

## 15.1 The kinetic theory of gases

Specification reference: 5.1.4

**Learning outcomes**

Demonstrate knowledge, understanding, and application of:

- amount of substance, measured in moles
- the Avogadro constant  $N_A$
- the model of the kinetic theory of gases and its assumptions
- pressure in terms of this model.

**Synoptic link**

You have met the kilogram along with the other SI base units in Topic 2.1, Quantities and units.



▲ **Figure 1:** An Avogadro Project sphere [in the centre of this measuring machine] is made of pure silicon and is the most spherical object ever made by humans – it is so perfectly spherical that if it were scaled up to the size of Earth, with a radius of 6370 km, its highest point would only be around 2 m above its lowest point

**Moving beyond the last artefact**

The kilogram remains the only SI unit defined by means of an artefact – the international prototype kilogram, kept in a vault near Paris. Several alternative options for a universal definition are currently being explored. One of these, which is gaining favour amongst the scientific community, is led by the International Avogadro Project and aims to relate the kilogram to the mass of a particular atom (Figure 1). Using painstakingly manufactured silicon spheres, the project's workers hope to define the kilogram as the mass of a precise number of silicon atoms. This approach is already used to define another SI unit, the **mole**.

**Particles and the mole**

In order to understand how gases behave, not only must we study macroscopic (large-scale) properties like mass and temperature, but we must also understand what is going on at the particle level.

We can express the number of atoms or molecules in a given volume of gas using moles (mol), the SI unit of measurement for the **amount of substance**. This is a base quantity and is different from the mass of a substance. The amount of a substance indicates the number of elementary entities (normally atoms or molecules) within a given sample of substance.

One mole is defined as the amount of substance that contains as many elementary entities as there are atoms in 0.012 kg (12 g) of carbon-12. This number is called **the Avogadro constant**,  $N_A$ , and has been measured as  $6.02 \times 10^{23}$ .

By definition, 1 mol of any substance contains  $6.02 \times 10^{23}$  individual atoms or molecules. Therefore the total number of atoms or molecules in a substance,  $N$ , is given by the equation

$$N = n \times N_A$$

where  $n$  is the number of moles of the substance.

**Molar mass**

The **molar mass**,  $M$ , of a substance is the mass of one mole of the substance. Knowing the molar mass allows us to calculate the mass  $m$  of a sample of a substance if we know the number of moles,  $n$ , and vice versa:

$$m = n \times M$$

The molar mass of an element is simple to determine from the **nucleon number** (also called the mass number). Helium-4 has a nucleon number of 4. As a result the molar mass of helium-4 is  $0.004 \text{ kg mol}^{-1}$  ( $4 \text{ g mol}^{-1}$ ). Similarly, one mole of uranium-238 would have a mass of  $0.238 \text{ kg}$  ( $238 \text{ g}$ ).

It becomes a little more complex when dealing with molecules. Nitrogen forms  $\text{N}_2$  molecules, that is, each molecule contains two nitrogen atoms, each with a molar mass of  $0.014 \text{ kg mol}^{-1}$ . The nucleon number of nitrogen is 14. Therefore the molar mass of nitrogen gas is  $0.028 \text{ kg mol}^{-1}$ .

A molecule of carbon dioxide ( $\text{CO}_2$ ) contains one carbon atom (nucleon number 12) and two oxygen atoms (nucleon number 16). Therefore the molar mass of carbon dioxide is  $0.044 \text{ kg mol}^{-1}$  ( $= 0.012 + 0.016 + 0.016$ ).

Table 1 gives the molar masses of these and some other common gases.

▼ **Table 1** Molar masses of some common gases

Substance	Elementary entities	Molar mass / $\text{kg mol}^{-1}$
hydrogen gas	$\text{H}_2$ molecules	0.002
helium gas	He atoms	0.004
oxygen gas	$\text{O}_2$ molecules	0.032
carbon dioxide gas	$\text{CO}_2$ molecules	0.044
neon gas	Ne atoms	0.020
argon gas	Ar atoms	0.040

- 1 Calculate the mass of  $4.0 \text{ mol}$  of helium gas.
- 2 Calculate the molar mass of methane ( $\text{CH}_4$ ). The molar mass of carbon is  $0.012 \text{ kg mol}^{-1}$  and the molar mass of hydrogen is  $0.001 \text{ kg mol}^{-1}$ .
- 3 Calculate the number of molecules in  $50 \text{ g}$  of carbon dioxide.

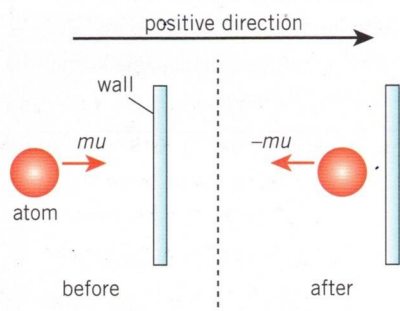
### Study tip

Mass represents the amount of matter in an object, measured in kg, whereas the amount of substance, measured in mol, indicates the number of elementary entities, such as atoms, ions, molecules, electrons, or other particles.

