Chapter 20

Ideal gases

LEARNING INTENTIONS

In this chapter you will learn how to:

- measure amounts of a substance in moles and find the number of particles using molar quantities
- solve problems using the equation of state $pV = nRT$ for an ideal gas
- deduce a relationship between pressure, volume and the microscopic properties of the molecules of a gas, stating the assumptions of the kinetic theory of gases
- relate the kinetic energy of the molecules of a gas to its temperature and calculate root-mean-square speeds.

BEFORE YOU START

- With a classmate, write down what you know about Brownian motion and what it shows about the molecules in a gas.
- Try to explain to a classmate, in terms of momentum change, why a ball hitting a wall exerts a force on it.
- List Newton's laws of motion.

THE IDEA OF A GAS

Figure 20.1 shows a weather balloon being launched. Balloons like this carry instruments high into the atmosphere, to measure pressure, temperature, wind speed and other variables.

The balloon is filled with helium so that its overall density is less than that of the surrounding air. The result is an upthrust on the balloon, greater than its weight, so that it rises upwards. As the balloon moves upwards, the pressure of the surrounding atmosphere decreases so that the balloon expands. The temperature drops, which tends to make the gas in the balloon shrink. In this chapter, we will look at the behaviour of gases as their pressure, temperature and volume change.

Figure 20.1: A weather balloon being launched.

20.1 Particles of a gas

We picture the particles of a gas as being fast-moving. They bounce off the walls of their container (and off each other) as they travel around at high speed (see Figure 20.2). How do we know that these particles are moving like this?

It is much harder to visualise the particles of a gas than those of a solid, because they move about in such a disordered way, and most of a gas is empty space. The movement of gas particles was investigated in the 1820s by a Scottish botanist, Robert Brown. He was using a microscope to look at pollen grains suspended in water, and saw very small particles moving around inside the water. He then saw the same motion in particles of dust in the air. It is easier in the laboratory to look at the movement of tiny particles of smoke in air. The particles are seen to be moving in a random, haphazard and jerky motion that we believe is caused by them being hit by invisible molecules of water or air around them. The pollen and dust particles are big enough to see in an ordinary microscope but air molecules are too small to see.

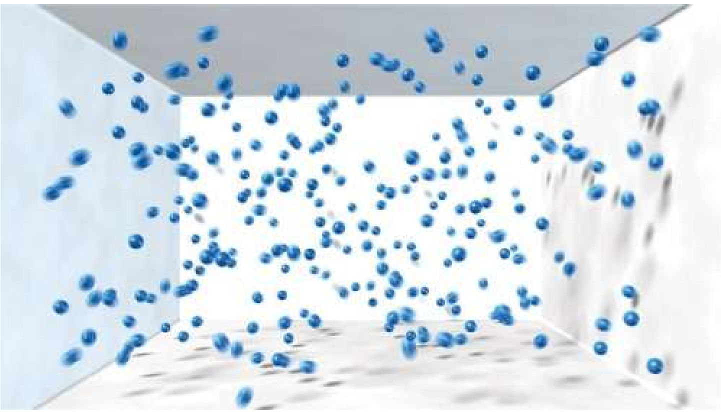

Figure 20.2: Particles of a gas – collisions with the walls of the container cause the gas' pressure on the container. (Particles do not have shadows like this. The shadows are added here to show depth.)

Fast molecules

For air at standard temperature and pressure (STP, −0 °C and 100 kPa), the average speed of the molecules is about 400 m s^{-1}. At any moment, some are moving faster than this and others more slowly. If we could follow the movement of a single air molecule, we would find that, some of the time, its speed was greater than this average; at other times, it would be less. The velocity (magnitude and direction) of an individual molecule changes every time it collides with anything else.

This value for molecular speed is reasonable. It is comparable to (but greater than) the speed of sound in air (approximately 330 m s^{-1} at STP). Very fast-moving particles can easily escape from the Earth's gravitational field. The required escape velocity is about 11 km s^{-1}. Since we still have an atmosphere, on average, the air molecules must be moving much more slowly than this value.

20.2 Explaining pressure

A gas exerts pressure on any surface with which it comes into contact. Pressure is a macroscopic property, defined as the force exerted per unit area of the surface.

The pressure of the atmosphere at sea level is approximately 100 000 Pa. The surface area of a typical person is 2.0 m^2. Hence the force exerted on a person by the atmosphere is about 200 000 N. This is equivalent to the weight of about 200 000 apples!

Fortunately, air inside the body presses outwards with an equal and opposite force, so we do not collapse under the influence of this large force. We can explain the macroscopic phenomenon of pressure by thinking about the behaviour of the microscopic particles that make up the atmosphere.

Figure 20.3 shows the movement of a single molecule of air in a box. It bounces around inside, colliding with the various surfaces of the box. At each collision, it exerts a small force on the box. The pressure on the inside of the box is a result of the forces exerted by the vast number of molecules in the box. Two factors affect the force, and hence the pressure, that the gas exerts on the box:

- the number of molecules that hit each side of the box in one second
- the force with which a molecule collides with the wall.

If a molecule of mass m hits the wall head-on with a speed v it will rebound with a speed v in the opposite direction. The change in momentum of the molecule is $2mv$. Since force is equal to rate of change of momentum, the higher the speed of the molecule the greater the force that it exerts as it collides with the wall. Hence, the pressure on the wall will increase if the molecules move faster.

If the piston in a bicycle pump is pushed inwards, but the temperature of the gas inside is kept constant, then more molecules will hit the piston in each second, but each collision will produce the same force because the temperature and therefore the average speed of the molecules is the same. The increased rate of collisions alone means that the force on the piston increases and thus the pressure rises. If the temperature of the gas in a container rises then the molecules move faster and hit the sides faster and more often; both of these factors cause the pressure to rise.

