

### **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.
- 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.

### **Fast molecules:**

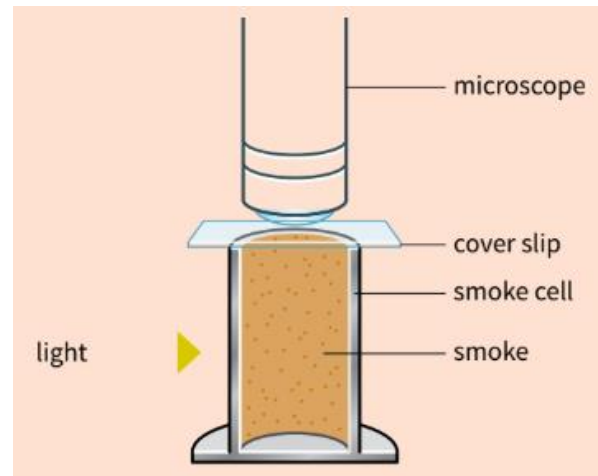
- For air at standard temperature and pressure (STP,  $-0^{\circ}\text{C}$  and 100 kPa), the average speed of the molecules is about  $400\text{ms}^{-1}$ .
- At any moment, some are moving faster than this and others more slowly.
- If we could follow the movement of a single air molecule, we would find 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  $330\text{ms}^{-1}$  at STP).
- Very fast-moving particles can easily escape from the Earth's gravitational field.
- The required escape velocity is about  $11\text{ km s}^{-1}$ .
- Since we still have an atmosphere, on average the air molecules must be moving much more slowly than this value.

### Path of a particle:

- The erratic motion of particles in water that Brown observed comes about because the particles are constantly bombarded by the much smaller, faster water molecules.
- This motion came to be known as Brownian motion, and it can be observed in both liquids and gases.
- Figure shows the sort of path followed by a particle showing Brownian motion. In fact, this is from a scientific paper by the French physicist Jean Perrin, published in 1911.
- He was looking at the movement of a single pollen grain suspended in water.
- He recorded its position every 30 s; the grid spacing is approximately  $3\mu\text{m}$ . From this he could deduce the average speed of the grain and hence work out details of the movement of water molecules.



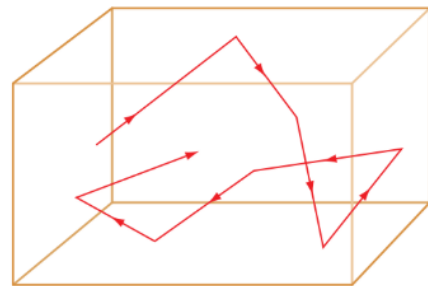
- The oxygen and nitrogen molecules that make up most of the air are far too small to see; they are much smaller than the wavelength of light.
- To observe the effect of the air molecules we have to look at something bigger.
- In this experiment, the smoke cell contains air into which a small amount of smoke has been introduced.
- The cell is lit from the side, and the microscope is used to view the smoke particles.
- The smoke particles show up as tiny specks of reflected light, although they are too small for any detail of their shape to be seen.
- What is noticeable is the way they move.
- If you can concentrate on a single particle, you will see that it follows a somewhat jerky and erratic path.
- This is a consequence of the repeated collisions between the smoke particles and air molecules.
- The erratic motion of the smoke particle provides direct evidence that the air molecules must:
  - be moving
  - also have haphazard motion.
- Since the air molecules are much smaller than the smoke grain, we can deduce that they must be moving much faster than the smoke grain if they are to affect it in this way.



(You may observe that all of the smoke particles in your field of view have a tendency to travel in one particular direction. This is a consequence of convection currents in the air. Also, you may have to adjust the focus of the microscope to keep track of an individual particle, as it moves up or down in the cell.)

### 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 000Pa.
- The surface area of a typical person is 2.0m<sup>2</sup>.
- Hence the force exerted on a person by the atmosphere is about 200 000N.
- 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 22.5 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.

## **Measuring gases:**

We are going to picture a container of gas, such as the box shown in [Figure](#).

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.

### **Pressure**

This is the normal force exerted per unit area by the gas on the walls of the container.

We saw in [in previous chapters](#) that this pressure is the result of molecular collisions with the walls of the container.

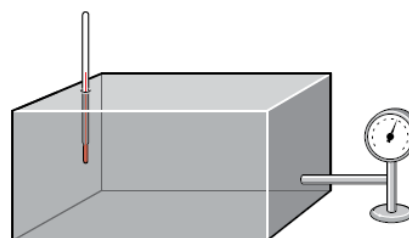
Pressure is measured in pascals, Pa ( $1 \text{ Pa} = 1 \text{ N m}^{-2}$ ).

### **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:

$$T (\text{K}) = \vartheta (^\circ\text{C}) + 273.15$$



### **Volume**

This is a measure of the space occupied by the gas. Volume is measured in m<sup>3</sup>.

### **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 defined as follows:

One mole of any substance is the amount of that substance which contains the same number of particles

as there are in 0.012 kg of carbon-12. (In this definition, 'particles' may be atoms, molecules, ions, etc.)

(In this definition, 'particles' may be atoms, molecules, ions, etc.)

One mole of any substance has a mass in grams which is numerically equal to the relative atomic or molecular mass of the substance.

For example, one mole of oxygen ( $O_2$ ) has a mass of about 32 g.

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 experimental value for  $N_A$  is  $6.02 \times 10^{23} \text{ mol}^{-1}$ .

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

10 mol of carbon contains  $10 \times 6.02 \times 10^{23} = 6.02 \times 10^{24}$  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.