## The kinetic theory of gases

Studying how the atoms or molecules in a gas behave suggests basic laws relating the motion of these particles at the microscopic scale to macroscopic properties like the temperature and pressure of the gas.

The **kinetic theory of matter** is a model used to describe the behaviour of the atoms or molecules in an **ideal gas**. Real gases have complex behaviour, so in order to keep the model simple a number of assumptions are made about the atoms or molecules in an ideal gas.



**▲ Figure 2** The change in momentum of the atom is  $-2mu$  and not zero. Momentum is a vector quantity

The assumptions made in the kinetic model for an ideal gas are as follows:

- The gas contains a very large number of atoms or molecules moving in random directions with random speeds.
- The atoms or molecules of the gas occupy a negligible volume compared with the volume of the gas.
- The collisions of atoms or molecules with each other and the container walls are perfectly elastic (no kinetic energy is lost).
- The time of collisions between the atoms or molecules is negligible compared to the time between the collisions.
- Electrostatic forces between atoms or molecules are negligible except during collisions.

Using these assumptions and Newton's laws of motion, we can explain how the atoms or molecules in an ideal gas cause pressure.

The atoms or molecules in a gas are always moving, and when they collide with the walls of a container the container exerts a force on them, changing their momentum as they bounce off the wall.

When a single atom collides with the container wall elastically, its speed does not change, but its velocity changes from  $+u \text{ m s}^{-1}$  to  $-u \text{ m s}^{-1}$ . The total change in momentum is  $-2mu$  (see Figure 2).

The atom bounces between the container walls, making frequent collisions. According to Newton's second law, the force acting on the atom is  $F_{\text{atom}} = \frac{\Delta p}{\Delta t}$ , where  $\Delta p = -2mu$  and  $\Delta t$  is the time between collisions with the wall. From Newton's third law, the atom also exerts an equal but opposite force on the wall.

A large number of atoms collide randomly with the walls of the container. If the total force they exert on the wall is  $F$ , then the pressure they exert on the wall is given by  $p = \frac{F}{A}$ , where  $A$  is the cross-sectional area of the wall.

## Summary questions

- 1 Calculate the number of elementary entities (atoms or molecules) in 3.0 mol of a substance. (2 marks)
- 2 Suggest why one mole of silicon has a different mass from one mole of aluminium. (2 marks)
- 3 A molecule of mass  $5.3 \times 10^{-26} \text{ kg}$  travelling at  $500 \text{ m s}^{-1}$  collides with a container wall. It collides at right angles to the wall. Calculate the change in the momentum of this molecule. (2 marks)
- 4 Calculate the number of moles there are in a substance containing:
  - a  $2.0 \times 10^{24}$  molecules
  - b  $1.5 \times 10^{17}$  atoms
  - c  $2.0 \times 10^{24}$  molecules. (3 marks)
- 5 a The molar mass of copper is  $64 \text{ g mol}^{-1}$  calculate the number of atoms in copper of mass 1.0 kg. (2 marks)  
 b The molar mass of uranium is  $235 \text{ g mol}^{-1}$ . Calculate the mass of a single atom of uranium. (2 marks)
- 6 The density of lead is  $11340 \text{ kg m}^{-3}$ . Each lead atom has a mass of  $3.46 \times 10^{-25} \text{ kg}$ . Calculate the number of moles of lead in a lead block with a volume of  $0.20 \text{ m}^3$ . (4 marks)

# 15.2 Gas laws

Specification reference: 5.1.4

## On the rise

Weather balloons are launched into the upper atmosphere to measure changes in temperature and pressure, and air currents and atmospheric pollutants. As the balloon rises, the atmospheric pressure around it drops, causing it to expand.

The relationships between the temperature, pressure, and volume of an ideal gas can be described by a few simple **gas laws**.

### Pressure and Volume

If the temperature and mass of gas remain constant then the pressure  $p$  of an ideal gas is inversely proportional to its volume  $V$ . This can be expressed as

$$p \propto \frac{1}{V} \quad \text{or} \quad pV = \text{constant}$$

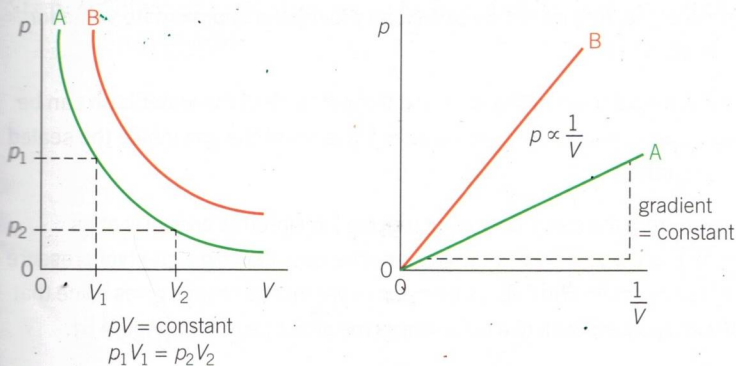
If a fixed mass of gas is kept in a sealed box, halving the volume of the box (slowly, to ensure the temperature remains constant) will compress the gas and double the pressure it exerts on the box.



