CHAPTER 11

Heat and Matter

11.1 INTRODUCTION

- Why is it that you can smell if a gas tap has been left on when you walk into a laboratory but you cannot smell the water spilt on the front bench?
- Have you ever wondered why you can smell perfume or aftershave lotion?
- Why are many of our anti-pollution laws, especially in very industrialised cities and nations such as some cities in America and Japan, concerned with gases?
- Can hot water freeze more rapidly than cold water?

The answer to each of these questions has something to do with the internal structure of gases, liquids and solids. In this chapter we will look at the theory underlying this structure and hence begin to understand the nature of gases.

11.2 THE KINETIC MODEL OF GASES

In the previous chapter we learnt that gases consist of particles that are relatively free in their ability to move compared with those of liquids and solids. These particles also exert almost no force on each other. Because of this the analysis of gas particles is easier. The understanding of the nature of these particles plays an important part in the understanding of heat, heating, and temperature.

To simplify the understanding of how the motion of the particles of a gas affects the properties of a gas, several assumptions are made about these particles.

Assumption 1 The particles of a gas are in constant random motion. They move at high speeds in straight lines unless they collide with the walls of the container or other particles. These collisions are elastic ('elastic' means they do not lose kinetic energy when they collide).

This helps us to explain why gases mix so readily and why gases fill containers.

Assumption 2 The particles of a gas are separated by large distances compared with the diameter of the particles, which are assumed to be negligible in size.

This explains why gases can be compressed and gas densities, in normal situations, are very small compared with those of solids and liquids.

Assumption 3 The force of attraction between particles is negligible, because they are large distances apart.

Assumption 4 Since heating a substance changes the motion of the particles of the substance, the temperature of a gas is a measure of the average speed or kinetic energy of the particles of the gas.

NOVEL CHALLENGE

Imagine a 1 cm square on your skin. Every second there are 10^{22} blows from air molecules. *Can you detect it? If you can't, give some reasons why you can't feel these blows. If the blows stopped, what would you feel?*

11.3 PRESSURE

The pressure of gases plays a major part in everyday life: the pressure of gases in the atmosphere affects the weather; the pressure of air in tyres affects the 'ride' of a car. But what is pressure and how do the particles of a gas exert a pressure?

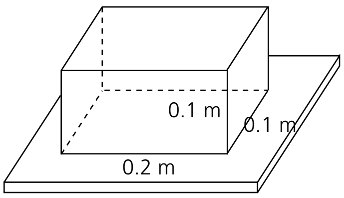
Pressure is the force per unit area ($P = F/A$)

Hence the unit of pressure is a newton per square metre (N m^{-2}) or the modern SI unit of the pascal (Pa), named in honour of the French scientist Blaise Pascal (1623–1666).

The interchanging of the terms 'force' and 'pressure' is common with new physics students but there are major differences that can be illustrated with the following example.

A rectangular solid of 2 kg mass is placed on a table as shown in Figure 11.1. The force this object exerts on the table is 20 N. (This is its weight.) But the pressure it exerts is determined by its area of contact:

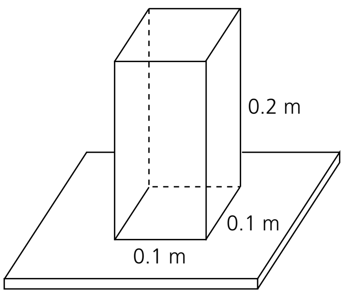
Figure 11.1
Pressure exerted by an object with the 0.2 m × 0.1 m face on the table.



$$P = \frac{20\ \text{N}}{0.2\ \text{m} \times 0.1\ \text{m}}$$
$$= \frac{20\ \text{N}}{0.02\ \text{m}^2}$$
$$= 1000\ \text{Pa}$$

But if the object is now placed on its end as shown in Figure 11.2, the force it exerts on the table will remain at 20 N, but the pressure is now:

Figure 11.2
Pressure exerted by an object with the 0.1 m × 0.1 m face on the table.



$$P = \frac{F}{A}$$
$$= \frac{20\ \text{N}}{0.1\ \text{m} \times 0.1\ \text{m}}$$
$$= \frac{20\ \text{N}}{0.01\ \text{m}^2}$$
$$= 2000\ \text{Pa}$$

It can be seen that if the area of contact is small the pressure is very large. Why do women wearing stiletto heels leave impressions on wooden or cork floors? (And it is not because they are heavy.)

- Where else is this effect seen?
- How does this affect our discussion of gases?

When each gas particle collides with the wall of the container it exerts a force on a small area of the wall. This collision produces pressure. Since gases contain many particles it is the constant collisions with the walls of the container that result in the pressure of the gas in the container. This can be seen when you blow up a balloon. When you start, it contains few particles, which make few collisions with the walls, resulting in low pressure. When the balloon contains more particles there are more collisions, exerting greater pressure on the walls, forcing the balloon to expand.

NOVEL CHALLENGE

A matchstick is placed in a test-tube of water. When you place your thumb over the top and press down, the match sinks. Propose a reason for this and test to see if we're lying!

THE GAS LAWS 11.4

The properties of a gas are easy to explain because the particles act independently without exerting any significant forces on each other. This is true except in the extremes, when the temperature is very low or when the pressure is high. In these circumstances the particles are maintained in close proximity to each other. The properties of gases that play a part in understanding the behaviour of gases are volume, pressure, temperature and the number of particles in the sample.

The relationships between these variables have been investigated for centuries and affect how we handle gases today.

Boyle's law

One of the earliest scientists to investigate the relationships between the above variables was the British chemist and physicist **Robert Boyle** (1637–91). By experimenting with gases he established that the volume of a gas decreased as the pressure of the gas increased. If the temperature of a confined gas sample was kept constant and the pressure on the gas increased by placing more mass on a piston, as shown in Figure 11.3, the volume of the gas changed, as shown in Figure 11.4. This suggested that pressure was inversely proportional to volume.

When the pressure was plotted against the inverse of volume, Boyle obtained a straight line, as shown in Figure 11.5. This indicated that pressure is directly proportional to the inverse of volume ($P \propto 1/V$),

or $$PV = \text{constant}$$

This relationship is known as **Boyle's law**, which states: For a fixed mass of gas at constant temperature the pressure of the gas varies inversely as the volume. This means for a particular sample of gas at constant temperature an increase in pressure from P_1 to P_2 causes a corresponding decrease in volume from V_1 to V_2.

$$P_1V_1 = \text{a constant} = P_2V_2$$

or $$P_1V_1 = P_2V_2$$

This is normally how Boyle's law is expressed when solving problems.

