CHAPTER 7

Materials and Models

We have applied Newton's laws of motion to the objects they were meant for: objects that are large enough to see or feel. In this chapter we use them to describe the mechanics of atoms and molecules. As we do that we have to keep in mind that Newton's laws and classical mechanics apply in the microscopic realm only to a limited extent, and that the ideas and methods of quantum mechanics may be necessary.

So far we have applied Newton's laws to "objects" without considering the material that they are made of or their internal structure. To treat them in terms of their atoms and molecules takes us from a few simple particles and unchanging objects to composite objects that consist of very large numbers of particles. The real systems are so complex that we approximate them with *models*, invented, imagined systems that, however, retain the essential properties of the systems that we seek to understand.

We begin this chapter by introducing the model called the *ideal gas*. It is an enormously fruitful model, which describes some of the most important properties of real gases, and, to some extent, also those of other materials. It also provides a bridge to a seemingly entirely different subject, that of heat and temperature.

In addition, it shows the correspondence between two very different aspects of the world around us. On the one hand there are the large-scale objects of our direct sensory experience. Our instruments show us that underlying this *macroscopic* world is a *microscopic* world that we are normally not aware of, the world of moving, vibrating, rotating, colliding atoms and molecules, absorbing, emitting, and exchanging energy.

7.1 Ideal systems and models: the ideal gas

How can we get started talking about the vastly complex real world? We know that we need to talk about one that is simpler, a *model* system, sometimes called an *ideal system*. Let's review the rules of the game. We decide what the model is and how it works. It is an invented system that shares some of the characteristics of the corresponding system in the real world.

The words *ideal* and *model* describe a system with properties that we make up and laws that we prescribe. We set the rules that we need to calculate the properties and behavior of our model system.

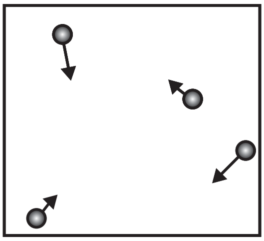
We can then compare the model and the real material to see to what extent their properties overlap. We can also ask what the model *predicts* for behavior under conditions that were not originally considered, and to see how the ideal and the actual systems then compare.

Here is the model that we will look at in some detail: it's a gas whose constituents (its atoms or molecules) are particles, i.e., they have no size or internal structure. They exert forces and experience forces only when they touch each other or the walls of their container. They move in accord with the laws of Newtonian mechanics. This model is called *the ideal gas*.

A real gas is very different. Its smallest units may be molecules, composed of two or more atoms, or single atoms, consisting of nuclei and electrons. They are not zero-size particles, and they exert forces on each other even when they don't touch. Nevertheless, the ideal-gas model describes and predicts the behavior of real gases very well under many circumstances.

Bouncing molecules: the microscopic point of view

The basic feature of the model that we call the ideal gas is that its components are always in motion and have only kinetic energy. They have no internal structure, no internal motion, and no internal energy. They exert no forces on each other except when they touch, so that there is no mutual potential energy. Since the model requires that these elementary components are point particles with no internal structure, it doesn't matter whether we call them atoms or molecules. (We'll call them molecules.) The figure shows a portion of a gas with just four molecules.



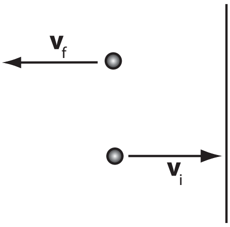
When the molecules collide with each other they can interchange energy and momentum in accord with the laws of conservation of energy and momentum. The total momentum of the system of which they are parts does not change. Neither does the total kinetic energy, since we have decided that in this model there is no other kind of energy.

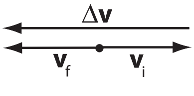
When we put the gas in a box or other container the molecules bounce off the walls. At each bounce the wall exerts a force on a molecule. From Newton's third law we know that there is at the same time a force *by* the molecule *on* the wall.

Our aim is to relate what the molecules are doing, as described by their *microscopic* variables, namely their velocities and kinetic energies, to the *macroscopic* variables that we observe and measure directly, namely the pressure (equal to the average force on the walls divided by the area of the walls) and the volume of the container.

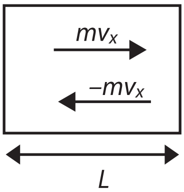
We start with a single molecule moving back and forth in a cubical box whose sides have length L and area $A = L^2$, with volume $V = L^3$. The molecule moves with an initial velocity $\mathbf{v}_\mathrm{i}$ in the x direction toward a wall that is at right angles to the x-direction. We assume that we can neglect the effect of the gravitational force on its path.

Like a ball hitting a solid wall at right angles to it, the molecule will bounce back along the same line, with its kinetic energy unchanged, and the direction of its momentum reversed. The kinetic energy is a scalar quantity that does not depend on direction, but the velocity and the momentum are vector quantities. The initial momentum vector $m\mathbf{v}_\mathrm{i}$ (where m is the mass of a molecule) and the momentum vector after the collision, $m\mathbf{v}_\mathrm{f}$, differ by the vector $m\mathbf{\Delta v}$, where $\mathbf{v}_\mathrm{i} + \mathbf{\Delta v} = \mathbf{v}_\mathrm{f}$.





Since all the velocities and momenta are along the x direction, we can call the initial momentum mv_x and the final momentum $-mv_x$. The change in momentum is $-2mv_x$, with a *magnitude* of $2mv_x$. Between a collision with one wall and a collision with the opposite wall the molecule moves a distance L in a time that we'll call Δt, so that $v_x \Delta t = L$, or $\Delta t = \frac{L}{v_x}$.



To find the force exerted by the molecule on the wall we use Newton's second law of motion. Instead of $F_\mathrm{net} = ma$ we use the momentum form. Since $a = \frac{\Delta v}{\Delta t}$ (the change in the velocity divided by the time it takes for the velocity to change), ma is equal to $\frac{\Delta(mv)}{\Delta t}$, i.e., the force is equal to the change in momentum divided by the time during which the momentum changes. For our single molecule the magnitude of the momentum change, $\Delta(mv)$, is $2mv_x$ at each collision, and this happens once in every time interval Δt, on one wall and then on the other, so that the average force is $\frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{L/v_x} = \frac{2mv_x^2}{L}$.

The molecule travels back and forth and contributes to the pressure on both walls. To find the pressure we need to divide the force by the area of both walls, $2L^2$, to get $\frac{2mv_x^2}{2L^3}$ or $\frac{mv_x^2}{V}$. This is the contribution to the pressure of a single molecule bouncing back and forth. For a gas of N molecules it is $\frac{Nmv_x^2}{V}$. We can also take into account that the velocities are not all the same, and use the average of mv_x^2, which we write as $\overline{mv_x^2}$, so that $P = \frac{N\overline{mv_x^2}}{V}$, which can be rewritten as $PV = N\overline{mv_x^2}$.

This is really the end of the derivation. But we can also look at what happens if the molecules do not just move along the x direction. In that case there are the additional velocity components v_y and v_z. The velocity v is related to them by $v^2 = v_x^2 + v_y^2 + v_z^2$. With a large number of molecules, randomly moving in all possible directions, all components will be equally represented, and their averages $\overline{v_x^2}, \overline{v_y^2}$, and $\overline{v_z^2}$ will be equal. $\overline{v^2}$ is then equal to $3\overline{v_x^2}$. This allows us to rewrite our result as $PV = \frac{1}{3}N\overline{mv^2}$, which we can also write as $PV = \left(\frac{2}{3}N\right)\left(\frac{1}{2}\overline{mv^2}\right)$.

We have achieved our goal. We now have a relation between the macroscopic variables, P and V, quantities that apply to the whole container with the gas in it, on the left, and the microscopic variables that refer to the molecules, i.e., their number and their average kinetic energy, on the right.

EXAMPLE 1

Joe and Jane are practicing tennis by hitting balls against a wall. The mass of a ball is 0.15 kg. The speed of each ball as it hits the wall is 20 m/s. There are 40 hits in one minute. Assume that the balls hit the wall at right angles and do not lose any kinetic energy when they bounce back.

(a) What average force does the wall experience in one minute?

(b) What is the average pressure on the section of the wall, whose area is 3 m^2, where the balls hit?

Ans.:

(a) $mv_x = 3$ kg m/s.

At one hit of a ball the momentum changes from mv_x to $-mv_x$. This is a change of $2mv_x = 6$ kg m/s. For 40 hits it is 240 kg m/s.

In a time of 60 s this is a rate of $\frac{240\,\text{kg m/s}}{60\,\text{s}} = F = 4\,\text{kg m/s}^2$, or 4 N.

(b) The pressure is $\frac{F}{A} = \frac{4}{3} = 1.33\,\text{N/m}^2$.

EXAMPLE 2

At atmospheric pressure (1.01×10^5 N/m^2) and room temperature the number of molecules in 1 m^3 of air is about 2.7×10^{25}. The average mass of an air molecule is about 5×10^{-26} kg. What is the average kinetic energy of a molecule?

Ans.:

$$PV = (\tfrac{2}{3}N)(\overline{\tfrac{1}{2}mv^2})$$
$$P = 1.01 \times 10^5,\ V = 1\,\text{m}^3,\ N = 2.7 \times 10^{25}$$
$$\overline{\tfrac{1}{2}mv^2} = 1.5\,\text{PV/N} = 5.6 \times 10^{-21}\,\text{J}$$

Atomic and molecular energies are most often expressed in *electron volts* (eV) where 1 eV $= 1.6 \times 10^{-19}$ J. Here the energy is .035 eV.

We can find the corresponding speed: $\sqrt{\overline{v^2}} = \sqrt{\frac{2K}{m}} = \sqrt{\frac{(2)(5.6\times10^{-21})}{5\times10^{-26}}} = \sqrt{2.24 \times 10^5} = 473$ m/s.

This is the square root of the average of the square of the speed. It is called the *root mean square speed*, v_{rms}.

You might think that it would be simpler just to say “average.” But since all directions are equally represented, the average velocity is zero! (For two velocities of 10 m/s in opposite directions, the average velocity is zero, but v_{rms} is $\sqrt{\frac{1}{2}(100 + 100)} = 10$ m/s.)