### Investigating Boyle's law

The relationship between the pressure of gas and its volume at a constant temperature was investigated by 1662 by Robert Boyle. He discovered the relationship  $p \propto \frac{1}{V}$ , which is now called **Boyle's Law**.

Boyle's experiments are simple to repeat in the classroom (Figure 2). If the pressure of a pressurised gas is slowly reduced, its volume increases. The gas must be in a sealed tube to ensure the amount of gas inside the tube remains fixed.



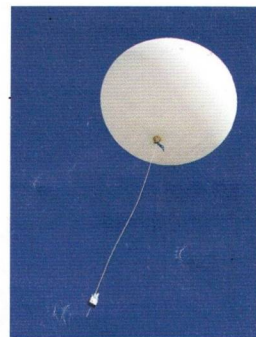
▲ **Figure 3** Pressure–volume graphs for two gases at different temperatures – the straight line through the origin in the second graph shows that  $p \propto \frac{1}{V}$

Each line on the graph relates to a gas at a specific temperature. In this case B is at a higher temperature than A. The lines are called **isotherms** as they represent how the pressure and volume are related at one fixed temperature.

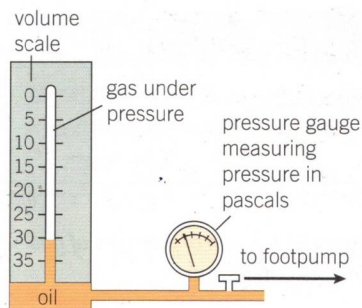
## Learning outcomes

Demonstrate knowledge, understanding, and application of:

- the equation of state of an ideal gas  $pV = nRT$ , where  $n$  is the number of moles
- techniques and procedures used to investigate  $pV = \text{constant}$  (Boyle's law) and  $\frac{p}{T} = \text{constant}$
- an estimation of absolute zero using variation of gas temperature with pressure.

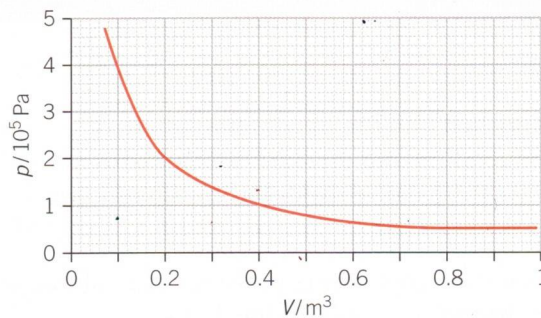


▲ **Figure 1** Weather balloons expand as they rise, eventually bursting and parachuting back to Earth



▲ **Figure 2** Apparatus for investigating how changing the volume of a gas affects the pressure of the gas (Boyle's law)

The graph in Figure 4 was produced in an investigation into Boyle's law.



▲ **Figure 4** A graph showing pressure against volume for a certain gas

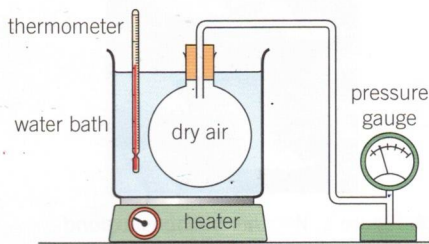
- 1 Explain why the pressure must be changed slowly.
- 2 Use the graph in Figure 4 to show that  $pV = \text{constant}$ .

## Pressure and temperature

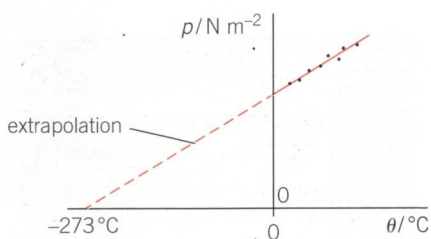
If the volume and mass of gas remain constant, the pressure  $p$  of an ideal gas is directly proportional to its absolute (thermodynamic) temperature  $T$  in kelvin. This relationship can be expressed as

$$p \propto T \quad \text{or} \quad \frac{p}{T} = \text{constant}$$

For a fixed mass of gas in a sealed container, doubling the temperature (say from 100 K to 200 K) will double the pressure the gas exerts on the container walls.



▲ **Figure 5** Apparatus used to determine absolute zero through investigating how the temperature of a gas affects its pressure



▲ **Figure 6** A graph of pressure of gas against its temperature



### Estimating absolute zero

Because the expression above requires the absolute temperature  $T$ , an investigation into the relationship between the pressure of a fixed volume and mass of gas and its temperature can provide an approximate value for absolute zero.

