ideal gas, in the

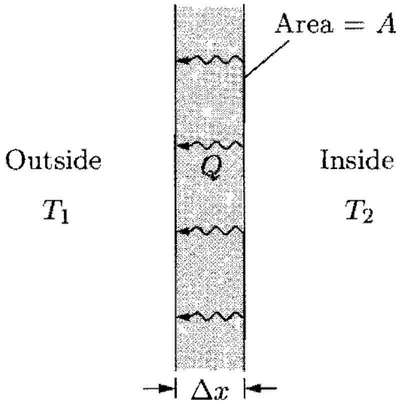

Figure 1.16. The rate of heat conduction through a pane of glass is proportional to its area A and inversely proportional to its thickness Δx.

following subsection. For now, though, let's just take Fourier's law as an empirical fact and treat k_t as a property that you need to measure for any material of interest.

Thermal conductivities of common materials vary by more than four orders of magnitude. In SI units (watts per meter per kelvin), a few representative values are: air, 0.026; wood, 0.08; water, 0.6; glass, 0.8; iron, 80; copper, 400. Again, good electrical conductors tend to be good thermal conductors. Note that the values for air and water apply to conduction only, even though convection can often be extremely important.

Back to our window, suppose it has an area of one square meter and a thickness of 3.2 mm (1/8 inch). Then if the temperature just inside the window is 20°C and the temperature just outside is 0°C, the rate of heat flow through it is

$$\frac{Q}{\Delta t} = \frac{(0.8\ \text{W/m}\cdot\text{K})(1\ \text{m}^2)(293\ \text{K} - 273\ \text{K})}{0.0032\ \text{m}} = 5000\ \text{watts.} \tag{1.61}$$

If this number seems absurdly high to you, you're right. My assumption of such a large temperature difference between "just inside" and "just outside" the window is unrealistic, because there is always a thin layer of still air on each side of the glass. The two air layers can provide many times more thermal insulation than the glass itself, bringing the heat loss down into the range of a few hundred watts (see Problem 1.57).

Problem 1.56. Calculate the rate of heat conduction through a layer of still air that is 1 mm thick, with an area of 1 m^2, for a temperature difference of 20°C.

Problem 1.57. Home owners and builders discuss thermal conductivities in terms of the ***R* value** (*R* for *resistance*) of a material, defined as the thickness divided by the thermal conductivity:

$$R \equiv \frac{\Delta x}{k_t}.$$

(a) Calculate the R value of a 1/8-inch (3.2 mm) piece of plate glass, and then of a 1 mm layer of still air. Express both answers in SI units.

(b) In the United States, R values of building materials are normally given in English units, $^\circ\text{F}\cdot\text{ft}^2\cdot\text{hr/Btu}$. A Btu, or British thermal unit, is the energy needed to raise the temperature of a pound of water by 1°F. Work out the conversion factor between the SI and English units for R values. Convert your answers from part (a) to English units.

(c) Prove that for a compound layer of two different materials sandwiched together (such as air and glass, or brick and wood), the effective total R value is the sum of the individual R values.

(d) Calculate the effective R value of a single piece of plate glass with a 1.0-mm layer of still air on each side. (The effective thickness of the air layer will depend on how much wind is blowing; 1 mm is of the right order of magnitude under most conditions.) Using this effective R value, make a revised estimate of the heat loss through a 1-m^2 single-pane window when the temperature in the room is 20°C higher than the outdoor temperature.

Problem 1.58. According to a standard reference table, the R value of a 3.5-inch-thick vertical air space (within a wall) is 1.0 (in English units), while the R value of a 3.5-inch thickness of fiberglass batting is 10.9. Calculate the R value of a 3.5-inch thickness of *still* air, then discuss whether these two numbers are reasonable. (Hint: These reference values include the effects of convection.)

Problem 1.59. Make a rough estimate of the total rate of conductive heat loss through the windows, walls, floor, and roof of a typical house in a cold climate. Then estimate the cost of replacing this lost energy over the course of a month. If possible, compare your estimate to a real utility bill. (Utility companies measure electricity by the **kilowatt-hour**, a unit equal to 3.6 MJ. In the United States, natural gas is billed in **therms**, where 1 therm = 10^5 Btu. Utility rates vary by region; I currently pay about 7 cents per kilowatt-hour for electricity and 50 cents per therm for natural gas.)