Example

A scuba diver releases a 1.0 cm^3 bubble of gas at a depth where the pressure is 4 atmospheres. What will be the volume of that gas at the surface where the pressure is 1 atmosphere (assuming the temperatures are the same)?

Solution

$$P_1V_1 = P_2V_2$$
$$4\text{ atm} \times 1\text{ cm}^3 = 1\text{ atm} \times V_2$$
$$V_2 = 4\text{ cm}^3$$

Note: the units of pressure and volume are not that important as long as they are consistent. That is, P_1 and P_2 have to have the same units and V_1 and V_2 as well. Some common units of pressure are pascals (Pa), mm of mercury (mmHg) and atmospheres (atm).

Figure 11.3
A device used to show the relationship between pressure and volume.

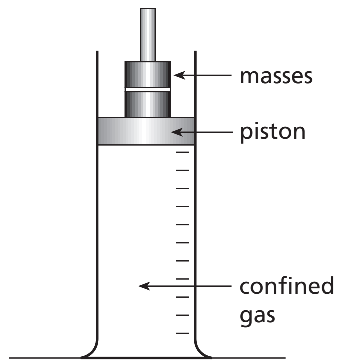


Figure 11.4
Pressure–volume relationship of a confined gas.

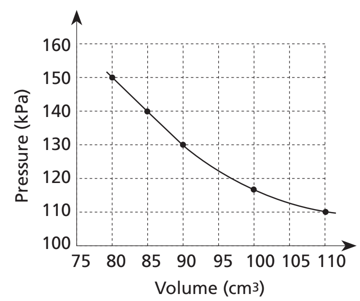
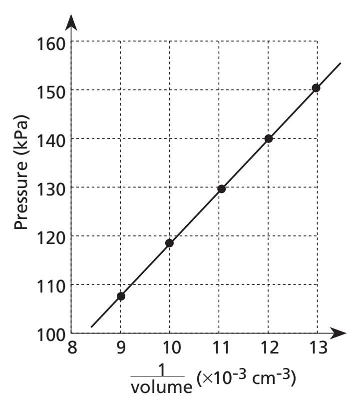


Figure 11.5
Pressure vs 1/volume graph to establish Boyle's law.



Questions

1. A balloon of volume 2.0 L contains air at 230 kPa. What would be the pressure of the gas when its volume is reduced to 0.50 L?
2. A hot-air balloon has a volume of 10 m^3 at sea-level. The balloon then rises to a height in the atmosphere where the pressure is 0.20 atmospheres. What would be the resulting volume of the balloon? (Assume constant temperature.)
3. A diver dives to a depth of 40 m in fresh water where he releases a toy balloon of volume 10 cm^3. What will be the size of the balloon when it reaches the surface? (The pressure increases at a rate of 1 atmosphere for every 10 m descent in fresh water.)
4. A student testing Boyle's law places masses on the top of a syringe as shown in Figure 11.6. With 500 g on the top of the syringe the volume is 50 mL. What mass will need to be placed on the piston for the volume to be 12.5 mL?

Figure 11.6
For question 4.

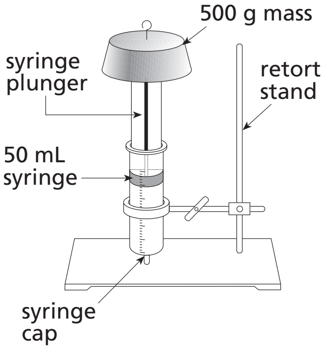
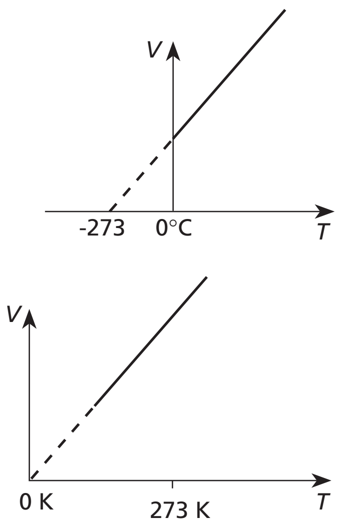


Figure 11.7
Volume–temperature relationship for a confined gas: notice that there is a direct relationship between the volume of the gas and its Kelvin temperature.



Charles' law

A French scientist, **Jacques Charles** (1746–1823), investigated the relationship between the volume of a confined gas and the temperature of a gas. For example, imagine heating a gas contained in a syringe in which the plunger is free to move and under atmospheric pressure. As the gas is heated the particles move more rapidly, making more frequent and forceful collisions with the walls and the plunger. The plunger will move outwards to a position that re-establishes the equilibrium between the pressure produced by the gas particles and atmospheric pressure. The pressure and number of particles remain constant but the volume of the gas increases with increasing temperature. This is shown graphically in Figure 11.7.

Notice that there is a direct relationship between volume of the gas and kelvin temperature.
That is:

$$V \propto T \text{ (kelvin)}$$

or $$\frac{V}{T} = \text{constant}$$

or $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Therefore, for a confined gas where the pressure remains constant the volume of the gas is directly proportional to its kelvin temperature. This is **Charles' law**.

This can very easily be seen by placing an inflated balloon in liquid nitrogen. The volume will shrink considerably. A good result can be seen by placing the balloon in a freezer.

When Charles did this experiment he could not cool a gas below −20°C so he had to extrapolate the graph to meet the temperature axis. This occurred at −273°C. This has startling implications. It would suggest that the volume of a gas at −273°C is zero. Charles' law is true for real gases except at low temperatures, and since no substance can exist as a gas below 2 K, it is theoretical and not practical outside this range.

Amontons' law

Guillaume Amontons (1663–1705) was a French physicist who in 1699 discovered that equal changes in temperature of a fixed volume of air produced equivalent variations in pressure ($P \propto T$). This law is sometimes referred to as Gay-Lussac's law. Before chemical fireworks were invented, the Chinese used to throw bamboo onto fires for amusement. The heat would increase the pressure of the gas, causing the pressure of the trapped gas to increase and making the chambers explode. That's why we don't throw pressure-pack spray cans onto a fire.

Questions

5 A balloon containing 40 cm^3 of air at 25°C is placed in the freezer where the temperature is −10°C. What will be its volume in the freezer?

6 At what temperature will a 500 cm^3 balloon of gas at 300 K have a volume of 300 cm^3, if the pressure remains constant?