With the set-up shown in Figure 5, the temperature of the water bath can be increased and the resulting increase in pressure of the gas inside the sealed vessel recorded.

At absolute zero the particles are not moving (the internal energy is at its minimum) so the pressure of the gas must be zero. Plotting a graph of pressure against temperature  $\theta$  in Celsius from the experimental results gives a line that can be extrapolated back to a point where the pressure is zero (Figure 6).

- 1 Explain why the volume of the gas must remain fixed.

- 2 The data in Table 1 was collected in an investigation into the pressure of a fixed mass and volume of gas as temperature changed.
- Plot a graph of pressure  $p$  of the gas against temperature  $\theta$  in  $^{\circ}\text{C}$  (range of  $\theta$ :  $-300^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ ). Use your graph to determine a value for absolute zero.
  - On your graph, sketch a second line to show the pattern you would expect if the experiment were repeated using the same mass of gas at a larger volume.

▼ **Table 1** Table showing the variation of pressure with temperature for a fixed mass of gas at a constant volume

$\theta/^{\circ}\text{C}$	$p/10^5\text{ Pa}$
10	1.41
20	1.45
30	1.51
40	1.57
50	1.61
60	1.66
70	1.70

## Combining the gas laws

By combining the two previously described gas laws we can show that for an ideal gas

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

If the conditions are changing from an initial state to a final state this can be written as

$$\frac{p_{\text{initial}} V_{\text{initial}}}{T_{\text{initial}}} = \frac{p_{\text{final}} V_{\text{final}}}{T_{\text{final}}} \quad \text{or simply} \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

### Worked example: Volume of a weather balloon

A weather balloon with a volume of  $2.0\text{ m}^3$  is launched on a day when the atmospheric pressure is  $101\text{ kPa}$  and the temperature is  $20^{\circ}\text{C}$  at ground level. It rises to a level where the air pressure is 20% of the pressure on the ground and the air temperature is  $-15^{\circ}\text{C}$ . Calculate the volume of the balloon at this altitude.

**Step 1:** First convert the temperatures into kelvin.

$$20^{\circ}\text{C} = 293\text{ K} \quad \text{and} \quad -15^{\circ}\text{C} = 258\text{ K}$$

**Step 2:** Select the equation you need and rearrange it to find the final volume.

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$V_2 = \frac{p_1 V_1 T_2}{p_2 T_1}$$

Substituting in known values in SI units gives

$$V_2 = \frac{1.01 \times 10^5 \times 2.0 \times 258}{0.2 \times 1.01 \times 10^5 \times 293} = 8.8\text{ m}^3 \quad (2 \text{ s.f.})$$

### Study tip

Remember, temperatures must be stated in kelvin when using ideal gas equations.

## The equation of state of an ideal gas

For one mole of an ideal gas, the constant in the combined relationship above is called the **molar gas constant**,  $R$ , and is equal to  $8.31\text{ J K}^{-1}\text{ mol}^{-1}$ . For  $n$  moles of gas the equation becomes

$$\frac{pV}{T} = nR \quad \text{or} \quad pV = nRT$$

This relationship is called the **equation of state of an ideal gas**. The molar gas constant is the same for all gases, as long as we can treat them as being ideal, so the equation above can be applied to trapped air in the laboratory or to helium in the atmosphere of distant stars.



### Worked example: A pressurised container

A  $3.50 \text{ m}^3$  pressurised container contains 425 moles of gas at  $25.0^\circ\text{C}$ . Calculate the pressure of the gas inside the container.

**Step 1:** Convert the temperature into kelvin.

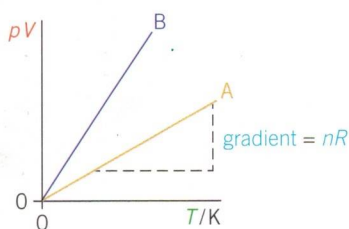
$$25.0^\circ\text{C} = 298 \text{ K}$$

**Step 2:** Select the equation you need and rearrange it to make the pressure the subject.

$$pV = nRT, \text{ hence } p = \frac{nRT}{V}$$

Substitute in known values and calculating the pressure of the gas inside the container.

$$p = \frac{425 \times 8.31 \times 298}{3.50} = 3.00 \times 10^5 \text{ Pa (3 s.f.)}$$



**▲ Figure 7** A graph of  $pV$  against  $T$  for a fixed amount of gas produces a straight line through the origin. Gas B produces a steeper line than gas A, as gas B contains a greater number of moles than A.

### Graphical analysis

A graph of  $pV$  against  $T$  for a fixed amount of gas produces a straight line through the origin ( $pV \propto T$ ). By considering the general equation of a straight line,  $y = mx + c$ , and the equation of state of an ideal gas,  $pV = nRT$ , we can see the gradient of the graph is equal to  $nR$ . The greater the number of moles of gas, the steeper the line becomes.