The macroscopic point of view

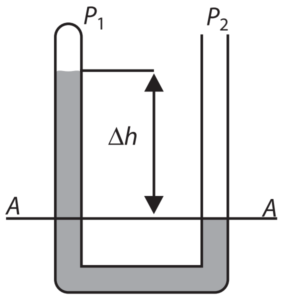
A number of pioneering scientists in the seventeenth and eighteenth centuries performed experiments on gases at different pressures and temperatures and with different volumes. Their results can be summarized by the relation that came to be known as *the ideal gas law*, $PV = nRT$. Here P is the pressure, V the volume, T the absolute temperature (measured in *kelvins*), and n is the amount of gas measured in *moles*. R is a proportionality constant, called the *universal gas constant*. In this section we review the work that led to the ideal gas law and examine the quantities P, T, and n.

Pressure

Water in a glass exerts a force on the bottom of the glass equal to the water’s weight, Mg. This is in addition to the weight of the air and the resulting *atmospheric pressure*. We can express the force of the water in terms of the height, h, and the density, ρ (Greek *rho*) of the water. The density is the mass per unit volume, and the volume is the height times the cross-sectional area. $\rho = \frac{M}{V}$ and $V = hA$, so that $Mg = \rho hAg$. The pressure on the bottom is $\frac{Mg}{A}$, which is equal to ρgh. The SI unit of pressure is N/m^2, which is also called the *pascal*, Pa, after Blaise Pascal (1623–1662), who, among other contributions, suggested correctly that atmospheric pressure should be smaller on top of a mountain. (1000 Pa = 1 kPa.)

The pressure, ρgh, is not only there at the bottom of a column of fluid. It is the pressure at the depth h regardless of the direction. If this were not so, a drop of water at that depth would not be in equilibrium, would experience a net force, and would accelerate.

EXAMPLE 3



The figure shows a U-tube partly filled with mercury. (Mercury, because it is a very dense liquid, with a density 13.6 times that of water.) The tube is open on the right side and closed on the left side. On the left side the mercury column is higher by $\Delta h = 10$ cm. What is the difference in pressure between the top of the mercury column on the left and the top of the mercury column on the right?

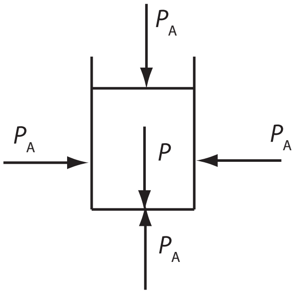
Ans.:

At the level marked *A* the pressures on the two sides are the same. Call the pressure above the mercury on the right side P_2 and on the left side P_1. P_2 is equal to P_1 plus the pressure of a column of mercury 10 cm high, $P_2 = P_1 + \rho g \Delta h$, where ρ is the density of mercury, 13.6×10^3 kg/m^3, and $\Delta h = 0.1$ m. The difference between P_2 and P_1 is $\rho g \Delta h = (13.6 \times 10^3)(9.8)(0.10) = 1.33 \times 10^4$ Pa.

EXAMPLE 4

What is the pressure on the bottom of a glass of water?

Ans.:

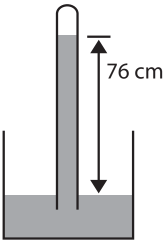


The pressure on the top of the water is the atmospheric pressure P_A. On the bottom there is the additional pressure $\rho g h$, where h is the height of the water. The total pressure on the bottom is $P = P_A + \rho g h$.

Atmospheric pressure also acts on the outside of the glass of water. It acts everywhere, including on the bottom of a glass sitting on a table. (There is some air between the glass and the table unless special efforts are made to exclude it.)

All of us live at the bottom of an ocean, not of liquid, but of air. The atmosphere is held to the earth by its weight. We are so used to the pressure that it exerts that we are normally not aware of it.

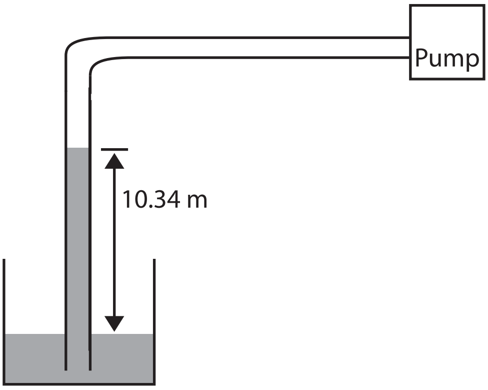
The first to understand the existence of atmospheric pressure and to measure it was Evangelista Torricelli (1608–1647). In 1643 he performed the following experiment. He took a glass tube closed at one end, with a length of about 1 m, and filled it with mercury. He put his finger over the open end, turned it upside down, and submerged the open end in a pool of mercury. Some of the mercury ran out of the tube into the pool, until the difference in height between the surface in the tube and the surface of the pool was about 0.76 m.



The pressure on the surface of the mercury pool (outside the U-tube) is just the atmospheric pressure. Inside the U-tube, above the mercury, there is no air and no atmospheric pressure. Inside the same tube, at the level of the mercury surface outside the tube, there is only the pressure of the mercury column.

In effect Torricelli produced a U-tube with the pressure of the column of mercury on one side and atmospheric pressure on the other. The two pressures are equal, so that what he showed is that the pressure of the air in the atmosphere is the same as that of a column of mercury whose height is 0.76 m.

It was known at that time that a suction pump can lift water only to a height of about 10.3 m. Torricelli's experiment showed why this is so. The situation is just as in his experiment, but with water instead of mercury. The pump removes the air (and its pressure) above the water. The atmospheric pressure forces water up.



With no pressure above the water, the pressure of the water column is equal to atmospheric pressure. Since the density of mercury is 13.6 times as great as that of water, the water column is 13.6 times as high as the mercury column. ($13.6 \times 0.76\,\text{m} = 10.34\,\text{m}$.)

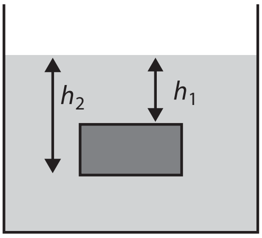
EXAMPLE 5

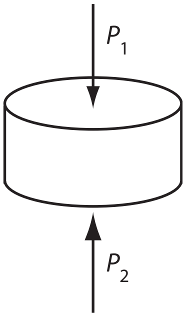
How large is atmospheric pressure in pascals when it is said to be "760 mm"? (The height of a column of mercury, here 760 mm, is often used as a measure of the pressure at its base.)

Ans.:
The density of mercury is $13.6 \times 10^3\,\text{kg/m}^3$. At the bottom of a column of mercury whose height is 760 mm or 0.76 m the pressure is $\rho g h = (13.6 \times 10^3)(9.8)(0.76) = 1.01 \times 10^5$ Pa or 101 kPa.

Atmospheric pressure at the surface of the earth varies, but is generally close to 101 kPa or 760 mm of mercury.

Archimedes' principle





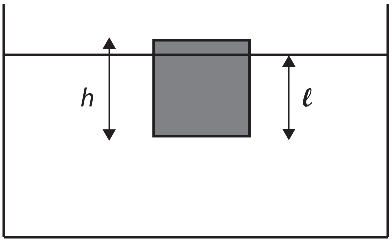
At the depth h_1 the pressure is atmospheric pressure (p_A) plus $\rho g h_1$. At the depth h_2 it is greater and equal to $p_A + \rho g h_2$. A disk with cross-sectional area A experiences the pressure P_1 downward at its top surface and the pressure P_2 upward at its bottom surface. There is a net pressure upward, $P_2 - P_1$, equal to $\rho g h_2 - \rho g h_1 = \rho g(h_2 - h_1)$ and hence a net upward force A times as large, equal to $\rho g(h_2 - h_1)A$. This force is called the *buoyant force*.

The volume of the disk is $(h_2 - h_1)A$. ρ is the density of the liquid, so that $\rho g(h_2 - h_1)A$ is the weight of the liquid that is displaced by the disk. That the magnitude of the buoyant force is equal to that of the weight of the displaced liquid is called *Archimedes' principle*.

EXAMPLE 6

A block of wood whose height is 10 cm, and whose density is $900\,\text{kg/m}^3$ floats in water. How much of the block is under water?

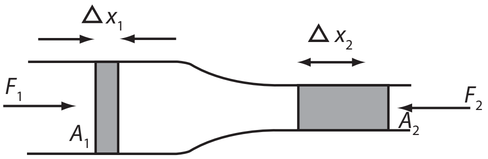
Ans.:
The block sinks until its weight is equal to the buoyant force. The net force on the block is then zero, and the block is in equilibrium. The block's weight is $Mg = \rho_{\text{wood}} A h g$, where $h = 10$ cm. Since $\rho_{\text{water}} = 1000\,\text{kg/m}^3$ it is also $.9 \rho_{\text{water}} A h g$.



If the wooden block is submerged to a distance ℓ, the buoyant force is $\rho_{\text{water}} A \ell g$. For it to be equal to the weight of the wooden block, $\ell = 0.9h$, and 9 cm of the block is submerged. The ratio $\frac{\ell}{h}$ is equal to the ratio of the densities $\frac{\rho_{\text{wood}}}{\rho_{\text{water}}}$.

Bernoulli's equation

So far we have considered only liquids at rest. We now look briefly at pressure in a flowing liquid.



The figure shows a liquid in a tube whose cross-sectional area changes from A_1 to A_2. Look at the part of the liquid that is shaded. It starts on the left, where the area is A_1. It is pushed to the right with a force $F_1 = P_1A_1$. Later the same volume is at the right where the area is A_2. The force in the opposite direction is $F_2 = P_2A_2$. As this amount of liquid moves to the right the distance through which it moves is different in the wide part and in the narrow part. It moves forward by Δx_1 in the wide part and by Δx_2 in the narrow part. The volumes $A_1\Delta x_1$ and $A_2\Delta x_2$ are the same.

The work done on this amount of liquid is $F_1\Delta x_1 - F_2\Delta x_2$, which is equal to $P_1A_1\Delta x_1 - P_2A_2\Delta x_2$. This amount of work is equal to the gain in kinetic energy, $\frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2$, where m is the mass of the liquid whose volume is $A_1\Delta x_1$ (or $A_2\Delta x_2$).