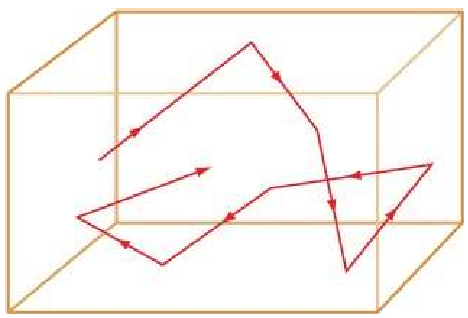

Figure 20.3: The path of a single molecule in an otherwise empty box.

Questions

1 State and explain, in terms of the kinetic model (the movement of molecules), what happens to the pressure inside a tyre when more molecules at the same temperature are pumped into the tyre.

2 Explain, using the kinetic model, why a can containing air may explode if the temperature rises.

20.3 Measuring gases

We are going to picture a container of gas, such as the box shown in Figure 20.4. There are four properties of this gas that we might measure: pressure, temperature, volume and mass. In this chapter, you will learn how these quantities are related to one another.

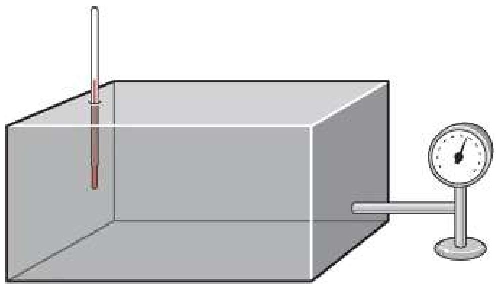

Figure 20.4: A gas has four measurable properties, which are all related to one another: pressure, temperature, volume and mass.

Pressure

This is the normal force exerted per unit area by the gas on the walls of the container. We saw in Chapter 7 that molecular collisions with the walls of the container produce a force and thus create a pressure. Pressure is measured in pascals, Pa (1 Pa = 1 N m^{-2}).

Temperature

This might be measured in °C, but in practice it is more useful to use the thermodynamic (Kelvin) scale of temperature. You should recall how these two scales are related:

$$T\ (\text{K}) = \theta\ (°\text{C}) + 273.15$$

Volume

This is a measure of the space occupied by the gas. Volume is measured in m^3.

Mass

This is measured in g or kg. In practice, it is more useful to consider the **amount** of gas, measured in moles. The mole is the SI unit of substance, not a unit of mass.

We have seen in Chapter 15 that each atom or molecule has a mass in unified atomic mass units (u), approximately equal to the number of nucleons (protons and neutrons) it contains.

We have also seen that 1 u = 1.66×10^{-27} kg.

Thus, each atom of carbon-12 has a mass:

$$\begin{aligned} 12\ \text{u} &= 12 \times 1.66 \times 10^{-27}\text{kg} \\ &= 1.99 \times 10^{-26}\text{kg} \end{aligned}$$

So, 0.012 kg of carbon-12 contains $\frac{0.012}{1.99\times10^{-26}} = 6.02 \times 10^{23}$ molecules.

A mole of any substance (solid, liquid or gas) contains a standard number of particles (molecules or atoms). This number is known as the **Avogadro constant**, N_A. The value for N_A is 6.02×10^{23} mol^{-1}. We can easily determine the number of atoms in a sample if we know how many moles it contains. For example:

2.0 mol of helium contains

$$2.0 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}\ \text{atoms}$$

10 mol of carbon contains

$$10 \times 6.02 \times 10^{23} = 6.02 \times 10^{24}\ \text{atoms}$$

We will see later that, if we consider equal numbers of moles of two different gases under the same conditions, their physical properties are the same.

Questions

3 The mass of one atom of carbon-12 is 12 u. Determine:

- **a** the mass of one atom of carbon-12 in kg, given that 1 u = 1.66×10^{-27} kg
- **b** the number of atoms and the number of moles in 54 g of carbon
- **c** the number of atoms in 1.0 kg of carbon.

4 **a** Calculate the mass in grams of a single atom of uranium-235 of mass 235 u.

- **b** A small pellet of uranium-235 has a mass of 20 mg. For this pellet, calculate:
  - **i** the number of uranium atoms
  - **ii** the number of moles.

5 'It can be useful to recall that 1.0 kg of ordinary matter contains in the order of 10^{26} atoms.' Making suitable estimates, test this statement.

20.4 Boyle's law

This law relates the pressure p and volume V of a gas. It was discovered in 1662 by Robert Boyle.

If a gas is compressed at constant temperature, its pressure increases and its volume decreases. A decrease in volume occupied by the gas means that there are more particles per unit volume and more collisions per second of the particles with unit area of the wall. Because the temperature is constant, the average speed of the molecules does not change. This means that each collision with the wall involves the same change in momentum, but with more collisions per second on unit area of the wall there is a greater rate of change of momentum and, therefore, a larger pressure on the wall.

Pressure and volume are inversely related.

We can write **Boyle's law** as:

The pressure exerted by a fixed mass of gas is inversely proportional to its volume, provided the temperature of the gas remains constant.

Note that this law relates two variables, pressure and volume, and it requires that the other two, mass and temperature, remain constant.

Boyle's law can be written as:

$$p \propto \frac{1}{V}$$

or simply:

$$pV = \text{Constant}$$

We can also represent Boyle's law as a graph, as shown in Figure 20.5. A graph of p against $\frac{1}{V}$ is a straight line passing through the origin, showing direct proportionality.

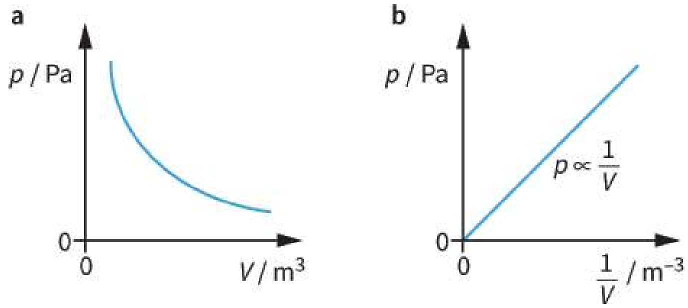

Figure 20.5: Graphical representations of the relationship between pressure and volume of a gas (Boyle's law).