## Summary questions

- 1 A sealed container contains 60 moles of gas at temperature of  $250 \text{ K}$  and a pressure of  $60\,000 \text{ Pa}$ . Calculate the volume of the container. (2 marks)
- 2 State the effect on the pressure of a fixed mass of gas at constant temperature if the volume of gas is:
  - a doubled;
  - b reduced to a third of its original value. (2 marks)
- 3 A fixed mass and volume of gas initially at a temperature of  $20^\circ\text{C}$  and pressure of  $300 \text{ kPa}$  is heated to  $100^\circ\text{C}$ . Calculate the change in pressure. (4 marks)
- 4 Using the values from Figure 4, plot a graph of  $p$  against  $\frac{1}{V}$ . Use this graph to determine the number of moles of gas used in the experiment. The temperature of the gas during the experiment was a constant  $20^\circ\text{C}$ . (4 marks)
- 5 Standard conditions for temperature and pressure (STP) are  $0^\circ\text{C}$  and  $100 \text{ kPa}$ . Calculate the volume occupied by  $1 \text{ mol}$  of air at STP. (3 marks)
- 6 Calculate the number of particles in a gas sample if, when the sample is in a sealed container of volume  $0.25 \text{ m}^3$  at a temperature of  $15^\circ\text{C}$ , the pressure inside the container is  $50 \text{ kPa}$ . (4 marks)
- 7 Use the equation of state of an ideal gas to estimate the amount of air in your lungs. (4 marks)

## 15.3 Root mean square speed

Specification reference: 5.1.4



### What happens when average velocity = $0 \text{ m s}^{-1}$ ?

We have already seen how the particles (atoms or molecules) in a gas move in random directions at different speeds. If we calculated the average velocity of the particles in a gas, because velocity is a vector the average would be  $0 \text{ m s}^{-1}$ . All the velocities of such a large number of particles would simply cancel out. So in order to describe the typical motion of particles inside the gas, we use a different measure, the **root mean square speed** (r.m.s. speed).

#### r.m.s. speed

In order to determine the r.m.s. speed, the velocity,  $c$ , of each atom or molecule in the gas is squared,  $c^2$ . Then the average of this squared velocity is found for all the gas particles, giving  $\bar{c^2}$  – the bar is a symbol for ‘mean’. This is the **mean square speed** of the gas particles. Finally the square root of this value is taken to give the r.m.s. speed, written as  $\sqrt{\bar{c^2}}$  or  $c_{\text{r.m.s.}}$ .

#### Learning outcomes

Demonstrate knowledge, understanding, and application of:

- the equation  $pV = \frac{1}{3}Nmc^2$  relating the number of particles and the mean square speed
- root mean square speed and mean square speed.

#### Worked example: Average speeds

A very small sample of gas contains just four molecules moving in one line. Their velocities in  $\text{m s}^{-1}$  are:  $-450$ ,  $-50$ ,  $100$ ,  $400$ . Calculate the mean velocity, the mean speed  $\bar{c}$ , and the r.m.s. speed.

**Step 1:** For the mean velocity, you must take account of the signs of the velocities, because they are vectors.

$$\text{mean velocity} = \frac{(-450 - 50 + 100 + 400)}{4} = 0 \text{ m s}^{-1}$$

**Step 2:** Speed is a scalar, so mean speed  $\bar{c}$  is calculated by ignoring the negative signs.

$$\bar{c} = \frac{(450 + 50 + 100 + 400)}{4} = 250 \text{ m s}^{-1}$$

**Step 3:** To determine the r.m.s. speed, first square the speeds, then determine the mean.

$$\begin{aligned} \text{mean square speed} = \\ \frac{(202\,500 + 2\,500 + 100\,000 + 160\,000)}{4} = 116\,250 \text{ m}^2 \text{ s}^{-2} \end{aligned}$$

$$c_{\text{r.m.s.}} = \sqrt{116\,250} = 340 \text{ m s}^{-1} \text{ (2 s.f.)}$$

The average speed  $\bar{c}$  is not the same as the r.m.s. speed.

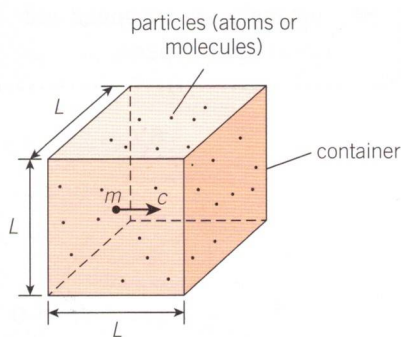


### Pressure at the microscopic level

The reason for our interest in r.m.s. speed is that it appears in the equation for the pressure and volume of a gas,

$$pV = \frac{1}{3}Nmc^2$$

where  $p$  is the pressure exerted by the gas,  $V$  is the volume of the gas,  $N$  is the number of particles in the gas,  $m$  is the mass of each particle and  $c^2$  is the mean square speed of the particles.