Since the density is equal to the mass divided by the volume, $\rho = \frac{m}{V}$, we can write $m = \rho V = \rho A_1\Delta x_1$ (or $\rho A_2\Delta x_2$), so that the change in kinetic energy is $(\frac{1}{2})(\rho A_2\Delta x_2)(v_2^2) - (\frac{1}{2})(\rho A_1\Delta x_1)(v_1^2)$. This is equal to $P_1A_1\Delta x_1 - P_2A_2\Delta x_2$.

The volume $A_1\Delta x_1$ (or $A_2\Delta x_2$) appears in each term and we can divide by it to get $P_1 - P_2 = \frac{1}{2}\rho v_2^2 - \frac{1}{2}\rho v_1^2$ or $P_1 + \rho v_1^2 = P_2 + \rho v_2^2$.

This relation, based on the law of conservation of energy, is called *Bernoulli's equation*, after Daniel Bernoulli (1700–1782). We see that in the wide part, where the speed of the flowing liquid is smaller, the pressure is larger. This is an important insight, with many applications.

There are, however, some major limitations. Bernoulli's equation assumes that the liquid flows smoothly, every part of it in the same direction. This is called *laminar flow*, in contrast to the much more common *turbulent flow*, where the motion is more complicated. The equation also ignores any loss of energy from frictional effects that result from the *viscosity* (the "stickiness") of the liquid.

With these limitations you may question the usefulness of the equation. But although its exact quantitative application is limited to special situations, *Bernoulli's principle*, namely the decrease in pressure where the liquid flows faster, is of great importance.

EXAMPLE 7

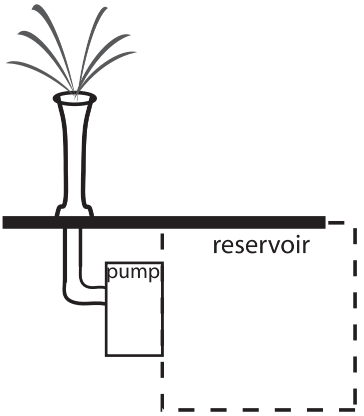
In a hurricane the wind blows horizontally across the 300 m^2 roof of a house with a speed of 30 m/s (67 mph). What is the resulting lifting force on the roof?

Ans.:
We are looking for the pressure difference that results from the change in speed of the air, from zero to 30 m/s. The density of air is 1.29 kg/m^3. $\Delta P = \frac{1}{2}\rho v^2 = (0.5)(1.29)(30^2) = 581$ Pa. $P = \frac{F}{A}$. $F = (581)(300) = 1.74 \times 10^5$ N, which is equivalent to the weight of 1.77×10^4 kg, or about 18 metric tons. (1 metric ton is 1000 kg.)

We came to Bernoulli's equation by using the fact that the work done on the liquid is equal to the increase in its kinetic energy, and then dividing each term by the volume. We can also include the potential energy. Since we are using the symbol P for pressure in this section, we will use $\mathcal{P}$ for potential energy.

We can use the system consisting of the fluid and the earth, with its kinetic and potential energies, and external work done on it: $K_1 + \mathcal{P}_1 + W = K_2 + \mathcal{P}_2$, where the subscripts 1 and 2 indicate two different positions in the fluid. As before, we divide each term by the volume, so that $\frac{1}{2}mv^2$ becomes $\frac{1}{2}\rho v^2$, and the work done on the liquid becomes $P_1 - P_2$. Similarly the difference in the potential energies, $Mgy_1 - Mgy_2$, becomes $\rho gy_1 - \rho gy_2$. The expanded Bernoulli equation is then $\frac{1}{2}\rho v_1^2 + \rho gy_1 + P_1 = \frac{1}{2}\rho v_2^2 + \rho gy_2 + P_2$.

EXAMPLE 8



A pump is 1.2 m below the surface of a reservoir. It provides the difference in pressure for a fountain 3 m above the surface of the reservoir, from which water shoots out with a speed of 2 m/s. What is the pressure difference that must be supplied by the pump?

Ans.:

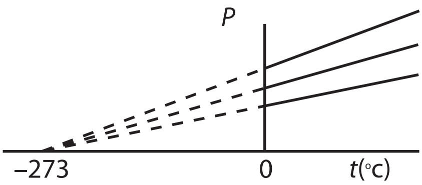
Assume that v_1, the velocity at the intake to the pump, is zero. Take the reference level to be at y_1, i.e., $y_1 = 0$. Bernoulli's equation then reduces to $P_1 - P_2 = \frac{1}{2}\rho v_2^2 + \rho g y_2$.

The density of water is 10^3 kg/m^3, so that $P_1 - P_2 = (\frac{1}{2})(10^3)(2^2) + (10^3)(9.8)(4.2) = 43.2 \times 10^3$ Pa.

Absolute temperature

After Torricelli's work a number of other discoveries were made in the seventeenth and eighteenth centuries in the study of gases. One is that the product of the pressure and the volume of a given amount of gas is constant if the temperature remains constant. This relation is usually called Boyle's law, after Robert Boyle (1627–1691). It is an empirical law. Like the other relations between pressure, volume, and temperature that we discuss next, it is approximate and subject to various limitations.

Another discovery was that at a given pressure the volume and the temperature are linearly related, in other words, the graph of volume against temperature is then a straight line. The graph of pressure against temperature is also a straight line. A particularly significant feature of this relation can be seen in the figure.



The straight lines of pressure against temperature are different for different volumes, but when they are extrapolated to lower pressures they converge at the point where the pressure is zero. At this point the temperature is −273°C. Since no lower pressure is possible, this is also the lowest possible temperature. It is called the *absolute zero* of temperature. Temperatures measured from absolute zero are called *absolute temperatures*, and the symbol T is used for them. (t is used for other temperature scales, such as the Celsius scale. On this scale 0°C is the temperature of melting ice and 100°C is the temperature of boiling water.) T (in K) $= t$ (in °C) $+ 273$.

The scale that starts at the absolute zero of temperature, and whose units are the same as for the Celsius scale, is called the Kelvin scale (after William Thomson, Lord Kelvin, 1824–1907). Its unit is called the *kelvin* (K). If T is the temperature on the Kelvin scale and t is the temperature on the Celsius scale, $T = t + 273$. On the Kelvin scale volume and temperature are proportional.

The two relations for pressure, volume, and temperature can be combined to say that $\frac{PV}{T}$ is constant for a given amount of gas. If we compare the pressure, volume, and absolute temperature at two different times, i.e., in two different *states* of a certain amount of gas, we can write $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$. Another way to write the same relation is that the product PV is proportional to T ($PV \propto T$), i.e., it is equal to a proportionality constant times T.

EXAMPLE 9

By what fraction does the pressure in a tire increase when the temperature goes from 20°C to 30°C?

Ans.:

Assume that the volume remains constant. The absolute temperature goes from $273 + 20$K or 293K to $273 + 30$K or 303K. The ratio is $\frac{303}{293} = 1.034$. The tire pressure increases by .034 of 3.4%.

So far we have considered a definite quantity or mass of gas. We can now incorporate the mass in our relation. If P and T are held constant, what can we say about V? For a given amount of gas it is constant, but what if the amount changes? Then the volume is proportional to the mass.

Experiments show that if the mass is measured in *moles* the relation between P, V, T and the mass is *universal*, i.e., independent of the kind of gas.

What Is a *Mole*?

In Chapter 1, we talked briefly about *atomic weight*. In the meantime we have also talked about mass, and you will not be surprised that we prefer talking about *atomic mass* rather than atomic weight. After all, your weight depends on where you are and is different at the top of a mountain from what it is at the bottom. And it is quite different on the moon. The mass remains the same, no matter where you are.

At first only relative masses were known, and one unit was assigned to hydrogen, which led to about four for helium, about 12 for carbon, and so on. Eventually it was realized that these numbers corresponded approximately to the number of particles in the nuclei of the various atoms.

To get exact numbers a standard was adopted, namely exactly 12 units (now called "atomic mass units," with the symbol *u*) for the most abundant kind of carbon, which is called "carbon 12" (^{12}C). It is the kind, or isotope, with six protons and six neutrons in its nucleus. It was then possible to assign atomic masses (in atomic mass units) to each element on the basis of measurements.

The quantity 12 grams of carbon 12 is called a mole of ^{12}C. (12 kg is a kilogram-mole.) The number of atoms in a mole is called *Avogadro's number*, given by the symbol N_A. A mole of hydrogen atoms consists of N_A atoms. A mole of hydrogen molecules consists of N_A molecules. Experiments show that N_A is 6.023×10^{23} molecules/mole or 6.023×10^{26} molecules/kg-mole.

If we measure the mass of gas by the number of moles, *n*, we can write the relation between *P*, *V*, *T* and the mass as $PV = nRT$, where *R* is the proportionality constant. Its value is determined from experiments and is about 8.31 J/mol K, but remember that the number depends on the units that are used.

The relation $PV = nRT$ summarizes the results of many experiments. This single statement describes how the macroscopic quantities P, V, T, and n are related, regardless of which kind of gas is being measured. It is therefore sometimes called the *universal gas law*. More often it is called the *ideal gas law* to emphasize that real gases follow it only approximately, as an "ideal" to be approached under special circumstances.

$PV = nRT$ is an empirical law, i.e., it is based on experiment. It represents a model. Real gases follow it more closely as the density decreases i.e., when the molecules are far apart and so have little interaction with each other.

EXAMPLE 10

What is the volume of 1 mole of gas at atmospheric pressure and 0°C?

Ans.:
$V = \frac{nRT}{P} = \frac{(1)(8.31)(273)}{1.01\times10^5} = 0.0225\,\text{m}^3$ or 22.5 liters.

We have to be careful with the units. We have not been sticking to SI units, since we have defined the mole as the number of molecules in 12 g of ^{12}C. *R* is then 8.31 J/mol K. If we were to use SI units consistently we would have to use the kg-mole, which is 10^3 as large. *R* is then also 10^3 as large, and equal to 8.31×10^3 J/kg-mol K. The volume of 1 kg-mole at the same pressure and temperature is $\frac{(1)(8.31\times10^3)(273)}{1.01\times10^5} = 22.5\,\text{m}^3$.