For solving problems, you may find it more useful to use the equation in this form:

$$p_1V_1 = p_2V_2$$

Here, p_1 and V_1 represent the pressure and volume of the gas before a change, and p_2 and V_2 represent the pressure and volume of the gas after the change. Worked example 1 shows how to use this equation.

WORKED EXAMPLE

1 A cylinder contains 0.80 m^3 of nitrogen gas at a pressure of 1.2 atmosphere (1 atm = 1.01×10^5 Pa). A piston slowly compresses the gas to a pressure of 6.0 atm. The temperature of the gas remains constant. Calculate the final volume of the gas.

Note from the question that the temperature of the gas is constant, and that its mass is fixed (because it is contained in a cylinder). This means that we can apply Boyle's law.

Step 1 We are going to use Boyle's law in the form $p_1V_1 = p_2V_2$. Write down the quantities that you know, and that you want to find out.

$$p_1 = 1.2 \text{ atm} \quad V_1 = 0.80 \text{ m}^3$$

$$p_2 = 6.0 \text{ atm} \quad V_2 = ?$$

Note that we don't need to worry about the particular units of pressure and volume being used here, so long as they are the same on both sides of the equation. The final value of V_2 will be in dm^3 because V_1 is in m^3.

Step 2 Substitute the values in the equation, rearrange and find V_2:

$$\begin{aligned} p_1V_1 &= p_2V_2 \\ 1.2 \times 0.8 &= 6.0 \times V_2 \\ V_2 &= \frac{1.2 \times 0.8}{6.0} \\ V_2 &= 0.16 \text{ m}^3 \end{aligned}$$

So the volume of the gas is reduced to 0.16 m^3.

The pressure increases by a factor of 5, so the volume decreases by a factor of 5.

Question

6 A balloon contains 0.04 m^3 of air at a pressure of 120 kPa. Calculate the pressure required to reduce its volume to 0.025 m^3 at constant temperature.

20.5 Changing temperature

Boyle's law requires that the temperature of a gas is fixed. What happens if the temperature of the gas is allowed to change? Figure 20.6 shows the results of an experiment in which a fixed mass of gas is cooled at constant pressure. The gas contracts; its volume decreases.

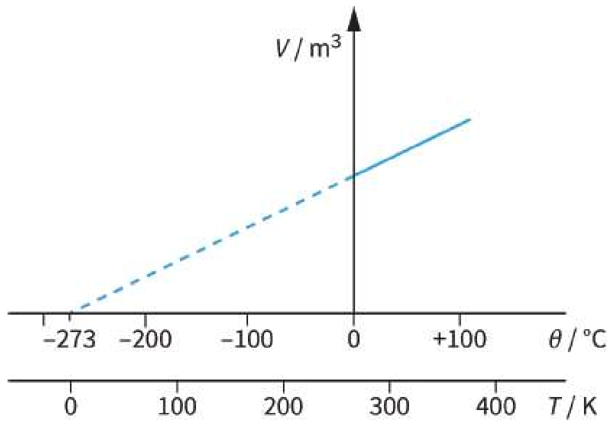

Figure 20.6: The volume of a gas decreases as its temperature decreases.

This graph does not show that the volume of a gas is proportional to its temperature on the Celsius scale. If a gas contracted to zero volume at 0 °C, the atmosphere would condense on a cold day and we would have a great deal of difficulty in breathing! However, the graph **does** show that there is a temperature at which the volume of a gas does, in principle, shrink to zero. Looking at the lower temperature scale on the graph, where temperatures are shown in kelvin (K), we can see that this temperature is 0 K, or absolute zero. (Historically, this is how the idea of absolute zero first arose.)

We can represent the relationship between volume V and thermodynamic temperature T as:

$$V \propto T$$

or simply:

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

Note that this relationship only applies to a fixed mass of gas and to constant pressure.

This relationship is an expression of **Charles's law**, named after the French physicist Jacques Charles, who in 1787 experimented with different gases kept at constant pressure.

If we combine Boyle's law and Charles's law, we can arrive at a single equation for a fixed mass of gas:

$$\frac{pV}{T} = \text{constant}$$

Shortly, we will look at the constant quantity that appears in this equation, but first we will consider the extent to which this equation applies to real gases.

KEY EQUATION

$$\frac{pV}{T} = \text{constant}$$

Fixed mass of gas.

Real and ideal gases

The relationships between p, V and T that we have considered are based on experimental observations of gases such as air, helium, nitrogen and so on, at temperatures and pressures around room temperature and pressure. In practice, if we change to more extreme conditions, such as low temperatures or high pressures, gases start to deviate from these laws as the gas atoms exert significant electrical forces on each other. For example, Figure 20.7 shows what happens when nitrogen is cooled down towards absolute zero. At first, the graph of volume against temperature follows a good straight line. However, as it approaches the temperature at which it condenses, it deviates from ideal behaviour and at 77 K it condenses to become liquid nitrogen.

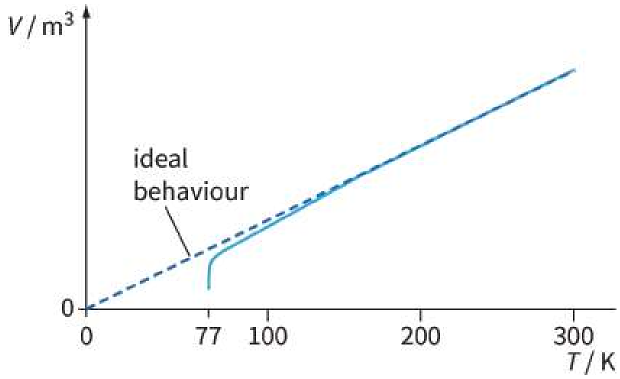

Figure 20.7: A real gas (in this case, nitrogen) deviates from the behaviour predicted by Charles's law at low temperatures.

Thus, we have to attach a condition to the relationships discussed earlier. We say that they apply to an **ideal gas**.

When we are dealing with real gases, we have to be aware that their behaviour may be significantly different from the ideal gas.