▲ **Figure 1** Gas particles (atoms or molecules) in a container



#### Derivation of $pV = \frac{1}{3}Nmc^2$

The equation  $pV = \frac{1}{3}Nmc^2$  can be derived by considering how the movement of atoms or molecules of gas inside a sealed box gives rise to pressure.

Consider a single gas particle (atom or molecule) making repeated collisions with a container wall. The container is a cube with sides  $L$ . The gas particle has mass  $m$  and velocity  $c$ . It hits the surface of the wall at right angles.

The elastic collision results in a change in momentum of magnitude  $2mc$  (see Topic 15.1, The kinetic theory of gases). The time  $t$  between collisions is the total distance covered by the particle divided by its speed. Therefore  $t = \frac{2L}{c}$ . According to Newton's second and third laws, the force exerted by the particle on the wall is:

$$\text{force} = \frac{\Delta p}{\Delta t} = 2mc \times \frac{c}{2L} = \frac{mc^2}{L}$$

If there are  $N$  particles in the container moving randomly, the average force exerted by each particle must be  $\frac{mc^2}{L}$ , where  $c^2$  is the mean square speed of the particles.

On average, because of the random motion of the gas particles, about  $\frac{1}{3}$  of the particles will be moving between two opposite faces of the container. Consequently the total force on one container wall of cross-sectional area  $L^2$  due to collisions from all of the particles must be

$$\text{force} = \frac{mc^2}{L} \times N \times \frac{1}{3} = \frac{Nmc^2}{3L}$$

Finally, the pressure  $p$  exerted by the gas must equal to the total force exerted by all the particles divided by the cross-sectional area of the wall. Therefore

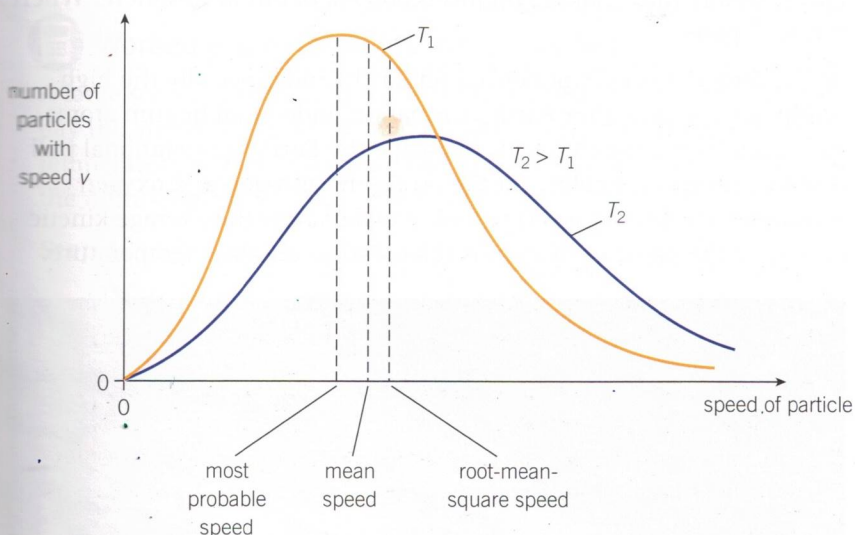
$$p = \frac{Nmc^2}{3L} \times \frac{1}{L^2} = \frac{Nmc^2}{3L^3} = \frac{Nmc^2}{3V}$$

where  $V$  is the volume of the container. Therefore  $pV = \frac{1}{3}Nmc^2$ .

- 1 Explain why, when considering the large number of particles in a sample of gas, it is a fair assumption that there must be about  $\frac{1}{3}$  of the particles moving between two opposite faces of the container.
- 2 State the other ideal gas assumptions required for this derivation.

### Distribution of particle speeds at different temperatures

The r.m.s. speed provides a useful way to describe the motion of the particles in a gas, but it is important to remember that it is an average. At any temperature, the random motion of the particles means that some are travelling very fast, whilst others are barely moving. The range of speeds of the particles in a gas at a given temperature is known as the **Maxwell-Boltzmann distribution**, shown in Figure 2.



▲ **Figure 2** The spread of speeds of particles in a gas is called the Maxwell-Boltzmann distribution, and is broader at the high temperature  $T_2$  than at the low temperature  $T_1$

Changing the temperature of the gas changes the distribution. The hotter the gas becomes, the greater the range of speeds. The most common (modal) speed and the r.m.s. speed increase, and the distribution becomes more spread out.