The surprising bridge to temperature

The number of molecules in one mole is Avogadro's number, N_A. The number of molecules in *n* moles, *N*, is therefore nN_A, so that $PV = \frac{N}{N_A}RT$. The constant $\frac{R}{N_A}$ is called Boltzmann's constant, *k*, so that $PV = NkT$. ($k = \frac{8.31}{6.023\times10^{23}} = 1.38 \times 10^{-23} \frac{\text{J}}{\text{molecule}-\text{K}}$.)

We now have two relations for the same quantity, *PV*, on the left-hand side. One is for the microscopic model of molecules flying freely except when they bounce into each other or off the walls. It is $PV = \left(\frac{2}{3}N\right)\left(\overline{\frac{1}{2}mv^2}\right)$. The other is for the approximate observed macroscopic behavior $PV = nRT$ or $PV = NkT$.

If both are to describe the same situation, the right-hand sides of the two relations must be the same, i.e., $\left(\frac{2}{3}N\right)\left(\overline{\frac{1}{2}mv^2}\right) = NkT$ or

$$\overline{\frac{1}{2}mv^2} = \frac{3}{2}kT.$$

This is one of those very special relations that provide a link between two different realms. We have here two different ways of looking at the same set of phenomena using two quite different languages. On the left-hand side is the average kinetic energy of a molecule. It provides a look at the microscopic constituents. On the right-hand side is the *temperature*. It is a macroscopic quantity, which characterizes the whole container of gas.

We see that the quantity that we observe on the macroscopic level as temperature is a manifestation of the motion, on the microscopic level, of the molecules: *the average kinetic energy of a* *molecule in a gas is proportional to the absolute temperature.* Moreover, this is so regardless of what kind of molecules we are talking about.

We first defined the ideal gas as a theoretical microscopic model with small, rigid molecules that have only kinetic energy. Then we used the relation $PV = nRT$ to describe the approximate experimental behavior of real gases. It is the confluence of the two approaches, the assumption that both describe the same system, that leads to the result $\overline{\frac{1}{2}mv^2} = \frac{3}{2}kT$.

This relation is only for the ideal gas of particles whose internal structure plays no role. But the conclusion that temperature is a manifestation of energy on the microscopic scale turns out to be universally valid, and is one of the great insights of science.

EXAMPLE 11

What are the average energy and the root-mean-square speed, v_{rms}, of oxygen molecules at a room temperature of 300 K(=27°C)?

Ans.:

It is important to stay with SI units for all of the calculations. Only if you use a consistent system of units (such as the SI system) do you know that the answer will also come out in the same system of units. (Remember that "constants" may have units also.) You may occasionally want to use other units, such as grams, moles, or electron volts, but the units on the two sides of an equation need to be the same. If there is any doubt it is best to include units in every term.

The energy is $\frac{3}{2}kT = (1.5)(1.38 \times 10^{-23})(300) = 6.21 \times 10^{-21}$ J.

We can express the energy in electron volts (eV), where 1 eV $= 1.6 \times 10^{-19}$ J. We can convert the energy from joules to electron volts by multiplying by $\frac{1\,\text{eV}}{1.6\times10^{-19}\,\text{J}}$ to get 0.039 eV.

The energy is kinetic energy, $\frac{1}{2}mv^2$, so that $\overline{v^2} = \frac{2E_K}{m}$.

One mole of oxygen molecules has 6.023×10^{23} molecules and a mass of 32 g. The mass of one molecule is therefore $\frac{32}{6.023\times10^{23}}\,\text{g} = 5.31 \times 10^{-23}\,\text{g} = 5.31 \times 10^{-26}$ kg.

$V_{\text{rms}} \quad \sqrt{\overline{v^2}} = \sqrt{\frac{(2)(6.21\times10^{-21})}{5.31\times10^{-26}}} = \sqrt{2.34 \times 10^5} =$ 484 m/s. Note that this is quite a high speed, larger than the speed of sound.

Internal energy and heat capacity

The only energy of a molecule of an ideal gas is its kinetic energy. For an amount of gas consisting of N molecules the energy is $(N)\left(\overline{\frac{1}{2}mv^2}\right)$, which we now see to be equal to $\frac{3}{2}nRT$. This is the *internal energy* of the gas, which we have previously called U.

Can we observe and measure the internal energy? We can measure how much energy it takes to *change* it, as, for example, by heating. The amount of added energy for each unit of temperature change is called the *heat capacity*, C. The heat capacity per unit mass is called the *specific heat capacity, c*.

We can see what the heat capacity is for our model. If we increase the internal energy U to $U+\Delta U$, the temperature will increase to $T+\Delta T$, and $U+\Delta U=\frac{3}{2}nR(T+\Delta T)$. We can subtract U from the left side and the equal quantity $\frac{3}{2}nRT$ from the right side, to leave $\Delta U = \frac{3}{2}nR\Delta T$. We see that the heat capacity, i.e., the amount of energy to change ΔT by one kelvin, is $\frac{3}{2}nR$.

For the ideal gas model the heat capacity is $\frac{3}{2}nR$. We can say that the model *predicts* a heat capacity of $\frac{3}{2}nR$. This is a remarkable result. It says that the specific heat capacity per mole of an ideal gas (its *molar heat capacity*) is $\frac{3}{2}R\left(= 12.5\frac{\text{J}}{\text{mol K}}\right)$, no matter what the gas is. Here are the experimentally observed molar heat capacities per mole for some gases. (These are the "noble" gases. Because of their complete electron shells they interact with each other only extremely weakly, and do not form molecules.)

Gas	*C* (J/mol K)
He	12.5
Ne	12.5
Ar	12.5
Kr	12.3

We see that the measured quantities are close to each other and to $\frac{3}{2}R$ for each of the gases. This is a major triumph for the model.

You notice that the list of gases does not include the common ones, oxygen, nitrogen, and hydrogen. The reason is that for these gases each molecule consists of two atoms. Each of these molecules has both kinetic and potential energy, and our model, which treats each as a particle, is inadequate.

EXAMPLE 12

6 J of energy is transferred by heating 1 g of neon (atomic mass 22.5 g/mol). What is the rise in temperature?

Ans.:

$$Q = \Delta U$$
$$\Delta U = \tfrac{3}{2}nR\Delta T$$
$$Q = C\Delta T, \text{ where } C = \tfrac{3}{2}nR$$
$$n = \tfrac{1}{22.5}$$
$$C = \tfrac{3}{2}\tfrac{1}{22.5}(8.31) = 0.554\,\text{J/K}$$
$$\Delta T = \tfrac{Q}{C} = \tfrac{6}{0.554} = 10.8\,\text{K}$$

EXAMPLE 13

0.1 kg of water at 80°C is mixed with 0.2 kg of water at 20°C. What is the final temperature?

Ans.:
Call the final temperature t. (Here there is no need to use absolute temperature, T. We use °C and the symbol t.) The 0.1 kg of water changes from 80°C to t, and gives up an amount of energy of $mc\Delta t = (0.1)(c)(80 - t)$. This amount of energy goes to the 0.2 kg of water, which gains $0.2(c)(t - 20)$. Since the two amounts of energy are the same, $(0.1)(c)(80 - t) = (0.2)(c)(t - 20)$, which leads to $t = 40$°C.

Heating

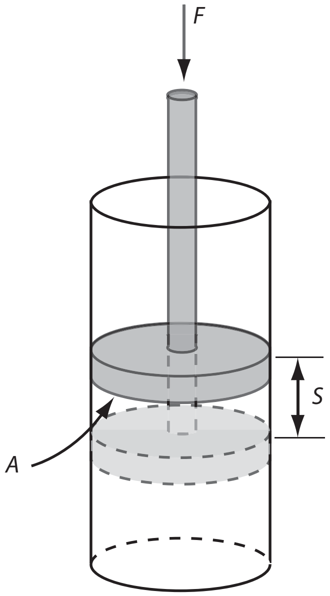
Let's look more closely at what happens when we increase the internal energy by heating. We'll talk about ideal gases, but the process is similar in all materials. We start with a container of gas at some temperature T and internal energy $\tfrac{3}{2}nRT$. We take a second container of gas, at a higher temperature, and bring the two gases into contact.

From the macroscopic point of view energy "flows" from the hotter to the cooler gas. The microscopic point of view helps us to understand how this happens. The molecules of the hotter gas move, on average, with greater speeds. When they collide with the molecules of the cooler gas they transfer some of their kinetic energy to them. The internal energy of the hotter gas decreases and it becomes cooler, and the internal energy of the cooler gas increases and it becomes hotter, until their temperatures are the same. There is then no further net transfer of energy, and the two gases are in *thermal equilibrium*.

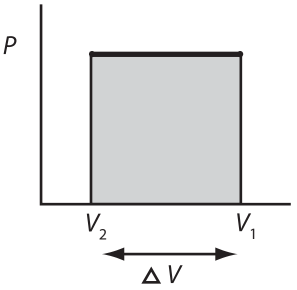
Note that we use the words *heat* and *heating* only for the *transfer* of energy. (The gas does not *have* heat energy.) The transfer of energy changes the *internal* energy, which in an ideal gas is the kinetic energy of the molecules.

Work

A second way in which the internal energy can be changed is by doing work. (We will again talk about an ideal gas, but the considerations are similar for other materials.) We know that work is done on an object when a force acts on it and it moves. We can do work on a gas by compressing it with a piston that moves in a cylinder. If the force, F, is applied with a piston, and the piston moves a distance s, the work done on the gas is Fs. We can write this as $(\tfrac{F}{A})(sA)$, where A is the cross-sectional area of the cylinder. $\tfrac{F}{A}$ is the pressure (P) applied to the gas and sA is the change in the volume (ΔV) of the gas in the cylinder. The work done on the gas can therefore be written as $P\Delta V$.



We can describe the process on a graph of P against V (a *PV diagram*.) In the figure the pressure is constant and the volume changes from V_1 to V_2. The magnitude of the work done on the gas is equal to that of the rectangle $P\Delta V$ under the curve. If the pressure is not constant, the work is still equal to the area under the curve.