An ideal gas is thus one for which we can apply the equation:

$$\frac{pV}{T} = \text{Constant for a fixed mass of gas}$$

20.6 Ideal gas equation

So far, we have seen how p, V and T are related. It is possible to write a single equation relating these quantities that takes into account the amount of gas being considered.

We can write the equation in the following form:

$$pV = nRT$$

where n is the amount (number of moles) of an ideal gas.

Or in the form:

$$pV = NkT$$

where N is the number of molecules and k is the Boltzmann constant described later in topic 20.8.

This equation is called the **equation of state** for an ideal gas (or the **ideal gas equation)**. It relates all four of the variable quantities discussed at the beginning of this chapter. The constant of proportionality R is called the universal molar gas constant. Its experimental value is:

$$R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Note that it doesn't matter what gas we are considering–it could be a very 'light' gas like hydrogen, or a much 'heavier' one like carbon dioxide. So long as it is behaving as an ideal gas, we can use the same equation of state with the same constant R.

KEY EQUATION

equation of state:

$$pV = nRT \text{ or } pV = NkT$$

Calculating the number *n* of moles

Instead of knowing the mass of one molecule in unified atomic mass units, sometimes we may be given the molar mass (the mass of one mole) and the mass of gas we are concerned with, to find how many moles are present. To do this, we use the relationship:

$$\text{number of moles} = \frac{\text{mass(g)}}{\text{molar mass}\left(\text{g mol}^{-1}\right)}$$

For example: How many moles are there in 1.6 kg of oxygen?

$$\text{molar mass of oxygen-16} = 32\ \text{g mol}^{-1}$$

$$\begin{aligned}\text{number of moles} &= \frac{1600\ \text{g}}{32\ \text{g mol}^{-1}} \\ &= 50\ \text{mol}\end{aligned}$$

(Note that this tells us that there are 50 moles of oxygen **molecules** in 1.6 kg of oxygen. An oxygen molecule consists of two oxygen atoms – its formula is O_2 – so 1.6 kg of oxygen contains 100 moles of oxygen **atoms**.)

Now look at Worked examples 2 and 3.

WORKED EXAMPLE

2 Calculate the volume occupied by one mole of an ideal gas at room temperature (20 °C) and pressure (1.013×10^5 Pa).

Step 1 Write down the quantities given.

$p = 1.013 \times 10^5\text{Pa}$ $\quad n = 1.0$

$T = 293$ K

Hint: *Note that the temperature is converted to kelvin.*

Step 2 Substituting these values in the equation of state gives:

$$
\begin{aligned}
V &= \frac{nRT}{P} \\
&= \frac{1\times 8.31\times 293}{1.103\times 10^5} \\
&= 0.0240\ \mathrm{m}^3 \\
&= 2.40\times 10^{-2}\mathrm{m}^3 \\
&= 24.0\ \mathrm{dm}^3
\end{aligned}
$$

Hint: *1 dm = 0.1 m; hence 1* $dm^3 = 10^{-3}\ m^3$.

This value, the volume of one mole of gas at room temperature and pressure, is well worth remembering. It is certainly known by most chemists.

3 A car tyre contains 0.020 m^3 of air at 27 °C at a pressure of 3.0×10^5 Pa. Calculate the mass of the air in the tyre. (Molar mass of air = 28.8 g mol^{-1}.)

Step 1 Here, we need first to calculate the number of moles of air using the equation of state. We have:

$p = 3.0 \times 10^5$ Pa $V = 0.02\ m^3$ T = 27 °C = 300 K

Hint: *Don't forget to convert the temperature to kelvin.*

So, from the equation of state:

$$
\begin{aligned}
n &= \frac{pV}{RT} \\
&= \frac{30\times 10^5\times 0.02}{8.31\times 300} \\
&= 2.41\ \mathrm{mol}
\end{aligned}
$$

Step 2 Now we can calculate the mass of air:

mass = number of moles × molar mass

mass = 2.41 × 28.8 = 69.4 g ≈ 69 g

Questions

For the questions that follow, you will need the following value:

$R = 8.31\ \mathrm{J\ mol^{-1}\ K^{-1}}$

7 At what temperature (in K) will 1.0 mol of a gas occupy 1.0 m^3 at a pressure of 1.0×10^4 Pa?

8 Nitrogen consists of molecules N_2. The molar mass of nitrogen is 28 g mol^{-1}. For 100 g of nitrogen, calculate:

a the number of moles

b the volume occupied at room temperature and pressure (20 °C; 1.01×10^5 Pa).

9 Calculate the volume of 5.0 mol of an ideal gas at a pressure of 1.0×10^5 Pa and a temperature of 200 °C.

10 A sample of gas contains 3.0×10^{24} molecules. Calculate the volume of the gas at a temperature of 300 K and a pressure of 120 kPa.

11 At what temperature would 1.0 kg of oxygen occupy 1.0 m^3 at a pressure of 1.0×10^5 Pa? (Molar mass of O_2 = 32 g mol^{-1}.)

12 A cylinder of hydrogen has a volume of 0.100 m^3. Its pressure is found to be 20 atmospheres at 20 °C.

a Calculate the mass of hydrogen in the cylinder.

b If it were instead filled with oxygen to the same pressure, how much oxygen would it contain?

(Molar mass of H_2 = 2.0 g mol^{-1}; molar mass of O_2 = 32 g mol^{-1};

1 atmosphere = 1.01×10^5 Pa.)

20.7 Modelling gases: the kinetic model

In this chapter, we are concentrating on the macroscopic properties of gases (pressure, volume, temperature). These can all be readily measured in the laboratory. The equation:

$$\frac{pV}{T} = \text{constant}$$

is an empirical relationship. In other words, it has been deduced from the results of experiments. It gives a good description of gases in many different situations. However, an empirical equation does not **explain** why gases behave in this way. An explanation requires us to think about the underlying nature of a gas and how this gives rise to our observations.

A gas is made of particles (atoms or molecules). Its pressure arises from collisions of the particles with the walls of the container; more frequent or harder collisions give rise to greater pressure. Its temperature indicates the average kinetic energy of its particles; the faster they move, the greater their average kinetic energy and the higher the temperature.