7 Twenty litres of oxygen at 30°C is cooled under constant pressure to −140°C. What will be the new volume of the gas?

8 A 100 cm^3 balloon is filled with hydrogen at 20°C. If the balloon is then released to rise in the atmosphere to a height where the temperature is −50°C, what will be the volume of the balloon? (Assume constant pressure.)

NOVEL CHALLENGE

Put a lit candle in a jar with no lid and place on a record turntable. Before starting the turntable predict whether the flame will point inwards or outwards. What if there is no jar?

The combined gas equation

Boyle's law, Charles's law and Amontons' law can be combined to obtain an equation that relates the pressure, volume and temperature of a fixed amount of gas.

Since:

- $V \propto 1/P$ (Boyle's law)
- $V \propto T$ (Charles's law)
- $P \propto T$ (Amontons' law)

then $$V \propto \frac{T}{P}$$

then $$\frac{PV}{T} = \text{constant}$$

That is, for a fixed mass of a particular gas:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This is called the **combined gas equation**. Notice that for this equation to hold, temperature has to be measured in kelvins. Pressure and volume can be in any units as long as they are consistent across the equation.

Example

A 0.20 L sample of gas at room temperature (20°C) and atmospheric pressure is heated to 200°C and allowed to expand to 0.30 L. What will be the new pressure of the gas?

Solution

- 20°C = (20 + 273) = 293 K.
- 200°C = (200 + 273) = 473 K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$1\text{ atm} \times 0.2\text{ L} / 293\text{ K} = P_2 \times 0.3\text{ L} / 473\text{ K}$$

$$(1 \times 0.2) / 293 \times 473 / 0.3 = P_2$$

$$P_2 = 1.08\text{ atm}$$

Questions

9 A tank of volume 0.025 m^3 containing a mixture of nitrogen and helium gas is used to inflate party balloons. The pressure in the tank is 2.0×10^7 Pa and at a temperature of 293 K. How many balloons of size 0.0010 m^3, at a temperature of 300 K and at atmospheric pressure, can be filled from the tank?

10 A tank containing 200 L of hydrogen gas at 20°C is kept under a pressure of 200 kPa. The temperature is raised to 90°C and the volume decreased to 150 L. What is the pressure of the gas in the container?

11 Oxygen gas is released from a cylinder at the rate of 10 m^3 per hour at atmospheric pressure. If it is sold at a pressure of 200 atm and has a volume of 2.0 m^3, for how long will it supply oxygen?

NOVEL CHALLENGE

Landmines are deadly explosives buried underground. They are about 10 cm by 10 cm in area and most require 500 kPa to detonate. What mass of person would it take to do that?

The ideal gas equation

The four variables previously discussed that affect the nature of a gas were:
- volume
- temperature
- pressure
- the number of particles in the gas.

So far in each of the previous laws we have considered the number of particles in the gas to be constant. Suppose we measure the temperature, pressure and volume of a gas and then keep the temperature and volume constant but introduce twice the number of particles into the container. What will happen to the pressure? Because the pressure of a gas is due to the collisions of the particles on the walls of the container, the pressure will be twice the original. There are twice as many particles so there are twice as many collisions. Pressure is therefore proportional to the number of particles in the container.

$$P \propto N$$

Since $P \propto 1/V$, and $P \propto T$, it then follows that:

$$P \propto TN/V$$

or

$$PV = kNT$$

where k is a gas constant called **Boltzmann's constant**, named after the Austrian physicist **Ludwig Boltzman** (1844–1906). The units of k are derived from the other variables in the equation.
- From the above, $k = PV/NT$.
- Therefore k has the units of Pa m^3 molecule^{-1} K^{-1} (or J K^{-1} molecule^{-1}).
- The value of k is 1.38×10^{-23} Pa m^3 molecule^{-1} K^{-1}.

SR Activity 11.1 EQUIVALENT UNITS

Show that the unit Pa m^3 molecule^{-1} K^{-1} is equivalent to J K^{-1} molecule^{-1}.

Because the number of particles in a gas is extremely large we use a **mole** as the unit for the amount or the number of particles. One mole is equal to 6.02×10^{23} particles. This number is called **Avogadro's number** (N_A), after the Italian scientist **Amedo Avogadro** (1776–1856). The enormously large value of Avogadro's number suggests how tiny and how numerous atoms must be. A mole of air can fit into a suitcase. Yet, if these molecules were spread uniformly over the Earth there would be 120 000 of them in every square centimetre. A second example to indicate the size of a mole is that one mole of tennis balls would fill a volume equal to three Moons.

In the previous equation if we change the number of particles to moles we also have to change the proportionality constant, producing the **ideal gas equation**:

$$PV = nRT$$

where R is the universal gas constant, and n is the number of moles of gas.

The value of R is 8.31 Pa m^3 mol^{-1} K^{-1} or 8.31 J K^{-1} molecule^{-1}.

Activity 11.2 CONVERSION OF UNITS

To convert the number of particles (N) to moles (n) we divide by Avogadro's number (N_A – 6.02×10^{23}). If we multiply k (1.38×10^{-23} Pa m^3 particle^{-1} K^{-1}) by the number of particles do we obtain 8.31?

Note 1: since the constant is in terms of standard units, all variables in the equations $PV = NkT$ or $PV = nRT$ have to be in standard units. That is, pressure needs to be measured in Pa, volume in m^3, and temperature in K.

Note 2: gases exist as either atoms or molecules. For example, helium, argon, and neon are single atoms whereas oxygen, hydrogen, and carbon dioxide exist as molecules containing two or more atoms. We use the term 'particles' to refer to both atoms and molecules.

Example 1

Find the number of particles in a 20 L sample of argon gas at a temperature of 273 K and at atmospheric pressure.

Solution

- P = 1 atm = 1.013×10^5 Pa.
- T = 273 K.
- V = 20 L = 20×10^{-3} m^3.

$$PV = NkT$$
$$1.013 \times 10^5 \text{ Pa} \times 20 \times 10^{-3} \text{ m}^3 = N \times 1.38 \times 10^{-23} \times 273 \text{ K}$$
$$N = 1.013 \times 10^5 \text{ Pa} \times 20 \times 10^{-3} \text{ m}^3/1.38 \times 10^{-23} \times 273 \text{ K}$$
$$N = 5.4 \times 10^{23} \text{ particles}$$

Example 2

Air has an average molecular weight (molar mass) of 29 g per mole. (That is, 1 mole of gas particles has a mass of 29 g.) What is the volume of 2.0 kg of air at atmospheric pressure and 20°C?