EXAMPLE 14

An ideal gas is compressed to $\frac{1}{3}$ of its initial volume by a piston in a cylinder.

(a) What is the change in the pressure if the temperature does not change?

(b) What is the change in the temperature if the pressure does not change?

(c) What is the change in the temperature if at the same time the pressure increases by a factor of 4?

Ans.:

(a) $PV = nRT$. If T does not change, PV remains constant, and $P_1V_1 = P_2V_2$, or $\frac{V_2}{V_1} = \frac{P_1}{P_2}$. Since $\frac{V_2}{V_1} = \frac{1}{3}$, $\frac{P_1}{P_2} = \frac{1}{3}$ and $P_2 = 3P_1$. The pressure increases by a factor of 3.

(b) Since P, n, and R are constant, $V \propto T$, and both the volume and the absolute temperature change by the same factor.

(c) $PV = nRT$. Since n and R are constant, $\frac{PV}{T}$ is constant, and $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$. $\frac{V_2}{V_1} = \frac{1}{3}$, $\frac{P_2}{P_1} = 4$, so that $\frac{T_2}{T_1} = (\frac{P_2}{P_1})(\frac{V_2}{V_1}) = \frac{4}{3}$.

The first law of thermodynamics

Both heating and doing work on a gas are processes that increase the internal energy of the gas. The initial internal energy of the gas (U_1), plus the energy transferred to it by heating it (Q) and doing work on it (W), is equal to its final internal energy (U_2). In this form and context the law of conservation of energy is called *the first law of thermodynamics*: $U_1 + Q + W = U_2$.

EXAMPLE 15

The pressure on a container with 18 moles of an ideal gas increases from 1 atmosphere to 2.5 atmospheres while the volume decreases from $0.4\,\text{m}^3$ to $0.2\,\text{m}^3$ along a straight line on a PV diagram.

(a) Draw a PV diagram.

(b) How much work is done on the gas?

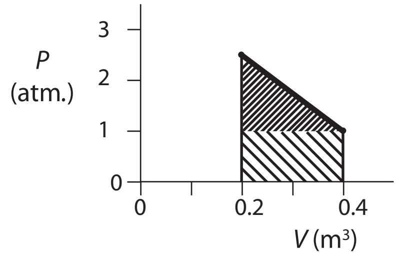
(c) What are the initial and final temperatures?

(d) What are the initial and final internal energies?

(e) How much heat is transferred to the gas during this process?

Ans.:

(a)



(b) Area under the line on the diagram: $(1)(.2) + (\frac{1}{2})(.2)(1.5) = .35$. This is in (atmospheres)(m^3) and has to be changed to SI units. 1 atmosphere $= 10^5$ Pa. The area in joules is therefore $.35 \times 10^5$ J. This is the work done on the gas.

(c) $T_1 = \frac{P_1V_1}{nR} = \frac{(10^5)(0.4)}{(18)(8.31)} = 267\,\text{K}$ or $-6°\text{C}$.
$T_2 = \frac{(2.5\times10^5)(0.2)}{(18)(8.31)} = 334\,\text{K}$ or $61°\text{C}$.

(d) $U_1 = nRT_1 = 4 \times 10^4$ J.
$U_2 = nRT_2 = 5 \times 10^4$ J.

(e) $U_1 + W + Q = U_2$.
$Q = 5 \times 10^4 - 4 \times 10^4 - 3.5 \times 10^4 = -2.5 \times 10^4 = -2.5 \times 10^4$ J.
2.5×10^4 J is transferred out of the gas.

Go to the PhET website (http://phet.colorado.edu) and open the simulation *Gas Properties*.

Explore the relationship between volume, pressure, and temperature, and the effect of work done or heat applied to a system.

7.2 Other systems: adding pieces from reality

The ideal-gas model assumes that the constituents have no internal structure and no forces between them except on contact. In this section we explore some other systems and the models that help us to understand their properties and behavior.

In contrast to what we have done so far, we will need to consider forces,within the molecules as well as those between them. These forces are electric forces, following Coulomb's law.

The gravitational forces are still there, but they are smaller by a huge factor, so that we can neglect them. The nuclear forces act only over distances much smaller than the size of atoms and play their role almost completely within the nuclei. On the other hand, in each atom the electrons are held to the nuclei by electric forces. The forces between atoms in molecules and solids, and those between molecules, are also entirely electric.

EXAMPLE 16

In a hydrogen atom the average distance between the proton and the electron is 0.53×10^{-10} m. The mass of the proton is 1.67×10^{-27} kg and the mass of the electron is 0.91×10^{-30} kg. The charge on each is $\pm 1.6 \times 10^{-19}$ C.

(a) What is the magnitude of the gravitational interaction between the two particles?

(b) What is the magnitude of the electric interaction between them?

(c) What is the ratio of the electric force to the gravitational force that they exert on each other?

Ans.:

(a) $F_g = G\frac{M_1 M_2}{r^2} = 1.67\times10^{-11}\frac{(1.67\times10^{-27})(0.91\times10^{-30})}{(0.53\times10^{-10})^2}$ $= 9.04 \times 10^{-48}$ N.

(b) $F_e = K\frac{Q_1 Q_2}{r^2} = 9 \times 10^9 \frac{(1.6\times10^{-19})^2}{(0.53\times10^{-10})^2} =$ 8.5×10^{-8} N.

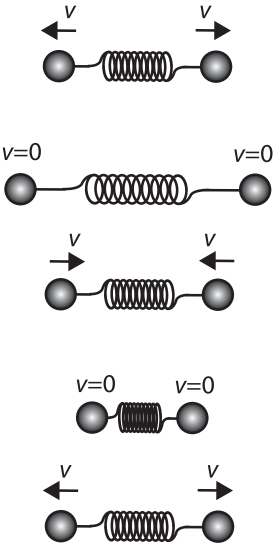
(c) $\frac{F_e}{F_g} = 0.9 \times 10^{40}$.

We will, for the time being, not consider what happens inside the nuclei. They have internal structure and internal energy, but their energy levels are separated by energies of the order of 10^5 times as large as those of atoms. The amount of energy that is required to change their energy is so large that we are justified in continuing to consider each nucleus to be a structureless particle.

Molecules

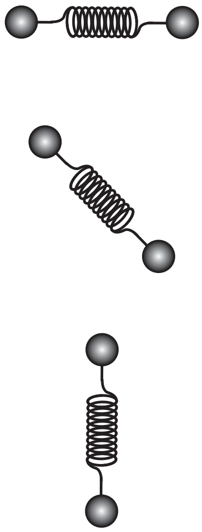
In molecules the interatomic electrical forces hold two or more atoms, the same kind or different, to each other. The molecules have internal motions of vibration and rotation, and as a result have additional kinetic and potential energies.

Diatomic molecules, such as those of hydrogen, nitrogen, and oxygen, consist of two atoms. They can be very successfully described by a model in which the force between the two atoms is represented by a spring. In this model the two atoms vibrate along the line that joins them.



Let's look at the vibrating motion in more detail. We'll assume that the spring follows Hooke's law, $F = -kx$. The vibrational motion of an object connected to a spring that follows Hooke's law is called *simple harmonic motion*. As each atom goes back and forth, its energy changes from kinetic to potential and back. At the two ends of the motion the atoms are stopped and all of the energy is stored in the spring as potential energy. In between, in the middle, no energy is stored in the spring and all of the energy is kinetic. On average, as the atoms vibrates, it turns out that there is just as much kinetic energy as potential energy. The diagram shows the model of a diatomic molecule in five different positions of its vibration.

Vibration is not the only possible motion. The molecules can also rotate about an axis perpendicular to the line that joins them. The diagram shows the model in three different positions as it rotates about an axis at right angles to the paper. In addition, it can rotate about a second axis that is also perpendicular to the line that joins the atoms, but lies in the plane of the paper. In this rotation one of the atoms starts by coming out of the paper, while the other one moves into the paper. (There is a third axis, joining the two atoms, but rotation around it contributes so little to the internal energy that we can neglect it.)



Just as for monatomic gases, we can find out about the internal energy of the gas by measuring the heat capacity. If we heat a monatomic gas, all the energy that we transfer to it becomes kinetic energy of the motion of the individual atoms. For the diatomic gas some of it becomes energy internal to the molecules, namely energy of vibration and energy of rotation. Because any added energy is divided between these various kinds of motion and their kinetic and potential energies, it now takes more energy to raise the temperature, and so the heat capacity is larger.

If we know how the energy is divided we can calculate the heat capacity. It turns out that at sufficiently high temperatures each part of the internal energy takes up an equal amount of energy. The vibrational energy has two such parts, the elastic potential energy of the spring and the kinetic energy, back and forth, of the vibrating motion. The rotational energy has to be counted as two parts, because the molecule can rotate about two different axes at right angles to each other, both of them perpendicular to the line joining the two atoms. (There is no potential energy associated with the rotational motion.) For the translational energy of the molecule as a whole we also have to count more than one part, because there are three different perpendicular directions, x, y, and z.

What we have called "parts of the energy" are called *degrees of freedom*. The rule that the energy is divided equally among them is called the *principle of equipartition of energy*. It holds as long as each kind of motion, i.e., each of the degrees of freedom, is equally accessible.

The energies are not all equally accessible when the energy is *quantized*, i.e., when only certain values of the energy are allowed. The energies between the allowed energy levels are then "forbidden" and are not accessible. At high temperatures the allowed energies are very close to each other, so that the forbidden energies do not play a determining role. The principle of equipartition therefore holds most closely at high temperatures. It fails at temperatures that are so low that the spacing between the allowed energies is of a size comparable to the *thermal energy*, ie., to about kT.

EXAMPLE 17

What is the internal energy of a mole of an ideal diatomic gas under the assumption that the principle of equipartition holds?

Ans.:
The internal energy of a diatomic molecule is $\frac{1}{2}kT$ for each degree of freedom (if the temperature is sufficiently high that the quantization of energy has no measurable effect). For one mole the internal energy is N_A times as large, or $\frac{1}{2}RT$. At room temperature (about 300 K), $\frac{1}{2}RT = (.5)(8.31)(300) = 1.25 \times 10^3$ J/mol for each degree of freedom.