The **kinetic theory of gases** is a theory that links these microscopic properties of particles (atoms or molecules) to the macroscopic properties of a gas. Table 20.1 shows the assumptions on which the theory is based.

On the basis of these assumptions, it is possible to use Newtonian mechanics to show that pressure is inversely proportional to volume (Boyle's law), volume is directly proportional to thermodynamic (kelvin) temperature (Charles's law), and so on. The theory also shows that the particles of a gas have a range of speeds – some move faster than others.

Learn the four assumptions of the kinetic theory shown in Table 20.1.

Assumption	Explanation/comment
A gas contains a large number of particles (atoms or molecules) moving at random that collide elastically with the walls and with each other.	Kinetic energy cannot be lost. The internal energy of the gas is the total kinetic energy of the particles.
The forces between particles are negligible, except during collisions.	If the particles attracted each other strongly over long distances, they would all tend to clump together in the middle of the container.
The volume of the particles is negligible compared to the volume occupied by the gas.	When a liquid boils to become a gas, its particles become much farther apart.
The time of collision by a particle with the container walls is negligible compared with the time between collisions.	The molecules can be considered to be hard spheres.

Table 20.1: The basic assumptions of the kinetic theory of gases.

The kinetic theory has proved to be a very powerful model. It convinced many physicists of the existence of particles long before it was ever possible to visualise them.

Molecules in a box

We can use the kinetic model to deduce an equation that relates the macroscopic properties of a gas (pressure, volume) to the microscopic properties of its molecules (mass and speed). We start by picturing a single molecule in a cube-shaped box of side l (Figure 20.8). This molecule has mass m, and is moving with speed c parallel to one side of the box (c is not the speed of light in this case). It rattles back and forth, colliding at regular intervals with the ends of the box and thereby contributing to the pressure of the gas. We are going to work out the pressure this one molecule exerts on one end of the box and then deduce the total pressure produced by all the molecules.

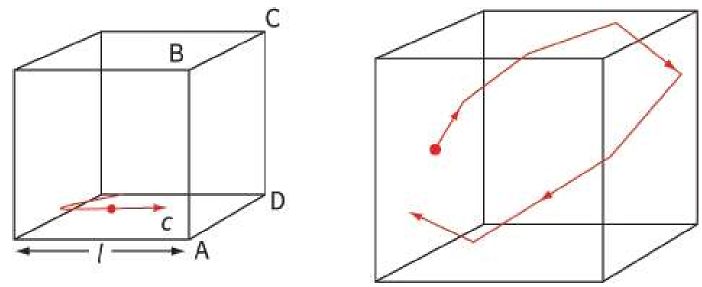

Figure 20.8: A single molecule of a gas, moving in a box.

KEY EQUATIONS

$$\text{force} = \frac{\text{change in momentum}}{\text{time taken}}$$

$$F = \frac{\Delta mv}{t}$$

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

$$P = \frac{F}{A}$$

Note: you need to be able to derive the final equation yourself.

You need to read through the proof carefully as you will need to be able to derive the final equation yourself.

The stages involved in this calculation are:

1. Find the change in momentum as a single molecule hits a wall at 90°.
2. Calculate the number of collisions per second by the molecule on a wall.
3. Find the change in momentum per second.
4. Find the pressure on the wall.
5. Consider the effect of having three directions in which the molecule can move.

As you go through the proof, see for yourself where each stage starts and finishes.

Consider a collision in which the molecule strikes side ABCD of the cube. It rebounds elastically in the opposite direction, so that its velocity is $-c$. Its momentum changes from mc to $-mc$. The change in momentum arising from this single collision is thus:

$$\begin{aligned} \text{change in momentum} &= -mc - (+mc) \\ &= -mc - mc = -2mc \end{aligned}$$

Between consecutive collisions with side ABCD, the molecule travels a distance of $2l$ at speed c. Hence:

$$\text{time between collisions with side ABCD} = \frac{2l}{c}$$

Now we can find the force that this one molecule exerts on side ABCD, using Newton's second law of motion. This says that the force produced is equal to the rate of change of momentum:

$$\begin{aligned} \text{force} &= \frac{\text{change in momentum}}{\text{time taken}} \\ &= \frac{2mc}{\left(\frac{2l}{c}\right)} \\ &= \frac{mc^2}{l} \end{aligned}$$

(We use $+2mc$ because now we are considering the force of the molecule on side ABCD, which is in the opposite direction to the change in momentum of the molecule.)

The area of side ABCD is l^2. From the definition of pressure, we have:

$$\text{pressure } p = \frac{\text{force}}{\text{area}} = \frac{\left(\frac{mc^2}{l}\right)}{l^2} = \frac{mc^2}{l^3}$$

This is for one molecule, but there is a large number N of molecules in the box. Each has a different velocity, and each contributes to the pressure. We write the average value of c^2 as $<c^2>$, and multiply by N to find the total pressure:

$$p = \frac{Nm<c^2>}{l^3}$$

But this assumes that all the molecules are travelling in the same direction and colliding with the same pair of opposite faces of the cube. In fact, they will be moving in all three dimensions equally.

If there are components c_x, c_y and c_z of the velocity in the x-, y- and z- directions then $c^2 = c_x^2 + c_y^2 + c_z^2$. There is nothing special about any particular direction and so $<c_x^2> = <c_y^2> = <c_z^2>$ and $< c_x^2 >= \frac{1}{3} < c^2 >$.

The equation for pressure worked out above involved just the component of the velocity in the x-direction and if c is the actual speed of the particle then we need to divide by 3 to find the pressure exerted.

$$p = \frac{1}{3}\left(\frac{Nm<c^2>}{l^3}\right)$$

Here, l^3 is equal to the volume V of the cube, so we can write:

$$p = \frac{1}{3}\left(\frac{Nm}{V}\right) < c^2 > \quad \text{or} \quad pV = \frac{1}{3}Nm < c^2 >$$

(Notice that, in the second form of the equation, we have the macroscopic properties of the gas – pressure and volume – on one side of the equation and the microscopic properties of the molecules on the other side.)