Problem 1.60. A frying pan is quickly heated on the stovetop to 200°C. It has an iron handle that is 20 cm long. Estimate how much time should pass before the end of the handle is too hot to grab with your bare hand. (Hint: The cross-sectional area of the handle doesn't matter. The density of iron is about 7.9 g/cm^3 and its specific heat is 0.45 J/g·°C).

Problem 1.61. Geologists measure conductive heat flow out of the earth by drilling holes (a few hundred meters deep) and measuring the temperature as a function of depth. Suppose that in a certain location the temperature increases by 20°C per kilometer of depth and the thermal conductivity of the rock is 2.5 W/m·K. What is the rate of heat conduction per square meter in this location? Assuming that this value is typical of other locations over all of earth's surface, at approximately what rate is the earth losing heat via conduction? (The radius of the earth is 6400 km.)

Problem 1.62. Consider a uniform rod of material whose temperature varies only along its length, in the x direction. By considering the heat flowing from both directions into a small segment of length Δx, derive the **heat equation**,

$$\frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2},$$

where $K = k_t/c\rho$, c is the specific heat of the material, and ρ is its density. (Assume that the only motion of energy is heat conduction within the rod; no energy enters or leaves along the sides.) Assuming that K is independent of temperature, show that a solution of the heat equation is

$$T(x,t) = T_0 + \frac{A}{\sqrt{t}}\, e^{-x^2/4Kt},$$

where T_0 is a constant background temperature and A is any constant. Sketch (or use a computer to plot) this solution as a function of x, for several values of t. Interpret this solution physically, and discuss in some detail how energy spreads through the rod as time passes.

Conductivity of an Ideal Gas

In a gas, the rate of heat conduction is limited by how *far* a molecule can travel before it collides with another molecule. The average distance traveled between collisions is called the **mean free path.** In a dilute gas the mean free path is many times larger than the average distance between molecules, because a molecule can pass by many of its neighbors before actually hitting one of them. Let me now make a rough estimate of the mean free path in a dilute gas.

For simplicity, imagine that all the molecules in a gas except one are frozen in place. How far does the remaining molecule travel between collisions? Well, a collision happens when the center of our molecule comes within one molecular diameter ($2r$, where r is the radius of a molecule) of the center of some other molecule (see Figure 1.17). Collisions would occur just as often if our molecule were twice as wide and all the others were points; let's therefore pretend that this is the case. Then, as our molecule travels along, it sweeps out an imaginary cylinder of space whose radius is $2r$. When the volume of this cylinder equals the average volume per molecule in the gas, we're likely to get a collision. The mean free path, ℓ, is roughly the length of the cylinder when this condition is met:

$$\begin{aligned}\text{volume of cylinder} &= \text{average volume per molecule}\\ \Rightarrow\quad \pi(2r)^2\ell &\approx \frac{V}{N}\\ \Rightarrow\quad \ell &\approx \frac{1}{4\pi r^2}\frac{V}{N}.\end{aligned} \tag{1.62}$$

The $\approx$ symbol indicates that this formula is only a rough approximation for ℓ, because I've neglected the motion of the other molecules as well as the variation in path lengths between collisions. The actual mean free path will differ by a numerical factor that shouldn't be too different from 1. But there's not much point in being more precise, because r itself is not well defined: Molecules don't have sharp edges,