Solution

- P = 1 atm = 1.013×10^5 Pa.
- T = 20°C = 293 K.
- n = 2 kg/29 g mole^{-1} = 68.97 mole.
- R = 8.31 m^3 Pa mol^{-1} K^{-1}.

$$PV = nRT$$
$$V = nRT/P$$
$$= 68.97 \times 8.31 \times 293/1.013 \times 10^5$$
$$= 1.66 \text{ m}^3$$

Questions

12 What is the pressure of 0.030 moles of hydrogen gas at 37°C if its volume is 80 mL?

13 A 0.50 L sample of oxygen gas has a pressure of 2.0 atm at a temperature of 80°C. How many molecules of oxygen are in the sample?

14 What amount of carbon dioxide gas occupies 2.0×10^{-4} m^3 at a pressure of 150 kPa and a temperature of 20°C?

15 A 500 mL sample of helium gas contains 2.0 moles of gas at 300 K.

(a) Find the pressure exerted by the particles.

(b) If the temperature is doubled and half of the gas escapes, what will be the new pressure?

TEMPERATURE AND KINETIC ENERGY 11.5

Let us now calculate the pressure of an ideal gas from kinetic theory. To simplify matters, we will consider a gas in a cubic vessel whose walls are perfectly elastic. Let each edge be of length d. Call the faces normal to the x axis (Figure 11.8) A_1 and A_2, each of area d^2. Consider a particle that has a velocity $\boldsymbol{v}$. We can resolve $\boldsymbol{v}$ into components $\boldsymbol{v}_x$, $\boldsymbol{v}_y$ and $\boldsymbol{v}_z$, the directions of the edges. If this particle collides with A_1 it will rebound, with its x component of velocity reversed. There will be no effect on $\boldsymbol{v}_y$ or $\boldsymbol{v}_z$, so the change in the particle's momentum $\Delta\boldsymbol{p}$ will be normal to A_1. Hence, the change in momentum of the particle will be:

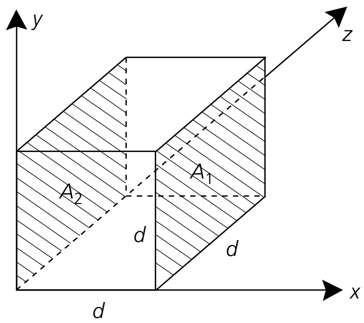


Figure 11.8
Motion of a particle in a box.

$$\Delta\boldsymbol{p} = \boldsymbol{p}_f - \boldsymbol{p}_i = -m\boldsymbol{v}_x - (m\boldsymbol{v}_x) = -2m\boldsymbol{v}_x$$

Thus the momentum imparted to A_1 will be $2m\boldsymbol{v}_x$ since the total momentum is conserved.

Suppose that this particle reaches A_2 without striking any other particle on the way. The time required to cross the cube will be $d/\boldsymbol{v}_x$. At A_2 it will again have its x component of velocity reversed and will return to A_1. Assuming no collisions in between, the round trip will take a time of $2d/\boldsymbol{v}_x$. Hence, the number of collisions per unit time this particle makes with A_1 is $\boldsymbol{v}_x/2d$, so the rate at which the particle transfers momentum to A_1 is:

$$2m\boldsymbol{v}_x \times \boldsymbol{v}_x/2d = m\boldsymbol{v}_x^2/d$$

To obtain the total force on A_1, that is, the rate at which momentum is imparted to A_1 by all the gas molecules, we must sum up $m\boldsymbol{v}_x^2/d$ for all the particles. Recall from Chapter 4 that $\boldsymbol{F}t = \Delta\boldsymbol{p}$, or $\boldsymbol{F} = \Delta\boldsymbol{p}/t$.

Then, to find the pressure, we divide this force by the area of A_1, namely d^2. If m is the mass of each molecule, we have:

$$\begin{aligned} P &= F/A \\ &= m\boldsymbol{v}_x^2/d/d^2 \text{ for one particle} \end{aligned}$$

The total pressure is:

$$P = m/d^3 \times (\boldsymbol{v}_{x1}^2 + \boldsymbol{v}_{x2}^2 + \boldsymbol{v}_{x3}^2 + \ldots \boldsymbol{v}_{xn}^2)$$

where $\boldsymbol{v}_{x1}$ is the x component of the velocity of particle 1, $\boldsymbol{v}_{x2}$ is that of particle 2, etc. If N is the total number of particles in the container and n is the number per unit volume, then $N/d^3 = n$ or $d^3 = N/n$. Hence:

$$P = mn(\boldsymbol{v}_{x1}^2 + \boldsymbol{v}_{x2}^2 + \boldsymbol{v}_{x3}^2 + \ldots \boldsymbol{v}_{xn}^2)/N$$

But mn is simply the mass per unit volume, that is, the density ρ of the gas we're considering. The quantity $(\boldsymbol{v}_{x1}^2 + \boldsymbol{v}_{x2}^2 + \boldsymbol{v}_{x3}^2 + \ldots \boldsymbol{v}_{xn}^2)/N$ is the average value of $\boldsymbol{v}_x^2$ for all particles in the container. Let us call this $\overline{\boldsymbol{v}_x^2}$.

Then:

$$P = \rho\overline{\boldsymbol{v}_x^2}$$

NOVEL CHALLENGE

French scientist Pierre Gassendi (1592–1655) said that the pressure of a gas doesn't depend on the weight of the gas in a container.
Was he correct? Could you have two equal rigid containers with the same mass of the same gas in each but exhibiting different pressures?

For any particle, $v^2 = v_x^2 + v_y^2 + v_z^2$ (Pythagoras's theorem). Because we have many particles and because they are moving entirely at random, the average values of v_x^2, v_y^2, and v_z^2 are equal and the value of each is exactly one-third the average value of v^2. There is no preference among the molecules for motion along any one of the three axes.

Hence, $\overline{v_x^2} = \frac{1}{3}\overline{v^2}$, so that:

$$\begin{aligned} P &= \rho v_x^2 = \tfrac{1}{3}\rho v^2 \\ &= \tfrac{1}{3} mn\ \overline{v^2} \\ &= \tfrac{1}{3} m\ \overline{v^2}\ n \\ &= \tfrac{1}{3} m\ \overline{v^2}\ N/d^3 \\ &= \tfrac{2}{3}\ \tfrac{1}{2}\ m\ \overline{v^2}\ N/V \\ &= \tfrac{2}{3}\ \overline{E_k}\ N/V \end{aligned}$$

From Chapter 9, kinetic energy $(E_k) = \frac{1}{2}\, m\, v^2$, so:

$$PV = \tfrac{2}{3}\ \overline{E_k}\ N$$

This can be equated to the general equation $PV = NkT$.

$$\text{Then} \qquad kT = \tfrac{2}{3}\ \overline{E_k}$$

$$\text{or} \qquad \tfrac{3}{2}\ kT = \overline{E_k}$$

Example

Find the average kinetic energy of the air particles, and the average speed of the nitrogen molecules in the laboratory at room temperature of 22°C.