KEY EQUATION

Pressure of an ideal gas:

$$p = \frac{1}{3}\left(\frac{Nm}{V}\right) < c^2 > \quad \text{or} \quad pV = \frac{1}{3}Nm < c^2 >$$

Finally, the quantity Nm is the mass of all the molecules of the gas, and this is simply equal to the mass M of the gas. So $\frac{Nm}{V}$ is equal to the density ρ of the gas, and we can write:

$$p = \frac{1}{3}\rho < c^2 >$$

So the pressure of a gas depends only on its density and the mean square speed of its molecules.

A plausible equation?

It is worth thinking a little about whether the equation $p = \frac{1}{3}\left(\frac{Nm}{v}\right) < c^2 >$ seems to make sense. It should be clear to you that the pressure is proportional to the number of molecules, N. More molecules mean greater pressure. Also, the greater the mass of each molecule, the greater the force it will exert during a collision.

The equation also suggests that pressure p is proportional to the average value of the speed squared. This is because, if a molecule is moving faster, not only does it strike the container harder, but it also strikes the container more often.

The equation suggests that the pressure p is inversely proportional to the volume occupied by the gas. Here, we have deduced Boyle's law. If we think in terms of the kinetic model, we can see that if a mass of gas occupies a larger volume, the frequency of collision between the molecules and unit area of wall decreases. The equation shows us not just that pressure will be lower but that it is inversely proportional to volume.

These arguments should serve to convince you that the equation is plausible; this sort of argument cannot prove the equation.

Questions

13 Check that the SI base units on the left-hand side of the equation:

$$p = \frac{1}{3}\left(\frac{Nm}{V}\right) < c^2 >$$

are the same as those on the right-hand side.

14 The quantity *Nm* is the total mass of the molecules of the gas, i.e. the mass of the gas. At room temperature, the density of air is about 1.29 kg m^{-3} at a pressure of 10^5 Pa.

a Use these figures to deduce the value of $<c^2>$ for air molecules at room temperature.

b Find a typical value for the speed of a molecule in the air by calculating $\sqrt{< c^2 >}$. How does this compare with the speed of sound in air, approximately 330 m s^{-1}?

20.8 Temperature and molecular kinetic energy

Now we can compare the equation $p = \frac{1}{3}\left(\frac{Nm}{v}\right) < c^2 >$ with the ideal gas equation $pV = nRT$. The left-hand sides are the same, so the two right-hand sides must also be equal:

$$\frac{1}{3}Nm < c^2 >= nRT$$

We can use this equation to tell us how the absolute temperature of a gas (a macroscopic property) is related to the mass and speed of its molecules. If we focus on the quantities of interest, we can see the following relationship:

$$m < c^2 >= \frac{3nRT}{N}$$

The quantity $\frac{N}{n} = N_{\mathrm{A}}$ is the Avogadro constant, the number of particles in 1 mole. So:

$$m < c^2 >= \frac{3RT}{N_A}$$

It is easier to make sense of this if we divide both sides by 2, to get the familiar expression for kinetic energy:

$$\frac{1}{2}m < c^2 >= \frac{3RT}{2N_A}$$

The quantity $\frac{R}{N_{\mathrm{A}}}$ is defined as the **Boltzmann constant**, k. Its value is 1.38×10^{-23} J K^{-1}. Substituting k in place of $\frac{R}{N_{\mathrm{A}}}$ gives

$$\text{kinetic energy} = \frac{1}{2}m < c^2 >= \frac{3}{2}kT$$

This is the average kinetic energy E of a molecule in the gas, and since k is a constant, the thermodynamic temperature T is proportional to the average kinetic energy of a molecule.

KEY EQUATION

Boltzmann constant:

$$k = \frac{R}{N_{\mathrm{A}}}$$

The mean translational kinetic energy of an atom (or molecule) of an ideal gas is proportional to the thermodynamic temperature.

It is easier to recall this as:

$$\text{mean translational kinetic energy of atom} \propto T$$

KEY EQUATION

mean translational kinetic energy of atom $\propto T$

We need to consider two of the terms in this statement. First, we talk about **translational** kinetic energy. This is the energy that the molecule has because it is moving from one point in space to another; a molecule made of two or more atoms may also spin or tumble around, and is then said to have rotational kinetic energy – see Figure 20.9.

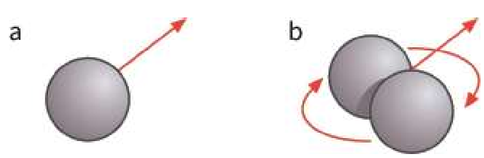

Figure 20.9: a A monatomic molecule has only translational kinetic energy. **b** A diatomic molecule can have both translational and rotational kinetic energy.

Second, we talk about **mean** (or average) kinetic energy. There are two ways to find the average kinetic energy (k.e.) of a molecule of a gas. Add up all the kinetic energies of the individual molecules of the gas and then calculate the average k.e. per molecule. Alternatively, watch an individual molecule over a period of time as it moves about, colliding with other molecules and the walls of the container and calculate its average k.e. over this time. Both should give the same answer.

The Boltzmann constant is an important constant in physics because it tells us how a property of microscopic particles (the kinetic energy of gas molecules) is related to a macroscopic property of the gas (its absolute temperature). That is why its units are joules per kelvin ($J\ K^{-1}$). Its value is very small ($1.38 \times 10^{-23}\ J\ K^{-1}$) because the increase in kinetic energy in J of a molecule is very small for each kelvin increase in temperature.

It is useful to remember the equation linking kinetic energy with temperature as 'average k.e. is three-halves *kT*'.

KEY EQUATION

$$\text{kinetic energy (of a molecule)} = \tfrac{3}{2}kT$$

Questions

15 The Boltzmann constant k is equal to $\frac{R}{N_A}$. From values of R and N_A, show that k has the value $1.38 \times 10^{-23}\ J\ K^{-1}$.

16 Calculate the mean translational k.e. of atoms in an ideal gas at 27 °C.

17 The atoms in a gas have a mean translational k.e. equal to 5.0×10^{-21} J. Calculate the temperature of the gas in K and in °C.