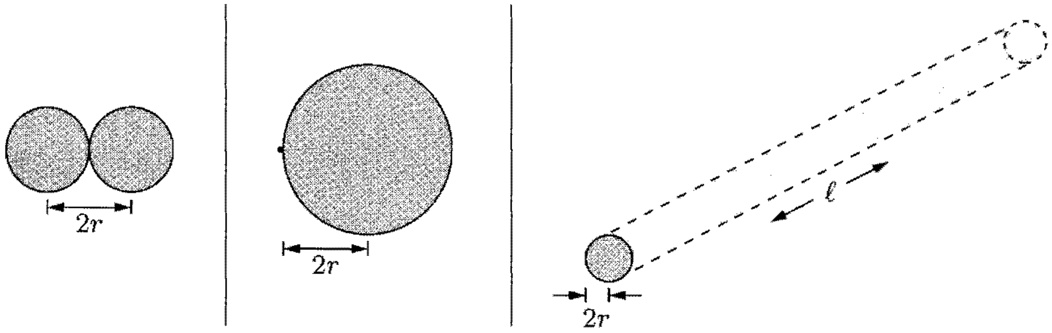

Figure 1.17. A collision between molecules occurs when their centers are separated by twice the molecular radius r. The same would be true if one molecule had radius $2r$ and the other were a point. When a sphere of radius $2r$ moves in a straight line of length ℓ, it sweeps out a cylinder whose volume is $4\pi r^2\ell$.

and most of them aren't even spherical.*

The effective radius of a nitrogen or oxygen molecule should be one or two ångstroms; let's say $r = 1.5$ Å $= 1.5 \times 10^{-10}$ m. Treating air as an ideal gas, the volume per particle is $V/N = kT/P = 4 \times 10^{-26}\ \text{m}^3$ at room temperature and atmospheric pressure. With these numbers, equation 1.62 predicts a mean free path of 150 nm, about 40 times greater than the average separation between air molecules. We can also estimate the average *time* between collisions:

$$\overline{\Delta t} = \frac{\ell}{\bar{v}} \approx \frac{\ell}{v_{\text{rms}}} \approx \frac{1.5 \times 10^{-7}\ \text{m}}{500\ \text{m/s}} = 3 \times 10^{-10}\ \text{s}. \tag{1.63}$$

Now back to heat conduction. Consider a small region within a gas where the temperature increases in the x direction (see Figure 1.18). The heavy dotted line in the figure represents a plane perpendicular to the x direction; my intent is to estimate the amount of heat that flows across this plane. Let Δt be the average time between collisions, so that each molecule travels a distance of roughly one mean free path during this time. Then, during this time, the molecules that cross the dotted line from the left will have started from somewhere within box 1 (whose thickness is ℓ), while the molecules that cross the dotted line from the right will have started from somewhere within box 2 (whose thickness is also ℓ). Both of these boxes have the same area A in the yz plane. If the total energy of all the molecules in box 1 is U_1, then the energy crossing the dotted line from the left is roughly $U_1/2$, since only half of the molecules will have positive x velocities at this moment. Similarly, the energy crossing the line from the right is half the total energy in box 2, or $U_2/2$. The net heat flow across the line is therefore

$$Q = \frac{1}{2}(U_1 - U_2) = -\frac{1}{2}(U_2 - U_1) = -\frac{1}{2}C_V(T_2 - T_1) = -\frac{1}{2}C_V\ell\frac{dT}{dx}, \tag{1.64}$$

where C_V is the heat capacity of all the gas in either box and T_1 and T_2 are the average temperatures in the two boxes. (In the last step I've used the fact that the distance between the centers of the two boxes is ℓ.)

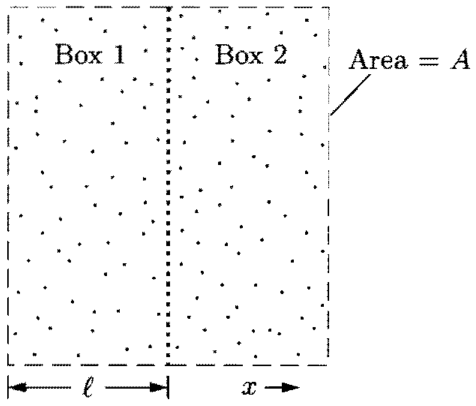

Figure 1.18. Heat conduction across the dotted line occurs because the molecules moving from box 1 to box 2 have a different average energy than the molecules moving from box 2 to box 1. For free motion between these boxes, each should have a width of roughly one mean free path.

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*For that matter, I haven't even given a precise definition of what constitutes a collision. After all, even when molecules pass at a distance, they attract and deflect each other somewhat. For a more careful treatment of transport processes in gases, see Reif (1965).