There are three degrees of freedom for the translational (linear) motion, two degrees of freedom for the vibrational motion, and two more degrees of freedom for the rotational motion, for a total of seven. The internal energy is 8.73×10^3 J/mol.

Phase changes

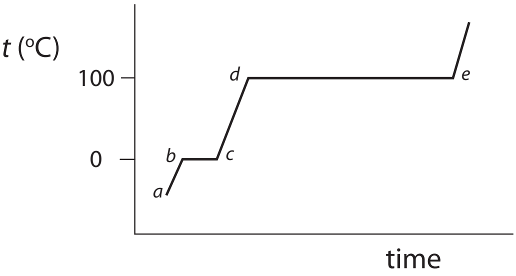
In a gas the molecules fly around freely. If the temperature goes down, the molecules slow down. In the ideal gas, where $PV = nRT$, the molecules can slow down until they don't move at all when the absolute temperature reaches zero. A real gas behaves differently. At some temperature it *condenses* and becomes a liquid. At some still lower temperature it freezes and becomes a solid.

When water freezes to become ice, boils to become steam, or evaporates to become water vapor, its molecules don't change. Ice, water, and steam are different *phases* of the same material.

The phases have different properties. Most obviously, their densities are very different. In the gas phase the molecules are far apart. In the liquid phase they are close to each other, but are still able to move. In the solid phase each atom or molecule has a fixed place about which it can vibrate.

We know that a phase change takes place at a fixed temperature. Water freezes and ice melts at 0°C. Water boils and steam condenses at 100°C. At each phase change the internal energy changes by a definite amount. When ice changes to water its internal energy increases by 80×10^3 cal/kg, or 333.5 kJ/kg, and this amount of energy, called the *heat of fusion*, needs to be supplied to it. When it boils, water requires the *heat of vaporization* of 540×10^3 cal/kg or 2.257×10^3 kJ/kg.

When a solid is heated, its temperature rises until it begins to melt. Further heat causes more and more of it to melt while the temperature remains the same. When all of it has melted the temperature rises again, until it reaches the boiling point. The phase change from liquid to gas then continues until all of the material has changed to the gas phase.



Here is a schematic graph to show the progression of the phases of water when it is heated at a steady rate, starting with ice. From *a* to *b* it is in the solid phase (ice), and warms until the melting point is reached at 0°C. The temperature then remains constant until all of the ice has melted at point *c*. The liquid water now warms to the boiling point, 100°C, point *d*. The temperature again remains constant, this time at 100°C, until all of the water has turned to steam at point *e*. With continued heating the temperature of the steam then continues to rise.

EXAMPLE 18

How much energy needs to be transferred to 0.2 kg of ice at −10°C to raise its temperature so that it is water at +10°C?

Ans.:
We will need to know the specific heat capacity of water, which is $c_{\mathrm{w}} = 10^3 \, \frac{\mathrm{cal}}{\mathrm{kg\ K}}$ or 4.18×10^3 J/kg K, and the specific heat capacity of ice, which is $c_{\mathrm{i}} = 2.09 \times 10^3$ J/kg K. If the heat of fusion h_{iw} is equal to 333.5×10^3 J/kg then the required energy is $10mc_{\mathrm{i}} + mh_{\mathrm{iw}} + 10mc_{\mathrm{w}} = (0.2)(10)(2.09 \times 10^3) + (0.2)(333.5 \times 10^3) + (0.2)(10)(4180) = 4.18 \times 10^3 + 66.7 \times 10^3 + 8.36 \times 10^3 = 75.1 \times 10^3$ J.

What happens from the microscopic point of view? What does our gas model of flying molecules suggest? As the temperature goes down and the molecules slow down, they spend more time near each other. The forces between them then have a greater chance to affect their motion. Eventually the disruptive effect of the ceaseless motion decreases sufficiently for the forces to bring about the *phase transition* from gas to liquid.

In the liquid phase the atoms or molecules continue to move, but their motion is much more confined. At the freezing (or melting) temperature there is again a phase transition as they become locked into place. The motion continues, but it is now a vibration around a fixed position.

In each of the phases or *states* of a material, the atoms or molecules are in motion, but not all with the same energy. There is a range or *distribution* of energies. In the liquid state, for example, some of the molecules move so rapidly that they are able to escape. This is the process of *evaporation*.

We can look at the progression from gas to solid as a path to greater order. The gas has the least amount of order as the molecules race around. In the solid the order is greatest as each atom assumes its position.

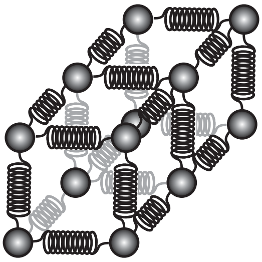
Both liquids and solids are called *condensed matter*. We will look at models for solids in the next section. In liquids the atoms or molecules are neither completely free to move nor locked into place. That makes them more difficult to describe, and there is no simple model. That's why we will not consider the microscopic aspects of liquids.

Condensed matter

Some solids consist of molecules held in place by the forces between them. This is so, for example, when large organic molecules form solids. In other solids the individual atoms are more likely to be the building blocks. When we talked about gases we called their constituents molecules. For solids it is usually more appropriate to think of the atoms.

In solids the interatomic forces are so strong that the atoms remain close to each other. The atoms vibrate about some equilibrium position, and so have both kinetic and potential energy. This vibration, the continuous shaking of the solid, is called its *thermal motion*. The sum of the kinetic and potential energies is the internal energy.

A model that we can call the *ideal solid* accounts for some of the thermal properties of solid materials. In this model the atoms are again without internal structure. They are connected to their neighbors by springs that represent the chemical bonds. The springs follow Hooke's law, $F = -kx$. The atoms vibrate about their equilibrium position. The internal energy is the energy of vibration, which is partly the kinetic energy of the motion and partly the elastic potential energy stored in the springs. Both of these energies increase when energy is transferred to the solid.



In this model the vibrational motion of each atom is *simple harmonic motion*, just as for the diatomic molecules that we discussed earlier. Again, as each atom vibrates, its energy changes from kinetic to potential and back. Again, on average, there is just as much kinetic energy as potential energy. This time, however, the vibration can be in any of the three directions, x, y, and z. We have to count the different parts of the energy, the different *degrees of freedom*, separately for each of these three directions. There is kinetic energy and potential energy along each axis, so that there are six degrees of freedom.

We can compare the average internal energy of an atom in the ideal solid to that of an atom in a monatomic ideal gas. The internal energy of the ideal gas is only kinetic. In the ideal solid, with the addition of an equal amount of potential energy, it is twice as large. In the model therefore, for a given number of atoms, the heat capacity is twice as large as for the ideal gas, namely $3R$ for one mole of material.

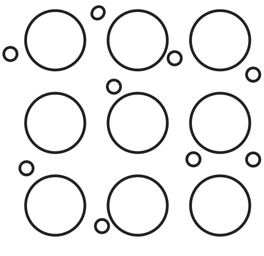
That this is in fact the case for a number of solids at and above room temperature was discovered experimentally by Pierre Dulong and Alexis Petit in 1819 and is known as the law of Dulong and Petit.

The model can be extended: as the vibration increases, eventually the springs no longer follow Hooke's law. They "break," and the atoms are cast adrift. The solid *melts*.

Metals

The model of atoms connected by springs cannot account for the phenomena that characterize metals, the most important of which is that they are good conductors of electricity. What characterizes metals is that some of the electrons in the atoms are separated from the nuclei to which the others are bound.

The simplest model that includes this possibility is the *free electron model*. In it one or more of the electrons from each atom becomes detached and "free." The free electrons can move throughout the material, leaving behind the remaining parts of the atoms, which are now positively charged ions. (In the figure the electrons are shown as the small circles.)



This model neglects the forces between the free electrons. They fly freely through the solid, and their only energy is kinetic energy, just as for the molecules of an ideal gas.

It would seem to be straightforward to see what the internal energy and hence the heat capacity are for this model. We expect the internal energy to be larger by the amount of the kinetic energy of the electrons. Since they are free to move, they act just like the molecules of an ideal gas. For a metal in which one electron from each atom is free, the model therefore leads to an additional energy of $\frac{3}{2}nRT$ and an additional heat capacity of $\frac{3}{2}R$ per mole.

This, however, is not observed! Experiments show that the heat capacity of metals is close to that of nonmetals. This was well known by the early part of the twentieth century. That a metal has free electrons was also well known. It was therefore a mystery that the free electrons did not seem to participate in the internal energy.

This is an example of a model that did not predict what was observed. The model seemed reasonable in terms of the knowledge at that time. Nevertheless its conclusions did not correspond to the observed facts. The discrepancy made it clear that in some fundamental way the nature of metals was not understood. Eventually it was learned that in metals electrons were indeed detached from the atoms, but that their behavior could not be described by classical mechanics.

There were other indications that the structure of atoms and the interactions between them were not understood. The turning point came in 1925 when quantum mechanics was first developed, and led to today's understanding of atomic phenomena. We discuss some of the principles of quantum mechanics later.

Chemical energy

The forces between atoms are stronger, and the atoms are held more tightly, in some molecules, and in some solids, than in others. Chemical transformations can take place, with atoms of one kind changing places with those of another. The positions and the momenta of the atoms, and of the electrons within them, change, as well as their potential and kinetic energies.

On the macroscopic scale we call the energy that is then released or absorbed *chemical* energy. On the microscopic scale it represents the changes in the kinetic and in the electric potential energies of the electrons and atoms.

Quantum theory

Except for our brief mention of the detachment of electrons in metals, we have not considered changes within atoms in this chapter. Such changes generally require more energy than changes that are external to the atoms.

Each system, whether it is a solid, a molecule, an atom, or a nucleus, can exist only with certain definite amounts of energy. They are said to be in particular *energy states*. The lowest state is called the *ground state*. The others are called *excited states*. It therefore takes a definite minimum amount of energy to change the state of a system. This energy gets larger as we go down in size to the atom and to the nucleus. It takes a minimum of 10.2 eV to change the energy of a hydrogen atom from its ground state to the first excited state. It takes 2.3 MeV to change a nucleus of nitrogen (^{14}N) from its ground state. In each of these cases a smaller amount of energy cannot be accepted by the system.