### Summary questions

- 1 Calculate the mean speed  $\bar{c}$ , mean squared speed  $\overline{c^2}$ , and r.m.s. speed  $c_{\text{r.m.s.}}$  of a small group of atoms with the following velocities:  $+100 \text{ m s}^{-1}$ ,  $-200 \text{ m s}^{-1}$ ,  $+150 \text{ m s}^{-1}$ ,  $-50 \text{ m s}^{-1}$ . (3 marks)
- 2 Describe how the speeds of the particles in a gas change as the temperature of the gas increases. (2 marks)
- 3 A gas cylinder contains nitrogen at a pressure of 800 kPa. The cylinder contains  $4.0 \times 10^{25}$  molecules and each molecule has a mass of  $4.7 \times 10^{-26} \text{ kg}$ . The r.m.s. speed of the molecules is  $450 \text{ m s}^{-1}$ . Calculate the volume of the cylinder. (3 marks)
- 4 Calculate the pressure inside the cylinder in question 3 if the r.m.s. speed of the molecules inside the cylinder increases to  $600 \text{ m s}^{-1}$ . (3 marks)
- 5 One mole of oxygen has a mass of 0.032 kg. An oxygen cylinder has a volume of  $0.020 \text{ m}^3$  at a pressure of 140 kPa. It contains 2.0 moles of oxygen. Calculate:
  - a the number of molecules inside the cylinder
  - b the mass of each molecule
  - c the r.m.s. speed of the oxygen molecules in the cylinder. (6 marks)

# 15.4 The Boltzmann constant

Specification reference: 5.1.4

## Learning outcomes

Demonstrate knowledge, understanding, and application of:

- the Boltzmann constant,  $k = \frac{R}{N_A}$
- $pV = NkT$ ,  $\frac{1}{2}mc^2 = \frac{3}{2}kT$
- internal energy of an ideal gas.

## Where is all the helium?

Helium is the second most abundant element in the universe. It makes up about 24% of the known mass of the universe, yet on Earth it is exceptionally rare, making up just 0.0005% of our atmosphere. Where has it all gone?

At the temperatures experienced on Earth, and especially the high temperatures soon after Earth's formation, individual helium atoms can reach high enough speeds to escape the Earth's gravitational pull and fly into space. Luckily for life on Earth, nitrogen and oxygen molecules are not so fast. This topic explains how the average kinetic energy of the particles in a gas is related to its absolute temperature.



▲ **Figure 1** Our atmosphere is approximately 78% nitrogen ( $N_2$ ), 21% oxygen ( $O_2$ ), and 1% argon (Ar), with other gases making up significantly less than 1% (carbon dioxide,  $CO_2$ , is the next highest, making up 0.04% at current levels)

## The Boltzmann constant

Ludwig Boltzmann was an Austrian physicist, whose greatest achievement was arguably his work on statistical mechanics. He applied Newtonian mechanics to gas particles in order to model the behaviour of gases. He was able to explain how the microscopic properties of particles in substances relate to the macroscopic properties of the gas, including temperature and pressure.

The **Boltzmann constant**,  $k$ , is named in his honour. As you will see later, it is used to relate the mean kinetic energy of the atoms or molecules in gas to the gas temperature. The Boltzmann constant is equal to the molar gas constant  $R$  divided by the Avogadro constant  $N_A$ :

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

## A second equation of state of an ideal gas

We can use the Boltzmann constant to express the equation of state of an ideal gas in another way. You can substitute the definition of  $k$  into the ideal gas equation  $pV = nRT$  to give  $pV = nkN_A T$

The number of particles in the gas sample,  $N$ , is equal to  $n \times N_A$ .  
Therefore  $pV = NkT$ .



### Worked example: Moles in the classroom

A large school classroom has a volume of  $600 \text{ m}^3$ . On a typical day the atmospheric pressure in the classroom is  $101 \text{ kPa}$  and the temperature is  $20^\circ\text{C}$ . Calculate the number of particles of gas and the number of moles of gas inside the classroom.

**Step 1:** Select the appropriate equation and rearrange for  $N$ .

$$pV = NkT \quad \text{or} \quad N = \frac{pV}{kT}$$

$$N = \frac{1.01 \times 10^5 \times 600}{1.38 \times 10^{-23} \times 293} = 1.49 \dots \times 10^{28} \text{ particles}$$

**Step 2:** Use  $N = n \times N_A$  to calculate the number of moles.

$$n = \frac{N}{N_A} = 2.5 \times 10^4 \text{ mol (2 s.f.)}$$

## Mean kinetic energy and temperature

By combining  $pV = \frac{1}{3}Nmc^2$  and  $pV = NkT$ , we can derive an expression which directly relates the mean kinetic energy of particles in a gas to the absolute temperature of the gas.

$$\frac{1}{3}Nmc^2 = NkT$$

The number of particles  $N$  is a constant and can be cancelled.

$$\frac{1}{3}mc^2 = kT$$

The left-hand side of the equation can be rewritten as  $\frac{1}{3}mc^2 = \frac{2}{3} \times \frac{1}{2} \times mc^2$ , which gives

$$\frac{2}{3} \times \left( \frac{1}{2}mc^2 \right) = kT$$

Rearranging gives  $\frac{1}{2}mc^2 = \frac{3}{2}kT$

The expression  $\frac{1}{2}mc^2$  is the mean average kinetic energy of the particles in the gas. Since all other values are constant,

$$E_k \propto T$$

This only applies if the temperature is measured in kelvin. Doubling the absolute temperature from  $50 \text{ K}$  to  $100 \text{ K}$  will double the average kinetic energy of the particles (atoms or molecules) in the gas.