Equation 1.64 confirms Fourier's law, that the rate of heat conduction is directly proportional to the difference in temperatures. Furthermore, comparison to equation 1.60 yields an explicit prediction for the thermal conductivity:

$$k_t = \frac{1}{2}\frac{C_V \ell}{A\,\Delta t} = \frac{1}{2}\frac{C_V}{A\ell}\frac{\ell^2}{\Delta t} = \frac{1}{2}\frac{C_V}{V}\ell\overline{v}, \tag{1.65}$$

where $\overline{v}$ is the average speed of the molecules. The quantity C_V/V is the heat capacity of the gas per unit volume, which can be evaluated as

$$\frac{C_V}{V} = \frac{\frac{f}{2}Nk}{V} = \frac{f}{2}\frac{P}{T}, \tag{1.66}$$

where f is the number of degrees of freedom per molecule. Recall, however, that ℓ for a gas is proportional to V/N. Therefore the thermal conductivity of a given gas should depend only on its temperature, through $\overline{v} \propto \sqrt{T}$ and possibly through f. Over limited ranges of temperature the number of degrees of freedom is fairly constant, so k_t should be proportional to the square root of the absolute temperature. Experiments on a wide variety of gases have confirmed this prediction (see Figure 1.19).

For air at room temperature and atmospheric pressure, $f = 5$ so $C_V/V = \frac{5}{2}(10^5\ \mathrm{N/m^2})/(300\ \mathrm{K}) \approx 800\ \mathrm{J/m^3{\cdot}K}$. Equation 1.65 therefore predicts a thermal conductivity of

$$k_t \approx \tfrac{1}{2}(800\ \mathrm{J/m^3{\cdot}K})(1.5\times10^{-7}\ \mathrm{m})(500\ \mathrm{m/s}) = 0.031\ \mathrm{W/m{\cdot}K}, \tag{1.67}$$

only a little higher than the measured value of 0.026. Not bad, considering all the crude approximations I've made in this section.

The preceding analysis of the thermal conductivities of gases is an example of what's called **kinetic theory**, an approach to thermal physics based on actual molecular motions. Another example was the microscopic model of an ideal gas presented in Section 1.2. While kinetic theory is the most direct and concrete approach to thermal physics, it is also the most difficult. Fortunately, there are

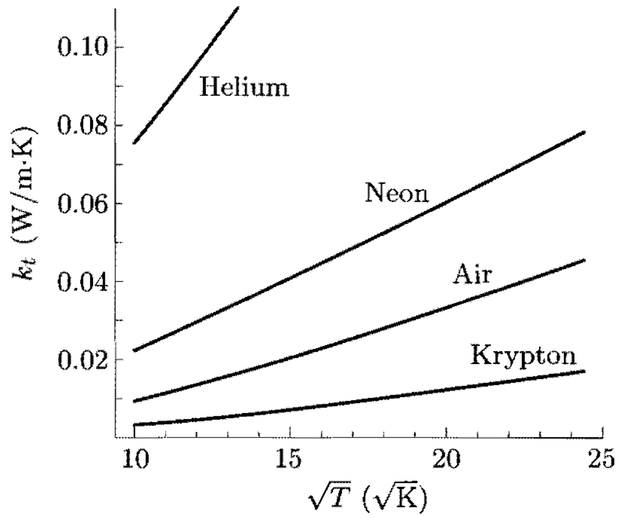

Figure 1.19. Thermal conductivities of selected gases, plotted vs. the square root of the absolute temperature. The curves are approximately linear, as predicted by equation 1.65. Data from Lide (1994).

much easier methods for predicting most of the *equilibrium* properties of materials, without having to know the details of how molecules move. To predict the *rates* of processes, however, we usually have to resort to kinetic theory.

> **Problem 1.63.** At about what pressure would the mean free path of an air molecule at room temperature equal 10 cm, the size of a typical laboratory apparatus?
>
> **Problem 1.64.** Make a rough estimate of the thermal conductivity of helium at room temperature. Discuss your result, explaining why it differs from the value for air.
>
> **Problem 1.65.** Pretend that you live in the 19th century and don't know the value of Avogadro's number* (or of Boltzmann's constant or of the mass or size of any molecule). Show how you could make a rough estimate of Avogadro's number from a measurement of the thermal conductivity of a gas, together with other measurements that are relatively easy.