Solution

$$\begin{aligned} \overline{E_k} &= \tfrac{3}{2}\ kT \\ &= \tfrac{3}{2}\ 1.38 \times 10^{-23} \times (22 + 273)\ \text{K} \\ &= 6.01 \times 10^{-21}\ \text{J} \end{aligned}$$

One mole of nitrogen molecules has a mass of 28 g, therefore the mass of a nitrogen molecule is $28/6.02 \times 10^{23}$ g, equals 4.65×10^{-26} kg.

$$\begin{aligned} \overline{E_k} &= \tfrac{1}{2} m\overline{v}^2 \\ 6.10 \times 10^{-21}\ \text{J} &= \tfrac{1}{2} 4.65 \times 10^{-26}\ \overline{v}^2 \\ v^2 &= 6.10 \times 10^{-21} \times 2/4.65 \times 10^{-26} \\ &= 2.6 \times 10^5 \\ \overline{v} &= 5.10 \times 10^2\ \text{m s}^{-1} \end{aligned}$$

(Notice that the speed of gas particles in the room is surprisingly high, 500 m s^{-1}, and if the gas under consideration was hydrogen the speed of the particles would be much greater.)

Questions

16 Find the average speed of the oxygen molecules in the above example. (The mass of oxygen is 32 g per mole.)

17 At a certain temperature a sample of oxygen has a pressure of 2.0×10^6 Pa, and a density of 4.0×10^{-3} g cm^{-3}. Find the average speed of the oxygen molecules of the gas.

PHYSICS FACT

It takes an alcohol molecule 6 months to travel from the front of your laboratory to the back (if the windows are closed). During this time it would collide 6000 times per second and travel a total distance of 60 million kilometres. Now that's a lot of 'Fly Buys'.

18 Samples of two ideal gases, argon and helium, are mixed and heated to 150°C. Find:
(a) the ratio of the average kinetic energy of the argon atoms to the average kinetic energy of the helium atoms;
(b) the ratio of the average velocity of the atoms of argon to the average velocity of the atoms of helium. (The mass of argon is 40 g mol^{-1}, and the mass of helium is 4 g mol^{-1}.)

19 A fluorescent light tube consists of a cylinder 1.2 m long with a diameter of 3 cm. It contains neon gas of density 1.12×10^{-3} g cm^{-3}. If it is heated to 80°C what pressure is the gas in the light? (Mass of neon = 20 g $mole^{-1}$.)

A FINAL NOTE — REAL GASES 11.6

The above equations are developed for ideal gases, that is, gases that consist of single atoms only. Therefore, all energy put into these gases by means of heat then goes into translational motion (Latin *trans* = 'across', *latio* = 'bringing') — motion in a straight line. That is, it makes the particles move faster in a certain direction. There are several ideal gases: helium, neon, argon, krypton, xenon, and radon. However, most gases have two or more atoms per molecule. For example, nitrogen does not, in gaseous form, exist as an individual atom but as a molecule that consists of two atoms bonded together. Other examples are oxygen (O_2), hydrogen (H_2) and carbon dioxide (CO_2). Energy put into these gases by means of heating does not all go into translational motion. Some goes into rotational motion — the atoms spin around as they travel along; and some goes into potential energy stored in the bonds of the atoms. Because of this, these gases deviate from the ideal gas equation.

Ideal gases are assumed to consist of particles that are insignificantly small and have no attractive force on each other. Real gas particles do have size so it is surprising that at normal temperatures and pressures they, in fact, obey the ideal gas equation very well. However, real gases deviate from the ideal gas equation as the temperature decreases and the pressure increases. At normal temperatures and pressures the particles of oxygen occupy very little volume compared with the total volume of the gas. The particles are moving so fast that they exert little attractive force on each other. But at low temperatures when they are moving slowly, or at high pressures when they are pushed close together, the attractive force is greater and the volume of the particles is significant compared with the volume of the gas. Under these conditions a real gas deviates from the behaviour indicated by the ideal gas equation.

THERMAL EXPANSION 11.7

So far we have looked at the effects of heat on gases. These effects are easier to understand because of the limited effect particles of the gas have on one another (except in collisions). The addition of heat affects the particles of the gas by making them move faster and thus expanding the gas or increasing its pressure on its container. Does the addition of heat have the same effect on the particles of solids and liquids?

Can you think of everyday examples where the addition of heat affects a solid or liquid?

- What causes the mercury in a thermometer to rise (Figure 11.9)?
- Why do trains make the 'clicky–clack' sound when moving over railway lines?
- Have you ever considered why people building ships or high-rise buildings in old movies use white-hot rivets to hold steel plates together? Why not use cold ones? They are easier to handle and do not lead to all those comical situations in cartoons.

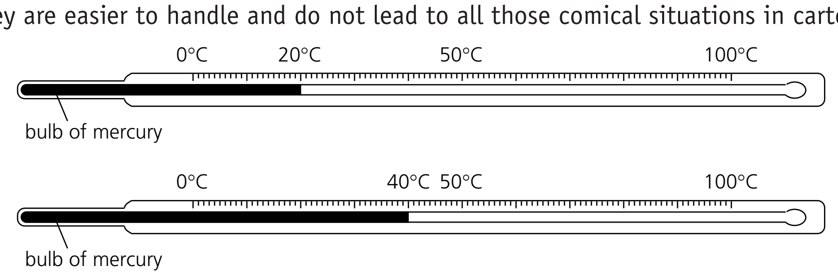


Figure 11.9
Expansion of mercury in a thermometer.

11.8 THERMAL EXPANSION OF SOLIDS

With very few exceptions all solids expand when they are heated and contract when they are cooled. But different substances expand at different rates. The rates at which solids expand can be found experimentally.

If we take a 1 m length of aluminium and heat it so as to change its temperature by 1°C, its length will expand by 23.8×10^{-6} m. This may not seem very much, and it is not, for everyday purposes, but when fine measurements are needed or the length is much longer or the temperature change much greater, thermal expansion is very significant.

The change in length of a 1 m length of a substance due to a temperature change of 1°C is called the **coefficient of linear expansion** (α). For example, the coefficient of linear expansion of Pyrex glass is 3.3×10^{-6} m °C^{-1}. This means that a 1 m length of Pyrex glass increases by 3.3×10^{-6} m if heated so as to change its temperature by 1°C. The coefficients of linear expansion of several common substances are given in Table 11.1.