The root-mean-square speed

You may have wondered how the mean-square speed $< c^2 >$ compares with the mean speed $< c >$.

The exact relationship depends on the distribution of the speeds of the molecules. If all the molecules have the same speed, then $< c > = \sqrt{< c^2 >}$.

But is this always the case?

Imagine three molecules with speeds 10, 20 and 30 $m\ s^{-1}$; (very low speeds for molecules, but easier for our calculations!).

$$\text{Their mean speed } < c > = \frac{(10+20+30)}{3} = 20\ \text{m s}^{-1}$$

Their square speeds are 10^2, 20^2 and 30^2.

So, their mean-square speed

$$< c^2 > = \frac{(10^2+20^2+30^2)}{3} = 467\ \text{m}^2\text{s}^{-2}$$

In this case, $\sqrt{< c^2 >} = 22\ \text{m s}^{-1}$, which is **not** the same as the mean speed.

Similarly, the mean of the square of the speeds $< c^2 > = 467\ m^2\ s^{-2}$ is **not** the same as the square of the mean of the speeds $(< c >)^2 = 400\ m^2\ s^{-2}$ in the example.

In general, the values for $< c >$ and $\sqrt{< c^2 >}$ are similar but, because they are **not** the same, we define a special quantity called the **root-mean-square speed** $c_{r.m.s.}$.

This is the square root of the mean-square-speed; that is:

$$c_{r.m.s} = \sqrt{< c^2 >}$$

In the example, for the three molecules, $c_{r.m.s} = 22\ m\ s^{-1}$.

KEY EQUATION

$$c_{r.m.s} = \sqrt{< c^2 >}$$

Root-mean-square speed, where $c_{r.m.s}$ is the root of the mean square speed.

Questions

18 Four molecules have speeds 200, 400, 600 and 800 m s^{-1}. Calculate:

- **a** their mean speed $< c >$
- **b** the square of their mean speed $< c >^2$
- **c** their mean-square speed $< c^2 >$
- **d** their root-mean-square speed $c_{r.m.s.}$.

19 Calculate the root-mean square speed of the molecules of hydrogen at 20 °C given that each molecule of hydrogen has mass 3.35×10^{-27} kg.

Mass, kinetic energy and temperature

Since mean k.e. ∝ T, it follows that if we double the thermodynamic temperature of an ideal gas (for example, from 300 K to 600 K), we double the mean k.e. of its molecules. It doesn't follow that we have doubled their speed; because k.e. ∝ v^2, their mean speed has increased by a factor of √2.

Air is a mixture of several gases: nitrogen, oxygen, carbon dioxide, etc. In a sample of air, the mean k.e. of the nitrogen molecules is the same as that of the oxygen molecules and that of the carbon dioxide molecules. This comes about because they are all repeatedly colliding with one another, sharing their energy. Carbon dioxide molecules have greater mass than oxygen molecules; since their mean translational k.e. is the same, it follows that the carbon dioxide molecules move more slowly than the oxygen molecules.

Questions

20 Show that, if the mean speed of the molecules in an ideal gas is doubled, the thermodynamic temperature of the gas increases by a factor of four.

21 A fixed mass of gas expands to twice its original volume at a constant temperature. How do the following change?

- **a** the pressure of the gas
- **b** the mean translational kinetic energy of its molecules.

22 Air consists of molecules of oxygen (molar mass = 32 g mol^{-1}) and nitrogen (molar mass = 28 g mol^{-1}). Calculate the mean translational k.e. of these molecules in air at 20 °C. Use your answer to calculate the root-mean-square speed of each type of molecule.

23 Show that the change in the internal energy of one mole of an ideal gas per unit change in temperature is always a constant. What is this constant?

REFLECTION

Without looking at your textbook, make a list of the kinetic theory equations and write down what each term in the equations means.

Write out a proof on your own of the main kinetic theory equation using momentum change and Newton's laws.

Write out the assumptions in your own words.

Show how kinetic theory relates temperature and molecular speed.

What things might you want more help with?

SUMMARY

For an ideal gas:

$$\frac{pV}{T} = \text{constant}$$

One mole of any substance contains N_A particles (atoms or molecules):

$$N_A = \text{Avogadro constant} = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

The equation of state for an ideal gas is:

$$pV = nRT \text{ for } n \text{ moles. } pV = NRT \text{ for } N \text{ molecules}$$

There are four assumptions of the kinetic theory:

1. Molecules move at random, colliding elastically with the walls.
2. The volume of the molecules is small compared to the volume of the container.
3. There are no forces between atoms in the gas.
4. The time of each collision is small compared to the time between collisions.

From the kinetic model of a gas, we can deduce the relationship:

$pV = \frac{1}{3}Nm < c^2 >$ where $< c^2 >$ is the mean-square speed of the molecules.

The mean translational kinetic energy E of a particle (atom or molecule) of an ideal gas is proportional to the thermodynamic temperature T:

$$E = \frac{1}{2}m < c^2 > = \frac{3}{2}kT$$

The root-mean-sqare speed is the square root of the mean square speed of the molecules:

$$c_{\text{r.m.s}} = \sqrt{< c^2 >}$$

EXAM-STYLE QUESTIONS

1 A gas is enclosed inside a cylinder that is fitted with a freely moving piston.

The gas is initially in equilibrium with a volume V_1 and a pressure p. The gas is then cooled slowly. The piston moves into the cylinder until the volume of the gas is reduced to V_2 and the pressure remains at p.

What is the work done on the gas during this cooling? **[1]**

A $\frac{1}{2}p(V_2 - V_1)$

B $p(V_2 - V_1)$

C $\frac{1}{2}p(V_2 + V_1)$

D $p(V_2 + V_1)$

2 An ideal gas is made to expand slowly at a constant temperature.

Which statement is correct? **[1]**

A The heat energy transferred to the gas is zero.

B The internal energy of the gas increases.

C The work done by the gas is equal to the heat energy added to it.

D The work done by the gas is zero.