Viscosity

Energy isn't the only thing that can spread through a fluid at the molecular level; another is *momentum.*

Consider the situation shown in Figure 1.20: two parallel solid surfaces moving past one another, separated by a small gap containing a liquid or gas. Let's work in the reference frame where the bottom surface is at rest and the top surface is moving in the $+x$ direction. What about the motion of the fluid? At normal temperatures the fluid molecules will be jostling with thermal velocities of hundreds of meters per second, but let's ignore this motion for the moment and instead ask about the average motion at the macroscopic scale. Taking a macroscopic view, it's natural to guess that just above the bottom surface the fluid should be at rest; a thin layer of fluid "sticks" to the surface. For the same reason (since reference frames are arbitrary), a thin layer "sticks" to the top surface and moves along with it. In between the motion of the fluid could be turbulent and chaotic, but let's assume that this is not the case: The motion is slow enough, or the gap is narrow enough, that the flow of the fluid is entirely horizontal. Then the flow is said to be **laminar**. Assuming laminar flow, the x velocity of the fluid will increase steadily in the z direction, as shown in the figure.

With only a few exceptions at very low temperatures, all fluids tend to resist this kind of shearing, differential flow. This resistance is called **viscosity**. The top layer of fluid gives up some of its forward momentum to the next layer down, which gives up some of its forward momentum to the next layer, and so on down to the bottom layer which exerts a forward force on the bottom surface. At the same time (by Newton's third law) the loss of momentum by the top layer causes it to exert a

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*Amedeo Avogadro himself, who died in 1856, never knew the numerical value of the number that was later named after him. The first *accurate* determination of Avogadro's number was not made until around 1913, when Robert Millikan measured the fundamental unit of electric charge. Others had already measured the charge-to-mass ratio of the proton (then called simply a hydrogen ion), so at that point it was easy to calculate the mass of the proton and hence the number of them needed to make a gram.

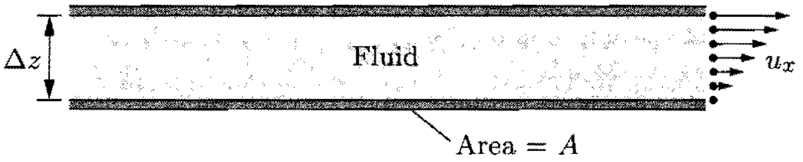

Figure 1.20. The simplest arrangement for demonstrating viscosity: two parallel surfaces sliding past each other, separated by a narrow gap containing a fluid. If the motion is slow enough and the gap narrow enough, the fluid flow is **laminar**: At the macroscopic scale the fluid moves only horizontally, with no turbulence.

backward force on the top surface. The more "viscous" the fluid, the more efficient the momentum transfer and the greater these forces will be. Air isn't very viscous; corn syrup is.

As with thermal conductivity, it isn't hard to guess how the viscous drag force depends on the geometry of the situation. The simplest guess (which turns out to be correct) is that the force is proportional to the common area of the surfaces, inversely proportional to the width of the gap, and directly proportional to the difference in velocity between the two surfaces. In the notation of Figure 1.20 (using u_x for the macroscopic velocity to distinguish it from the much faster thermal velocities),

$$F_x \propto \frac{A \cdot (u_{x,\text{top}} - u_{x,\text{bottom}})}{\Delta z} \qquad \text{or} \qquad \frac{F_x}{A} \propto \frac{\Delta u_x}{\Delta z}. \tag{1.68}$$

The constant of proportionality is called the **coefficient of viscosity** or simply the **viscosity** of the fluid; the standard symbol for this coefficient is η, the Greek letter eta. Our formula for the force is then

$$\frac{|F_x|}{A} = \eta \frac{du_x}{dz}, \tag{1.69}$$

where I've put absolute value bars around F_x because it could represent the force on either plate, these two forces being equal in magnitude but opposite in direction. The force per unit area has units of pressure (Pa or $\mathrm{N/m^2}$), but please don't *call* it a pressure because it's exerted parallel to the surface, not perpendicular. The correct term for such a force per unit area is **shear stress**.