Our consideration of the ideal gas showed that the average kinetic energy per molecule is $\frac{3}{2}kT$. Let's see how much that is. Boltzmann's constant, k, is equal to 1.38×10^{-23} J/molecule-deg. At room temperature, with T about 300 K, $\frac{3}{2}kT$ is about 0.04 eV. This is the average kinetic energy per molecule in a gas. The amount of energy that can be exchanged between molecules when they collide is therefore also about 0.04 eV. It takes about 250 times as much energy to raise the energy of a hydrogen atom from that of its lowest state. (For other atoms the amount of energy is different, but it is of the same order of magnitude.) We see that in most collisions between hydrogen atoms the amount of energy that can be transferred is not enough to change the internal energy of the atoms.

This is a fact of great importance. After all, it was the starting point of our discussion of the ideal gas that its constituents behave as particles without internal structure or internal energy. If the kinetic energy (of about $\frac{3}{2}kT$) were large enough to change the internal energy of an atom, the assumption of a rigid atom, one that is unchanged by collisions, would not have been appropriate or fruitful.

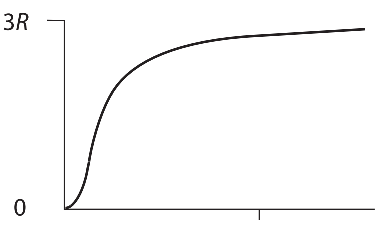
Suppose for a moment that there were no such minimum energy. Even a small amount of energy given to an atom, either in collisions or in any other way, could then become internal kinetic and potential energy of the atom. The assumption that we made in the ideal gas model that the atoms have no internal energy, and are like rigid marbles without internal structure, could not be made. The real gas would behave quite differently, and the ideal gas model that we have discussed here would not represent its properties.

The definite, finite energy required to change the energy of an atom, as well as that of a molecule or solid, plays a crucial role in the stability of these structures. If they were able to accept any amount, no matter how small, they would have properties quite different from those of a model that treats the atoms or molecules as particles.

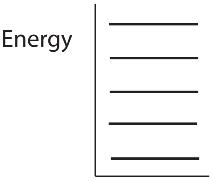
If this had been understood when the ideal gas model was developed, the *quantization* of energy and the *quantum theory* might have been discovered much earlier than they were, by a much more circuitous route, by Planck in 1900.

Back to heat capacities

The heat capacities of all solids decrease as the temperature is lowered. The molar heat capacities are then no longer $3R$, as expected from the law of Dulong and Petit. The graph shows the specific heat capacity of silver as a function of temperature.



Again the model's predictions do not correspond to what is observed. It was Einstein, in 1907, who first realized why the old model was inadequate: it did not take into account the quantization of energy, i.e., the fact that individual atoms, as well as solid materials, can exist only with definite energies separated from each other.



The figure shows an *energy level diagram.* Each horizontal line represents one of the allowed energies. For a particle in simple harmonic motion (i.e., vibrating as if attached to a spring following Hooke's law) the energy levels are equally spaced.

Just as in the ideal gas, the internal energy is higher at higher temperatures. At temperatures near room temperature and higher, the spacing between the possible energies is small compared to the internal energy and the fact that the energy is quantized does not play a significant role. As the temperature decreases, on the other hand, the internal energy becomes smaller, and the spacing between the energy levels plays a more important role.

We saw earlier that when there is potential energy in addition to kinetic energy, the heat capacity is larger. In general, the heat capacity is larger when there are more kinds of energy and more ways for the energy to be distributed. This time we have the opposite situation. Because the energy is quantized there are gaps between the allowed energies. There are fewer possible values of the energy and the heat capacity is smaller.

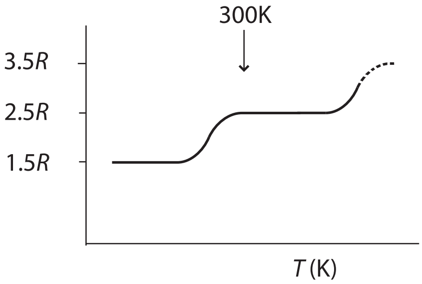
This is a good example of how the limits of one model led to the invention of a different model. In this case it led to important new knowledge, and the confirmation of the quantization of energy, which had been discovered a short time earlier.

Diatomic gases

The heat capacity of the monatomic gases is $\frac{3}{2}nR$, i.e., $\frac{1}{2}nR$ for each of the three degrees of freedom, represented by mv_x^2, mv_y^2, and mv_z^2. For the diatomic gases there are two more degrees of freedom for the vibrational motion's additional kinetic and potential energies, and another two for the rotations about the two axes. With contributions of $\frac{1}{2}nR$ for each, you expect heat capacities of $\frac{7}{2}nR$.

Gas	C (J/mol K)
H_2	20.4
N_2	20.8
O_2	21.1
CO	21.0

The table shows heat capacities per mole for some of the diatomic gases at room temperature, and they are seen to be only about $\frac{5}{2}R(=20.8\,\text{J/mol K})$. Where did the other two degrees of freedom go?



Here is a schematic graph of the molar heat capacity of hydrogen as a function of temperature. We see that at sufficiently high temperatures the heat capacity really does go up toward $\frac{7}{2}R$. To see what happens to the heat capacity at lower temperatures we have to look at the spacing of the energy levels of the hydrogen molecule. It turns out that for the rotational motion the spacing is much smaller than for the vibration. So much so that room temperature is "high" for the rotational motion and "low" for the vibrational motion. At room temperature the molecules don't vibrate, but they do rotate, leading to the $\frac{5}{2}R$ molar heat capacity. At much lower temperatures the spacing between the rotational energy levels also becomes significant (compared to kT), and the molar heat capacity decreases to $\frac{3}{2}R$.

The spacing between the vibrational levels is 0.53 eV, so that the energy available, on average, at room temperature, equal to kT, or about 0.025 eV, is insufficient to raise the energy of the molecules from that of the ground state. In other words, the molecules can vibrate only at much higher temperature. On the other hand, the energy difference between the ground state and the first excited rotational state is about 7×10^{-3} eV. Since this is much smaller than kT at room temperature, there is enough energy at room temperature to populate many of the rotational energy levels. The energy of the molecules then includes the rotational energy. This can be seen in the heat capacity, which is $\frac{5}{2}R$, representing both the translational and the rotational degrees of freedom.

7.3 Summary

Whenever we talk about materials, whether they are gases, liquids, or solids, we have to remember that we are dealing with enormous numbers of particles—the atoms and molecules of which the material is made. It is remarkable how much we can say about these complex systems by using simple models. We look in detail at one of the most successful models, the *ideal gas*. What we observe with our senses are the large-scale or *macroscopic* objects. Each is made of small particles (atoms, molecules) on the *microscopic* scale. The microscopic features are those of the particles and their motion. The discussion of the ideal gas shows how the microscopic features are related to the properties that we observe on the macroscopic scale, such as pressure, volume, and temperature.

On the microscopic level we think in terms of the number of molecules, N. On the macroscopic level we think in terms of the number of moles, n. The two are linked by *Avogadro's number*, N_A, the number of molecules in a mole: $N=nN_A$.

A real gas consists of particles that move freely. They have both kinetic energy and mutual potential energy as they move toward and away from each other. Together, the sum of these two kinds of energy for all of the molecules is the internal energy (often called *thermal* energy) of the gas. Each atom and molecule also has internal energy, but since these energies do not change so easily they can often be ignored when we talk about the properties of gases.

For the model that we call the ideal gas we make several assumptions. It consists of particles that have no internal energy or internal structure and no size. There are no forces between them except when they collide, so that there is no mutual potential energy. The only energy of an ideal gas is the kinetic energy of its particles. The sum of the kinetic energies of the particles is the internal energy of the gas.

From our knowledge of mechanics we showed that $PV = \frac{1}{3}N\overline{mv^2}$ or $PV = \frac{2}{3}N\overline{\frac{1}{2}mv^2}$. Here P is the pressure ($P = \frac{F}{A}$), N is the number of particles, and $\overline{\frac{1}{2}mv^2}$ is the average energy per particle.

Empirically, i.e., from observation and experiment, a relation followed approximately by many gases is $PV = nRT$. Here n is the number of moles and T is the absolute temperature, i.e., the temperature measured from absolute zero, the lowest possible temperature, equal to zero kelvins (0 K) and to −273°C. R is the *universal gas constant*. By comparing the relation from the application of mechanics to the motion of the particles to the empirical macroscopic relation we see that $\overline{\frac{1}{2}mv^2} = \frac{3}{2}kT$, where k (Boltzmann's constant) is equal to $\frac{R}{N_A}$. The relation shows that the average energy per particle is proportional to the absolute temperature. The relation is for the *ideal gas*, but the conclusion that the particles of a gas have greater average energy at higher temperature is always true.

That shows what temperature is: when energy is transferred to an object (as by heating), it becomes energy of its constituents, i.e., internal energy. We detect and perceive the higher internal energy as higher temperature. A change in the internal energy can also accompany a change of structure, i.e., a *phase change* such as that from solid to liquid or from liquid to gas.

The pressure at the bottom of a column of liquid of height h is ρgh, where ρ is the density of the liquid. Normal atmospheric pressure is about the same as the pressure at the bottom of a column of mercury whose height is 76 cm.

In a flowing liquid, energy considerations lead to *Bernoulli's equation*, $\frac{1}{2}\rho v_1^2 + \rho g y_1 + P_1 = \frac{1}{2}\rho v_2^2 + \rho g y_2 + P_2$.

The work done on a gas when its volume changes is $P\Delta V$.

7.4 Review activities and problems

Guided review

1. A cubical box, 1 cm to the side, holds 1000 molecules, each with a mass of 10^{-25} kg. The molecules move back and forth in the x direction with speeds of 1000 m/s.

(a) What is the magnitude of the momentum of each molecule?

(b) What is the change of momentum when a molecule hits a wall?