## Synoptic link

You have met the equation  $N = n \times N_A$  in Topic 15.1, The kinetic theory of gases.

## Study tip

All gas atoms and molecules have the same mean kinetic energy  $E_k$  at a given temperature, with

$$E_k = \frac{3}{2}kT$$

or

$$E_k = (2.07 \times 10^{-23})T$$



### Worked example: The speed of a helium atom

A helium atom has a mass of  $6.64 \times 10^{-27}$  kg. Calculate the r.m.s. speed of helium atoms in a gas at a temperature of  $15.0^\circ\text{C}$ .

**Step 1:** Convert the temperature into kelvin:  $15.0^\circ\text{C} = 288\text{ K}$

**Step 2:** Rearrange the relationship  $\left(\frac{1}{2}m\overline{c^2}\right) = \frac{3}{2}kT$  to make  $\overline{c^2}$  the subject.

$$m\overline{c^2} = 3kT$$

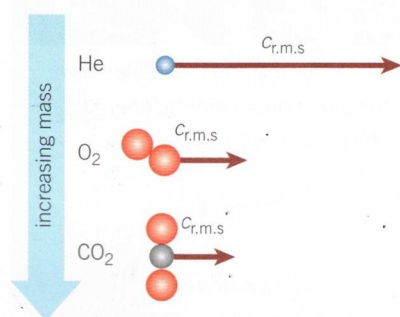
$$\overline{c^2} = \frac{3kT}{m}$$

Take the square root to give  $c_{\text{r.m.s.}} = \sqrt{\frac{3kT}{m}}$

Finally, substitute in the values in SI units

$$c_{\text{r.m.s.}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 288}{6.64 \times 10^{-27}}} = 1.34 \times 10^3 \text{ m s}^{-1} \text{ (3 s.f.)}$$

The r.m.s. speed of the helium atom is about  $1.3\text{ km s}^{-1}$ .



**▲ Figure 2** The kinetic energy of the particles in different gases is the same at a given temperature, but their r.m.s. speeds vary, with lighter particles moving much faster

### Particle speeds at different temperatures

At a given temperature the atoms or molecules in different gases have the same average kinetic energy. The oxygen molecules and helium atoms around you, in spite of their different masses, have the same mean kinetic energy. However, as the particles have different masses their r.m.s. speeds will be different.

This explains why there is very little helium in the Earth's atmosphere. Helium atoms have a very small mass, which in turns means higher r.m.s. speeds. According to the Maxwell-Boltzmann distribution, some helium atoms have greater speeds than the r.m.s. speed. Over time, these faster-moving helium atoms have escaped from the Earth's atmosphere. The escape velocity for the Earth is about  $11\text{ km s}^{-1}$ .

### The internal energy of an ideal gas

The internal energy of a gas is the sum of the kinetic and potential energies of the particles inside the gas. One of the assumptions of an ideal gas (Topic 15.1) states that the electrostatic forces between particles in the gas are negligible except during collisions. This means that there is no electrical potential energy in an ideal gas. All the internal energy is in the form of the kinetic energy of the particles. Doubling the temperature of an ideal gas doubles the average kinetic energy of the particles inside the gas and therefore also doubles its internal energy.

## Summary questions

- Describe what happens to the absolute temperature of a gas if the r.m.s. speed of the particles in the gas:
  - increases
  - doubles
  - increases by a factor of 5. (5 marks)
- Show that the Boltzmann constant  $k$  has a value of  $1.38 \times 10^{-23} \text{ J K}^{-1}$ . (2 marks)
- A gas canister has a volume of  $0.50 \text{ m}^3$ . The pressure inside the canister is  $450 \text{ kPa}$  and the temperature is  $18^\circ\text{C}$ . Calculate the number of particles of gas and the number of moles of gas inside the canister. (4 marks)
- Explain why doubling the temperature of a real gas does not double the internal energy of the gas. (2 marks)
- Show that the units of the Boltzmann constant are  $\text{J K}^{-1}$ . (2 marks)
- An oxygen molecule ( $\text{O}_2$ ) has a mass of  $5.3 \times 10^{-26} \text{ kg}$ . Calculate the r.m.s. speed of an oxygen molecule at room temperature ( $20^\circ\text{C}$ ). (4 marks)
- Compare the kinetic energy and the r.m.s. speed at room temperature of a helium atom of mass  $6.6 \times 10^{-27} \text{ kg}$  with your answer to question 6. (4 marks)