From equation 1.69 you can see that the coefficient of viscosity has units of pascal-seconds in the SI system. (Sometimes you'll still see viscosities given in a unit called the **poise**; this is the cgs unit, equal to a dyne-second per cm^2, which turns out to be 10 times smaller than the SI unit.) Viscosities vary enormously from one fluid to another and also vary considerably with temperature. The viscosity of water is 0.0018 Pa·s at 0°C but only 0.00028 Pa·s at 100°C. Low-viscosity motor oil (SAE 10) has a room-temperature viscosity of about 0.25 Pa·s. Gases have much lower viscosities, for example, 19 μPa·s for air at room temperature. Surprisingly, the viscosity of an ideal gas is *independent* of its pressure and *increases* as a function of temperature. This strange behavior requires some explanation.

Recall from the previous subsection that the thermal conductivity of an ideal gas behaves in a similar way: It is independent of pressure and increases with temperature in proportion to $\sqrt{T}$. Although the *amount* of energy carried by a parcel of gas is proportional to the density of particles N/V, this dependence cancels in k_t because the mean free path, which controls *how far* the energy can travel at once, is proportional to V/N. The temperature dependence of k_t comes from the remaining factor of $\overline{v}$, the average thermal speed of the gas molecules (see equation 1.65).

In exactly the same way, the transfer of horizontal momentum vertically through a gas depends on three factors: the momentum density in the gas, the mean free path, and the average thermal speed. The first two factors depend on the particle density, but this dependence cancels: Although a dense gas carries *more* momentum, random thermal motions transport that momentum through *less distance* at a time. The molecules do move *faster* at high temperature, however. According to this picture the viscosity of a gas should be proportional to $\sqrt{T}$ just like the thermal conductivity, and experiments confirm this prediction.

Why, then, does the viscosity of a liquid *decrease* as its temperature increases? In a liquid the density and the mean free path are essentially independent of temperature and pressure, but another factor comes into play: When the temperature is low and the thermal motions are slow, the molecules can better latch onto each other as they collide. This binding allows a very efficient transfer of momentum from one molecule to another. In the extreme case of a solid, the molecules are more or less permanently bonded together and the viscosity is almost infinite; solids *can* flow like fluids, but only on geological time scales.

Problem 1.66. In analogy with the thermal conductivity, derive an approximate formula for the viscosity of an ideal gas in terms of its density, mean free path, and average thermal speed. Show explicitly that the viscosity is independent of pressure and proportional to the square root of the temperature. Evaluate your formula numerically for air at room temperature and compare to the experimental value quoted in the text.

Diffusion

Heat conduction is the transport of *energy* by random thermal motions. Viscosity results from the transport of *momentum*, which in gases is accomplished mainly by random thermal motions. A third entity that can be transported by random thermal motions is *particles*, which tend to spread from areas of high concentration to areas of low concentration. For example, if you drop a drop of food coloring into a cup of still water, you'll see the dye gradually spreading out in all directions. This spreading out of particles is called **diffusion**.*

Like the flow of energy and momentum, the flow of particles by diffusion obeys an equation that is fairly easy to guess. Just as heat conduction is caused by a temperature difference and viscous drag is caused by a velocity difference, diffusion is caused by a difference in the *concentration* of particles, that is, the number of particles per unit volume, N/V. In this section (and only in this section) I'll use the

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*Problem 1.22 treats the simpler process of a gas escaping through a hole into a vacuum, called **effusion**.