(c) What is the time between collisions of a molecule with one wall?

(d) What is the average force on one of the walls perpendicular to the x direction?

(e) What is the pressure?

2. A cubical box, 1 cm to the side, holds 10^{19} molecules of an ideal gas, each with a mass of 10^{-25} kg. The pressure is 8×10^4 N/m^2.

(a) What is the average kinetic energy per molecule?

(b) What is v_{rms}?

3. A U-tube contains oil whose density is 0.92 times that of water. The height of the column of oil on one side is 15 cm greater than that on the other side. What is the difference in the pressures above the oil on the two sides?

4. What is the total pressure at the bottom of a lake at a depth of 30 m?

5. (a) A hole in the ground is filled with water to a depth of 30 m. A pump is put next to the top of the hole to pump out the water through a tube to the bottom of the hole. What happens when the pump is turned on?

(b) What would be a better arrangement to pump out the water?

6. An iceberg whose density is 900 kg/m^3 floats in a lake, 90% submerged. When the iceberg melts, will the level of the lake rise, fall, or remain the same?

7. To separate two pieces of paper whose area is 10 cm by 10 cm, you blow across them with an air speed of 2 m/s. What is the resulting force on each?

8. A pump that produces a pressure difference of 70 kPa is 0.8 m below ground level. A faucet

connected to it is on the second floor, 5 m above ground level. What is the speed of the water coming out of the faucet?

9. As a balloon rises, its volume goes from $10\,\text{m}^3$ to $12\,\text{m}^3$. The temperature goes from 20°C to −20°C. The initial pressure in the balloon is 1.1 atmospheres. What is the final pressure in atmospheres?

10. (a) How many moles of air are in the balloon of the previous question?

(b) What is the mass of air in the balloon? (The average molecular mass is about 29 g/mol.)

11. The main constituents of air are oxygen and nitrogen. What is the ratio of v_{rms} for oxygen to that of nitrogen?

12. How much energy does it take to heat 1 mole of a monatomic ideal gas through 18°C?

13. 1 kg of water ($C = 4.18\,\frac{\text{J}}{\text{g K}}$) at 50°C is mixed with 0.2 kg of ethanol ($C = 2.46\,\frac{\text{J}}{\text{g K}}$) at 0°C. What is the final temperature?

14. The pressure on five liters of an ideal gas in a container with a movable wall is raised by 50%. The temperature goes from 20°C to 80°C. What is the final volume?

15. Two moles of an ideal gas go through a process during which 10^4 J of work is done on it without any change in temperature. Is there a heat transfer, and if there is, what are its magnitude and direction?

16. The distance between the two protons in a hydrogen molecule is 1.5×10^{-10} m. What is the net force between them?

17. At room temperature hydrogen molecules rotate freely, but do not vibrate. (The difference between the vibrational energy levels is much larger than kT.) What is the internal energy of one mole of hydrogen at 0°C?

18. An ice block whose mass is 2 kg is at 0°C. It is put into a container with 10 kg of water at 50°C. What is the final temperature?

Problems and reasoning skill building

1. In the relation $v_{\text{rms}} \propto m^x$, where m is the molecular mass, what is x?

2. About how many molecules are in $1\,\text{mm}^3$ of air?

3. The internal energy of an ideal gas is $\frac{3}{2}nRT$. Why does the internal nuclear energy not get counted?

4. A scuba diver has 2.5 liters ($= 2.5 \times 10^{-3}\text{m}^3$) of air in his lungs when he is 10 m below the surface. He holds his breath as he rises. What will the volume (in liters) be when he reaches the surface?

5. A balloon is filled with air at 20°C and has a volume of $4 \times 10^{-3}\,\text{m}^3$ at atmospheric pressure. It is then submerged and tied to a coral reef, where the pressure is 250 kPa and the balloon's volume is $1.58 \times 10^{-3}\,\text{m}^3$.

(a) What is the temperature (in °C) at the reef?

(b) What are the internal energies of the gas at the surface and at the reef?

(c) Is work being done? By what? Can you tell how much?

(d) Is heat being transferred? By what and to what? How can you tell?

6. 0.3 moles of an ideal gas at atmospheric pressure is enclosed in a container whose volume, V, is fixed. It is first submerged in ice water. Later it is submerged in boiling water.

(a) Describe the changes in the macroscopic quantities, T and P, in words. Calculate the final values of T and P.

(b) Describe the changes in the microscopic quantity v_{rms} in words. Calculate v_{rms} at both temperatures.

(c) Draw a graph of P against T for this process.

(d) Calculate the change in the internal energy.

(e) Is there a heat transfer? In what direction? How large is it?

7. A copper coin whose mass is 5 g is dropped 400 m from a building. Air resistance causes it to slow down so that it has a velocity of 45 m/s just before it hits the ground. What is the change in the temperature of the coin as it falls? ($C =$ 0.39 kJ/kg.) Assume that all of the dissipated energy goes to the coin.

8. What is the amount of energy that must be removed from 2 kg of water at 20°C to change it to ice at −10°C? (The specific heat capacity

is 4.18 $\frac{\text{kJ}}{\text{kg K}}$ for water and 2.09 $\frac{\text{kJ}}{\text{kg K}}$ for ice. The heat of fusion is 334 kJ/kg and the heat of vaporization is 2.26×10^3 kJ/kg.)

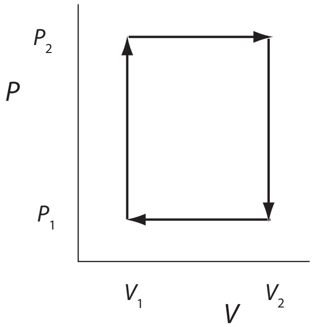
Multiple choice questions

1. 4 mol of an ideal gas is compressed at a constant pressure of 110 kPa from 0.25 m^3 to 0.12 m^3.

The increase in internal energy is about
- (a) 21 kJ
- (b) 36 kJ
- (c) −21 kJ
- (d) −14 kJ

2. An ideal gas is in a container whose volume is V at a pressure P. The rms speed of the molecules is v_{rms}. When V increases by a factor of 4, and P decreases by a factor of 2, v_{rms} is multiplied by a factor of
- (a) $\frac{1}{2}$
- (b) 4
- (c) 2
- (d) $\sqrt{2}$
- (e) $\frac{1}{4}$

3.

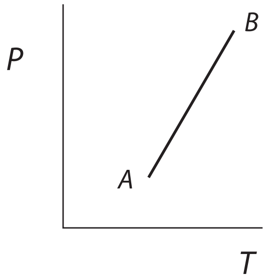


An ideal gas is initially at P_1 and V_1. It changes along the path shown in the PV diagram. In one cycle (from the starting point all around and back to the same point on the diagram) the net work done by the gas is
- (a) $V_2(P_2 - P_1)$
- (b) $P_2V_2 - P_1V_1$
- (c) $(P_2 - P_1)(V_2 - V_1)$
- (d) $P_2(V_2 - V_1)$
- (e) P_1V_1

4. 7.4×10^{-3} m^3 of neon is at a pressure of 470 kPa and a temperature of 87°C. (The atomic mass of neon is 20.2 g/mol.) The mass of the gas (in kg) is about
- (a) 0.014
- (b) 0.023
- (c) 0.096
- (d) 0.059
- (e) 0.0014

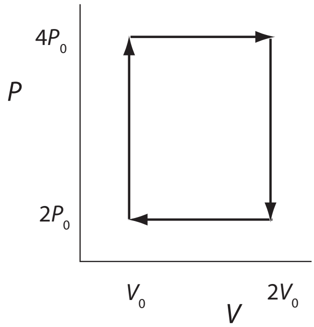
The pressure of one mole of an ideal gas is reduced from 100 kPa to 50 kPa without changing the volume of 2×10^{-2} m^3. How much heat, in kJ, is released by the gas during this process?
- (a) 2.5
- (b) 1.0
- (c) 3.0
- (d) 6.0
- (e) 1.5

5. The graph shows P plotted against T for a process that takes one mole of an ideal gas from point A to point B. Which of the following is correct?



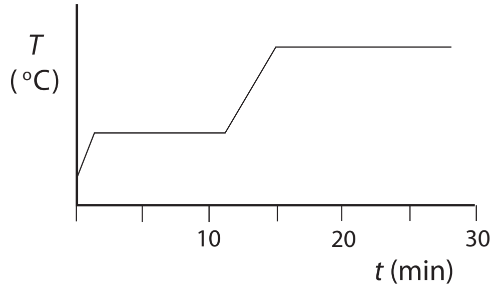
- (a) The volume increases.
- (b) The volume decreases.
- (c) The volume remains the same.
- (d) Any one of the above is possible.
- (e) none of the above is possible.

6. The diagram describes a cyclic process for an ideal gas. How much work (in J) is done in one cycle if $P_0 = 8.1 \times 10^5$ Pa and $V_0 = 7.0 \times 10^{-3}$ m^3?



(a) 11,300
(b) 4320
(c) 21,200
(d) 22,600
(e) 43,200

7. A compound has a solid phase, a liquid phase, and a gas phase. A sample of this material is heated at a constant rate. The graph shows the temperature as a function of time. Which of the following conclusions can be drawn from this graph?



(a) The sample never boiled.

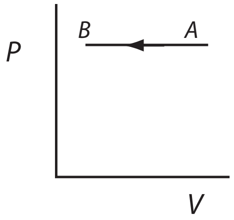
(b) The heat of fusion is greater than the heat of vaporization.

(c) After 5 min the sample is partly solid and partly liquid.

(d) The heat capacity of the solid phase is greater than that of the liquid.

(e) After 20 min the sample is totally liquid.

8. The figure shows a process from point *A* to point *B* for an ideal gas. Select the correct answers from the following:



(a) Work is done on the gas (*W* is positive).
Work is done by the gas (*W* is negative).
(b) The internal energy increases.
The internal energy decreases.
(c) Heat is transferred to the gas.
Heat is transferred from the gas.

9. When *P* and *V* of a certain amount of gas are both raised by 50%, v_{rms} is multiplied by a factor of
(a) 0.5
(b) 1.5
(c) 2.25
(d) 3
(e) 5