3 **a** State how many atoms there are in:

i a mole of helium gas (a molecule of helium has one atom) **[1]**

ii a mole of chlorine gas (a molecule of chlorine has two atoms) **[1]**

iii a kilomole of neon gas (a molecule of neon has one atom). **[1]**

b A container holds four moles of carbon dioxide of molecular formula CO_2. Calculate:

i the number of carbon dioxide molecules there are in the container **[1]**

ii the number of carbon atoms there are in the container **[1]**

iii the number of oxygen atoms there are in the container. **[1]**

[Total: 6]

4 A bar of gold-197 has a mass of 1.0 kg. Calculate:

a the mass of one gold atom in kg. **[1]**

b the number of gold atoms in the bar **[1]**

c the number of moles of gold in the bar. **[2]**

(An atom of gold contains 197 nucleons and has a mass of 197 u.)

[Total: 4]

5 A cylinder holds 140 m^3 of nitrogen at room temperature and pressure. Moving slowly, so that there is no change in temperature, a piston is pushed to reduce the volume of the nitrogen to 42 m^3.

a Calculate the pressure of the nitrogen after compression. **[2]**

b Explain the effect on the temperature and pressure of the nitrogen if the piston is pushed in very quickly. **[1]**

[Total: 3]

6 The atmospheric pressure is 100 kPa, equivalent to the pressure exerted by a column of water 10 m high. A bubble of oxygen of volume 0.42 cm^3 is released by a water plant at a depth of 25 m. Calculate the volume of the bubble when it reaches the surface. State any assumptions you make. **[4]**

7 A cylinder contains 4.0×10^{-2} m^3 of carbon dioxide at a pressure of 4.8×10^5 Pa at room temperature.

Calculate:

a the number of moles of carbon dioxide **[2]**

b the mass of carbon dioxide. **[2]**

(Molar mass of carbon dioxide = 44 g or one molecule of carbon dioxide has mass 44 u.)

[Total: 4]

8 Calculate the volume of 1 mole of ideal gas at a pressure of 1.01×10^5 Pa and at a temperature of 0 °C. **[2]**

9 A vessel of volume 0.20 m^3 contains 3.0×10^{26} molecules of gas at a temperature of 127 °C. Calculate the pressure exerted by the gas on the vessel walls. **[3]**

10 **a** Calculate the root-mean-square speed of helium molecules at room temperature and pressure. (Density of helium at room temperature and pressure = 0.179 kg m^{-3}.) **[3]**

b Compare this speed with the average speed of air molecules at the same temperature and pressure. **[2]**

[Total: 5]

11 A sample of neon is contained in a cylinder at 27 °C. Its temperature is raised to 243 °C.

a Calculate the kinetic energy of the neon atoms at:

i 27 °C **[3]**

ii 243 °C. **[1]**

b Calculate the ratio of the speeds of the molecules at the two temperatures. **[2]**

[Total: 6]

12 A truck is to cross the Sahara desert. The journey begins just before dawn when the temperature is 3 °C. The volume of air held in each tyre is 1.50 m^3 and the pressure in the tyres is 3.42×10^5 Pa.

a Explain how the air molecules in the tyre exert a pressure on the tyre walls. **[3]**

b Calculate the number of moles of air in the tyre. **[3]**

c By midday the temperature has risen to 42 °C.

i Calculate the pressure in the tyre at this new temperature. You may assume that no air escapes and the volume of the tyre is unchanged. **[2]**

ii Calculate the increase in the average translational kinetic energy of an air molecule due to this temperature rise. **[2]**

[Total: 10]

13 The ideal gas equation is $pV = \frac{1}{3}Nm < c^2 >$.

a State the meaning of the symbols *N*, *m* and $< c^2 >$. **[3]**

b A cylinder of helium-4 contains gas with volume 4.1×10^4 cm^3 at a pressure of 6.0×10^5 Pa and a temperature of 22 °C. You may assume helium acts as an ideal gas and that a molecule of helium-4 contains 4 nucleons, each of mass 1.66×10^{-27} kg.

Determine:

i the amount of gas in mol **[3]**

ii the number of molecules present in the gas **[2]**

iii the root-mean-square speed of the molecules. **[3]**

[Total: 11]

14 **a** State what is meant by an ideal gas. **[2]**

b A cylinder contains 500 g of helium-4 at a pressure of 5.0×10^5 Pa and at a temperature of 27 °C. You may assume that the molar mass of helium-4 is 4.0 g.

Calculate:

i the number of moles of helium the cylinder holds **[1]**

ii the number of molecules of helium the cylinder holds **[1]**

iii the volume of the cylinder. **[3]**

[Total: 7]

15 **a** One assumption of the kinetic theory of gases is that molecules undergo perfectly elastic collisions with the walls of their container.

i Explain what is meant by a perfectly elastic collision. **[1]**

ii State three other assumptions of the kinetic theory. **[3]**

b A single molecule is contained within a cubical box of side length 0.30 m. The molecule, of mass 2.4×10^{-26} kg, moves backwards and forwards parallel to one side of the box with a speed of 400 m s^{-1}. It collides elastically with one of the faces of the box, face P.

i Calculate the change in momentum each time the molecule hits face P. **[2]**

ii Calculate the number of collisions made by the molecule in 1.0 s with face P. **[2]**

iii Calculate the mean force exerted by the molecule on face P. **[2]**

[Total: 10]

16 **a** A cylinder contains 1.0 mol of an ideal gas. The gas is heated while the volume of the cylinder remains constant. Calculate the energy required to raise the temperature of the gas by 1.0 °C. **[2]**

b Calculate the root-mean-square speed of a molecule of hydrogen-1 at a temperature of 100 °C.

(Mass of a hydrogen molecule = 3.34×10^{-27} kg.) **[3]**

c Calculate, for oxygen and hydrogen at the same temperature, the ratio

$$\frac{\text{root mean square speed of a hydrogen molecule}}{\text{root mean square speed of an oxygen molecule}}$$

(Mass of an oxygen molecule = 5.31×10^{-26} kg.) **[2]**

[Total: 7]