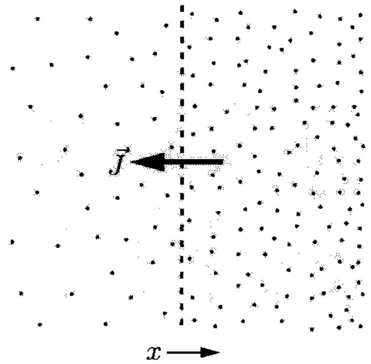

Figure 1.21. When the concentration of a certain type of molecule increases from left to right, there will be **diffusion**, a net flow of molecules, from right to left.

symbol n for particle concentration. To keep the geometry simple, imagine a region where n for a certain type of particle increases uniformly in the x direction (see Figure 1.21). The **flux** of these particles across any surface is the net number that cross it per unit area per unit time; the symbol for particle flux is $\vec{J}$. Then, in analogy with equations 1.60 and 1.69, we would probably guess that $|\vec{J}|$ is proportional to dn/dx. Again, this guess turns out to be correct under most circumstances. Using the symbol D for the constant of proportionality, we can write

$$J_x = -D\frac{dn}{dx}. \tag{1.70}$$

The minus sign indicates that if dn/dx is positive, the flux is in the negative x direction. This equation is known as **Fick's law**, after the 19th century German physiologist Adolf Eugen Fick.

The constant D is called the **diffusion coefficient**; it depends both on the type of molecule that is diffusing and on what it is diffusing through. In SI units (m^2/s), diffusion coefficients in water near room temperature range from 9×10^{-9} for H^+ ions to 5×10^{-10} for sucrose to a few times 10^{-11} for very large molecules such as proteins. Diffusion in gases is faster: For CO molecules diffusing through air at room temperature and atmospheric pressure, $D = 2 \times 10^{-5}\ \mathrm{m}^2/\mathrm{s}$. Other small molecules diffusing through air have similar D values. As you would probably expect, diffusion coefficients generally increase with increasing temperature.

Although diffusion is extremely important on the small scales of biological cells, cloud droplets, and semiconductor fabrication, the small D values quoted above indicate that it is not an efficient mechanism for large-scale mixing. As a quick example, consider a drop of food coloring added to a glass of water. Imagine that the dye has already spread uniformly through half of the glass. How long would it take to diffuse into the other half? According to Fick's law, I can write very roughly

$$\frac{N}{A\,\Delta t} = D\frac{N/V}{\Delta x}, \tag{1.71}$$

where N is the total number of dye molecules, Δx is about 0.1 m and $V \approx A \cdot \Delta x$. I've written the particle flux in terms of the same N to indicate that I want Δt to be the time for approximately all (that is, half) of the molecules to cross from one side of the glass to the other. I don't know how big a molecule of food coloring is, but it can't be too different in size from sucrose so I'll guess $D = 10^{-9}$ m^2/s. Solving for Δt then gives 10^7 seconds, or almost four months. If you actually perform an experiment with water and food coloring, you'll probably find that they mix *much* faster than this, due to bulk motion of the water—convection. You *can* see the diffusion, though, if you look very closely at the interface between the colored and clear water.

Problem 1.67. Make a rough estimate of how far food coloring (or sugar) will diffuse through water in one minute.

Problem 1.68. Suppose you open a bottle of perfume at one end of a room. Very roughly, how much time would pass before a person at the other end of the room could smell the perfume, *if* diffusion were the only transport mechanism? Do you think diffusion *is* the dominant transport mechanism in this situation?

Problem 1.69. Imagine a narrow pipe, filled with fluid, in which the concentration of a certain type of molecule varies only along the length of the pipe (in the x direction). By considering the flux of these particles from both directions into a short segment Δx, derive **Fick's second law**,

$$\frac{\partial n}{\partial t} = D\,\frac{\partial^2 n}{\partial x^2}.$$

Noting the similarity to the heat equation derived in Problem 1.62, discuss the implications of this equation in some detail.

Problem 1.70. In analogy with the thermal conductivity, derive an approximate formula for the diffusion coefficient of an ideal gas in terms of the mean free path and the average thermal speed. Evaluate your formula numerically for air at room temperature and atmospheric pressure, and compare to the experimental value quoted in the text. How does D depend on T, at fixed pressure?

Humans are to a large degree sensitive to energy fluxes rather than temperatures, which you can verify for yourself on a cold, dark morning in the outhouse of a mountain cabin equipped with wooden and metal toilet seats. Both seats are at the same temperature, but your backside, which is not a very good thermometer, is nevertheless very effective at telling you which is which.

—Craig F. Bohren and Bruce A. Albrecht,
Atmospheric Thermodynamics (Oxford
University Press, New York, 1998).