This expansion is more significant if we have greater lengths of materials or the temperature changes by more than 1°C.

For example, if we have a 4 m length of aluminium and change its temperature by 1°C, its length will increase by:

$$4 \times 23.8 \times 10^{-6} \times 1 \text{ m} = 9.52 \times 10^{-5} \text{ m}$$

Table 11.1 COEFFICIENTS OF LINEAR EXPANSION OF COMMON SUBSTANCES

SUBSTANCE	COEFFICIENT OF LINEAR EXPANSION $\alpha \times 10^{-6}$ m °C^{-1}
Diamond	1.2
Glass (Pyrex)	3
Glass (crown)	9
Platinum	9
Steel	10
Iron	12
Brick and concrete	12
Copper	17
Brass	19
Silver	18.8
Aluminium	23.8
Zinc	26.3
Rubber	80

If we have a 1 m length of aluminium and increase its temperature by 100°C, its length will change by 23.8×10^{-6} m every change of 1°C, giving a total increase in length of:

$$23.8 \times 10^{-6} \times 100 \text{ m} = 23.8 \times 10^{-4} \text{ m}$$

Changing the temperature of a 4 m length of aluminium by 100°C causes a change in length of:

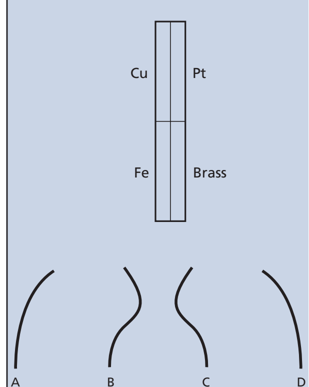
$$\begin{aligned} 23.8 \times 10^{-6} \times 4 \text{ m} \times 100\text{°C} &= 9.52 \times 10^{-3} \text{ m} \\ &= 9.52 \text{ mm} \end{aligned}$$

NOVEL CHALLENGE

When water freezes it expands and can crack pipes; therefore water can do work when it freezes. Where does this energy come from, especially as heat is being removed? Sounds stupid!

NOVEL CHALLENGE

When a rod made up of four metals as shown in the diagram is heated, which of the following diagrams represents its final shape.
What about if it is cooled?



NOVEL CHALLENGE

The General Electric building in New York has thousands of slabs of Italian Travertine marble bolted on as a skin. Each slab is 6000 mm x 3000 mm. The temperatures in NY can vary from −23°C to +38°C, over which temperature range the length of the slabs increase by 3 mm.
What is the coefficient of linear expansion of marble? How would these slabs be attached to the building so that they didn't crack on expansion or contraction? If a slab was bolted at each corner, how far away from the face of the building would it bow out? Do any buildings in your city have them? Email the authors and it will be added to the next edition.

NOVEL CHALLENGE

In the old days before welding was invented, ships were made by riveting steel sheets together. Rivets are small lengths of steel with a flat head on one end. They were heated to a high temperature and inserted through a hole drilled in the sheets. The rivets were then struck with a hammer to bend the other end over. Why were they heated? Wouldn't they shrink away from the insides of the hole?

This may have important consequences in everyday activities.

The reverse is also true. Cooling a 4 m length of aluminium from 100°C to 0°C will cause it to contract by 9.52 mm.

This expansion may not seem very much but if the length is big enough and the temperature rise large enough the expansion will be noticeable. For example, in the early 1800s, steam had just been introduced to power the factories. Steam pipes in the cotton mills were often over 400 feet (130 m) long and with temperature rises from a cold 10°C to 400°C the increase in length was such that a carpenter's ruler could be used to measure it. Leading industrialists of the time were enthusiastic in promoting the type of learning needed to deal with the new technology of steam. They saw the academic approach of the universities of the time as being useless in factories. Hence, they supported the establishment of craft guilds and mechanics' institutes to teach 'real-life' knowledge. Universities have changed a lot since then.

Expansion formula A formula to help find the change in length of a substance due to thermal expansion of solids is:

$$\Delta L = L_i \, \alpha \, \Delta T$$

where ΔL is the change in length, L_i is the original length of the solid, ΔT is the change in temperature.

It also should be noted that because a solid has three length measurements — length, width and height — all three expand and contract, therefore the volume of a solid changes with temperature change.

This property of solids to expand and contract with temperature change can be an advantage as well as a disadvantage in everyday life.

Can you think of some advantages and disadvantages?

Have you worked out why hot rivets are used yet? This is an advantage.

Other examples where these properties have to be considered include:

- The fitting of gear wheels to axles. If the axle is cooled in liquid nitrogen it contracts and the gear wheel will slip on more easily. When the axle warms up to normal temperature it makes a very tight fit.
- Telephone and electrical cables are hung loosely between poles to allow for contraction in cold weather conditions.
- Bimetallic strips that consist of two dissimilar metals of equal length are used in fire alarms. (See Figure 11.10.)
- Bridges and rail lines have expansion gaps to allow for expansion in hot conditions to stop buckling.
- Next time you pass a large building or concrete paths check for rubber expansion gaps that allow for the expansion of the concrete, to stop cracking.

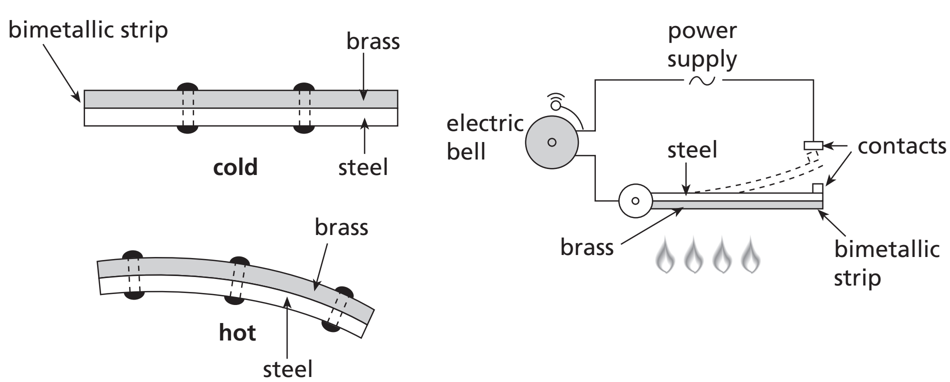


Figure 11.10 Bimetallic strip used in a fire alarm.

- The coefficients of expansion of the iron used for reinforcing concrete and of the concrete itself have to be similar. If they expand at different rates the concrete will crack, and with continual expansion and contraction it may break away from the iron.
- Fillings in teeth and the teeth themselves need to have similar coefficients of expansion. Why?
- Crown glass shatters when you pour boiling water into it but Pyrex does not.
- In aircraft manufacture, rivets are often cooled in dry ice before insertion and then allowed to expand to a tight fit.
- Pipes in refineries often include an expansion loop so that the pipe will not buckle as the temperature rises.

NEI Activity 11.3 THERMAL EXPANSION

Houses with steel roofs on a timber frame will creak when a cloud passes overhead on a hot summer's day. What's going on here? In your response, you should provide quantitative data to support your claim.

Example

An electric company strung an aluminium wire between two piers 200.0 m apart on a day when the temperature was 25°C. They strung it tight so that it would not sag. Find the length of the wire when the temperature fell to –25°C on a cold winter's night? What might happen? What should have been done to prevent this occurring? This does happen in countries that have wide variations in temperature.

Solution

$$\begin{aligned}\Delta L &= L_i\, \alpha\, \Delta T \\ &= 200.0 \text{ m} \times 23.8 \times 10^{-6} \times 50°\text{C} \\ &= 2.38 \times 10^{-1} \text{ m} \\ &= 23.8 \text{ cm} \\ \therefore L &= 200.0 - 0.238 \\ &= 199.862 \text{ m}\end{aligned}$$

PHYSICS UPDATE

Modern train lines are welded together, so they have no expansion gap. How is expansion allowed for so that the lines don't buckle? In the past, fairly light wooden sleepers were used but today heavy steel or concrete sleepers (300 kg) are used and this physically prevents expansion. The force of expansion builds up but it is insufficient to lift the weight of the tracks and sleepers so they just get compressed. If you don't think this can be true, ring *Queensland Rail* and talk to a track engineer.

NOVEL CHALLENGE

A steel ruler has a hole in one end. When the ruler is heated, does the hole get bigger, smaller or stay the same? Be careful — even some science texts get it wrong.

Questions

20 A 3.0 m steel girder is used in the construction of a bridge. If the least and greatest recorded temperatures in the region where the bridge is to be built are –10°C and 45°C, what allowance would need to be made for expansion and contraction, if it was fixed in place when the temperature was 20°C?

21 A very modern car engine is to be made of ceramic material with a coefficient of expansion of 1.8×10^{-6} m °C^{-1}.
(a) What would be the increase in the diameter of the 5.0 cm piston if the temperature of the engine changed from 10°C to 180°C?
(b) How does this compare with an engine made of iron?
(c) How do normal car engines allow for this expansion?

22 An expansion gap between 5.0 m iron railway lines was set at 2.0 mm on a day when the temperature was 10°C. To what temperature would the lines have to increase before they begin to buckle?

23 A 100 m long iron water pipe was laid in the ground on a hot summer's day when the temperature was 25°C. By what length would it have contracted if the ground temperature fell to –15°C?

THERMAL EXPANSION OF LIQUIDS 11.9

A very common device making use of the expansion of liquids is a thermometer. As the temperature increases, the mercury or alcohol in the thermometer increases in volume and moves up the fine tube. Other examples include the explosion of bottles filled with liquid and left in the hot sun.

As liquids take the shape of the container we are mainly interested in the volume changes of liquids with temperature. Again these changes can be found experimentally. The **coefficients of volume expansion**, β, of some common liquids are given in Table 11.2.

Table 11.2 COEFFICIENTS OF VOLUME EXPANSION OF LIQUIDS

LIQUID	COEFFICIENT OF VOLUME EXPANSION $\beta \times 10^{-4}$ m °C^{-1}
Mercury	1.82
Water	2.07
Petrol	9.55
Turpentine	9.73
Alcohol	11.2
Acetone	14.87
Ether	16.56

NOVEL CHALLENGE

The coefficient of volume expansion (β) for iron is 0.36×10^{-4}. *How many times greater is this than the coefficient of linear expansion (α)? Propose a proof for this.*

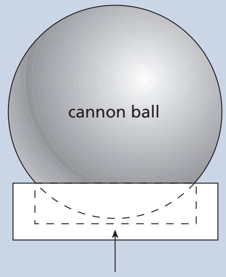
As with solids, the change in volume of liquids can be found by the formula:

$$\Delta V = \beta\, V_i\, \Delta T$$

where ΔV is the change in the volume of the liquid, β is the coefficient of volume expansion, V_i is the initial volume of the liquid, ΔT is the change in temperature.

NOVEL CHALLENGE

In days gone by, warships had cannons mounted on the decks with the iron cannonballs resting in shallow brass ashtray-shaped containers called 'brass monkeys'. These would invariably fill with water as the sea washed over the decks. In the Atlantic ocean sometimes it would get so cold that sailors would say: 'It's cold enough to freeze the balls off a brass monkey'. *What do you suspect they meant?*



Example

What would be the increase in the volume of 0.20 L of acetone if it was heated from 10°C to 40°C?

Solution

$$\begin{aligned} \Delta V &= \beta\, V_i\, \Delta T \\ &= 14.87 \times 10^{-4} \times 0.20 \times (40 - 10) \\ &= 89.2 \times 10^{-4}\ \text{L} \\ &= 8.9 \times 10^{-3}\ \text{L} \end{aligned}$$

Questions

24 By what volume would 25 L of alcohol increase if its temperature was increased from 10°C to 50°C?

25 How much extra petrol would you get if you bought 50 L at 5.0°C instead of at 40°C?

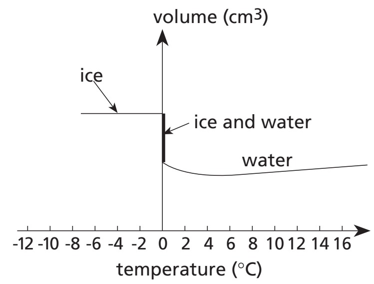
26 A student measured 500 mL of water into a measuring cylinder at a temperature of 25°C and placed it in the refrigerator where the temperature was 4.0°C. What will be the measurement on the measuring cylinder? (Assume the cylinder does not contract.)

11.10 THE ABNORMAL EXPANSION OF WATER

Most liquids contract with a decrease in temperature. Water is different. Water in fact expands as it cools below a certain temperature. Why do soft drink bottling companies leave air at the top of bottles of soft drink? But expansion also is seen if a bottle of soft drink is left in a freezer. Consider the graph (Figure 11.11) showing the change in volume of water with temperature changes.

As water is cooled it contracts as expected with all liquids; however, at approximately 4°C it stops contracting. Between 4°C and 0°C it actually expands as temperature decreases. This is due to the rearrangement of the particles that make up water. This rearrangement takes up more volume. A certain amount of water therefore has a minimum volume and a maximum density at 4°C. When water freezes at 0°C it undergoes considerable expansion. The volume of 100 mL of water changes to 109 mL of ice. This is very important in cold countries. Unless water pipes are very well insulated the water in them will freeze and this may cause the pipes to burst.

Figure 11.11
The change in the volume of water with temperature.



This abnormal (or anomalous) expansion of water can cause many problems:

- In cold climates the water in the engine block and radiator of a car can freeze and the expansion can shatter the engine. 'Antifreeze' is usually added to the water to lower its freezing point and to prevent freezing from occuring. It also raises the boiling point. Can you see the use of this?
- When water freezes in pipes in your house it can cause them to crack. Some people leave taps dripping to prevent this happening. Do you think that this would work?

— Practice questions

The relative difficulty of these questions is indicated by the number of stars beside each question number: * = low; ** = medium; *** = high.

Review — applying principles and problem solving

***27** A cylinder contains 0.50 m^3 of helium gas at 2.0 atm. What volume of gas is able to escape if it is released into the atmosphere?

****28** An oxygen cylinder releases gas at the rate of 4 $m^3\ h^{-1}$ at atmospheric pressure. If it is sold at a pressure of 200 atm and has a volume of 2 m^3, for what time will it supply oxygen?

***29** A container of gas has a pressure of 80 cm of Hg when its volume is 800 cm^3 and its temperature is 60°C. What will be its pressure when its temperature is increased to 90°C, and its volume is reduced to 400 cm^3?

****30** Two cylinders of volumes 2.0 m^3 and 3.0 m^3 are at pressures 4.0 atm and 6.0 atm respectively. If they are then joined by a thin, short tube, what will be the new pressure in each?

***31** What is the effect on the volume of a gas **(a)** whose pressure is tripled at the same time as its temperature is halved; **(b)** whose pressure is kept constant while twice the number of molecules are added at the same temperature?

***32** What volume will two moles of gas occupy at a pressure of 8.2×10^4 N m^{-2} and a temperature of 290 K?

***33** A container has a volume of 20.0 L at a temperature of 360 K. Gas is forced into the container until the pressure is 2.0×10^5 N m^{-2}. How many molecules of gas are there in the container now?

***34** A flask is open to the atmosphere at room temperature of 26°C. To what temperature must the flask be heated before only two-thirds of the original number of molecules remain in the flask?

***35** A cylinder has a volume of 1.5 m^3 and contains neon gas at a pressure of 1.0×10^{-1} cm height of mercury at the temperature of 20°C. What is the number of particles in the cylinder?

****36** A flask contains gas at a temperature of 30°C and a pressure of 2.0×10^3 Pa. Find the number of molecules per cubic metre in the flask.

****37** If we have a cylinder of volume 4.4 m^3 containing 5.0×10^{22} molecules at a pressure of 3 atm, what will be the average kinetic energy of the centre of mass motion of the molecules?

***38** Find the average kinetic energy of translation of a molecule at 24°C.

***39** How much energy is needed to raise the temperature of 1 mol of a monatomic gas by 10°C?

***40** A steel water pipe line of 2000 m is fixed in place on a day when the temperature was 30°C. What will be its new length when the temperature drops to –20°C?

***41** The space between 10 m steel railway lines is 8.0 mm at 5.0°C. What would be the space at 30°C?

****42** Mercury has a density of 13.6 g cm^{-3} at 20°C. What would be the density of mercury at 100°C?

****43** The data given in Table 11.3 were collected by heating a 50 cm copper rod in a water bath. From the data calculate the coefficient of linear expansion for copper.

Table 11.3

TEMPERATURE	LENGTH (CM)
20	50.000
40	50.017
60	50.033
80	50.052
100	50.070

***44** Explain why iron and not steel is used to reinforce concrete.

Extension — complex, challenging and novel

*****45** Twenty-five percent of the energy put into a certain non-monatomic gas causes increased rotation and vibration of the atoms within the molecule. How much energy is required to raise the temperature of 2 mol of this gas from 10°C to 35°C?

*****46** If 2 mol of helium at 50°C is mixed with 4 mol of argon at 20°C, find the final temperature of the mixture.

*****47** Gas X is monatomic, and gas Y has one-quarter of its total energy involved as energy within the molecules.

(a) If 2 mol of X at 70°C is mixed with 1 mol of Y at 25°C, find the final temperature of the mixture.

(b) If 2 mol of Y at 80°C is mixed with 2 mol of X at 35°C, find the final temperature of the mixture.

*****48** A bubble expands to three times its original volume while rising from the bottom to the surface of a lake.

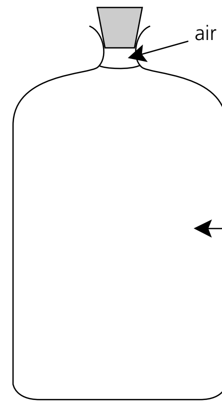
(a) Assuming that the lake throughout is at the same temperature as the surrounding atmosphere, how deep is the lake?

(b) If there had been a temperature increase from 7.0°C at the bottom to 27°C at the surface, by what factor would the bubble have expanded?

*****49** Two glass flasks, one of which has twice the volume of the other, are connected by a thin tube of negligible volume. They contain dry air at a temperature of 20°C and a pressure of 76 cm of mercury. The larger flask is then immersed in steam at 100°C and the smaller in melting ice at 0°C. Neglecting any change in volume of the flasks, find the resulting pressure in them.

*****50** A 500 mL flask as shown in Figure 11.12 was filled almost to the top with acetone at 20°C. It was inadvertently left on the bench in the sunlight on a hot day when the temperature reached 32°C. Assuming no acetone changed to vapour, calculate the pressure of the air in the neck of the flask. (Neglect the expansion of the flask itself as this is small compared with the expansion of acetone.)

Figure 11.12
For question 50.



*****51** A new type of temperature scale has been created by Martians. Measurements of a gas held at constant pressure give the following data. The temperature is in degrees Martian (°M) which has the same size *degree* as in the Celsius and Kelvin scales:

Temperature (°M)	90	120	150
Volume (L)	30	45	60

Create an equation that converts a temperature on the Martian scale into a temperature on the Celsius scale. It should look something like the Celsius/Kelvin conversion equation (K = °C + 273).

°M = ?