### 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, its pressure increases and its volume decreases.
- 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:

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

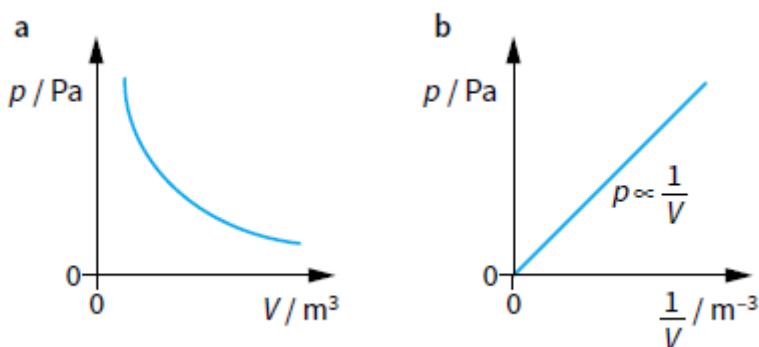
or simply:

$$pV = \text{constant}$$

- We can also represent Boyle's law as a graph, as shown in.
- A graph of  $p$  against  $1/V$  is a straight line passing through the origin, showing direct proportionality.
- For solving problems, you may find it more useful to use the equation in this form:

$$p_1 V_1 = p_2 V_2$$

- 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.

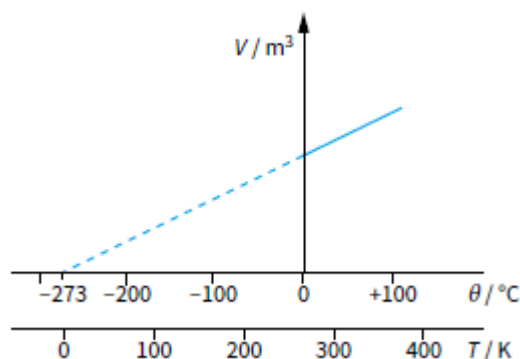




### Changing temperature:

- 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 22.8 shows the results of an experiment in which a fixed mass of gas is cooled at constant pressure.



- The gas contracts; its volume 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.
- The relationship above 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.

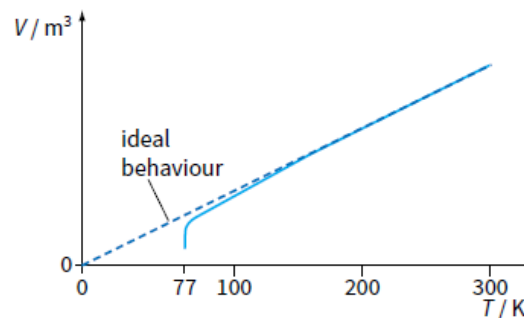
- If we combine Boyle's law and Charles's law, we can arrive at a single equation for a fixed mass of gas:

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

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

### Real and ideal gases:

- The relationships between  $p$ ,  $V$  and  $T$  that we have considered above are based on experimental observations of gases such as air, helium, nitrogen, etc., 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 22.9](#) 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.
- Thus we have to attach a condition to the relationships discussed above.
- 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 equation:



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

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

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

for a fixed mass of gas.

### 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 which takes into account the amount of gas being considered.
- If we consider  $n$  moles of an ideal gas, we can write the equation in the following form:

$$pV = nRT$$

- This equation is called the **ideal gas equation** or the **equation of state** for an ideal gas.
- 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  $R$ .

### Calculating the number $n$ of moles:

- Sometimes we know the mass of gas we are concerned with, and then we must find how many moles this represents.
- To do this, we use the relationship:

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

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

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

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

- (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  $\text{O}_2$  – so 1.6 kg of oxygen contains 100 moles of oxygen atoms.)

## 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 which links these microscopic properties of particles (atoms or molecules) to the macroscopic properties of a gas.

- **Table** 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.

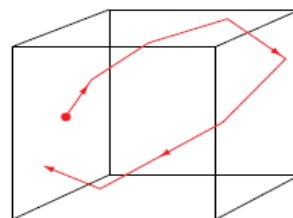
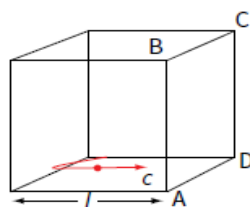
Assumption	Explanation/comment
A gas contains a very large number of particles (atoms or molecules).	A small 'cube' of air can have as many as $10^{20}$ molecules.
The forces between particles are negligible, except during collisions.	If the particles attracted each other strongly over long distances, they would all tend to clump together in the middle of the container. The particles travel in straight lines between collisions.
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.
Most of the time, a particle moves in a straight line at a constant velocity. The time of collision with another particle or with the container walls is negligible compared with the time between collisions.	The particles collide with the walls of the container and with each other, but for most of the time they are moving with constant velocity.
The collisions of particles with each other and with the container are perfectly elastic, so that no kinetic energy is lost.	Kinetic energy cannot be lost. The internal energy of the gas is the total kinetic energy of the particles.

- The theory also shows that the particles of a gas have a range of speeds – some move faster than others.

- Things are different when a gas is close to condensing.
- At temperatures a little above the boiling point, the molecules of a gas are moving more slowly and they tend to stick together – a liquid is forming.
- So we cannot consider them to be moving about freely, and the kinetic theory of gases must be modified.
- This is often how physics progresses.
- A theory is developed which explains a simple situation.
- Then the theory is modified to explain more complex situations.
- 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 which 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  $l$ .
- 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.
- 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:

$$\text{force} = \frac{\text{change in momentum}}{\text{time taken}} = \frac{2mc}{2l/c} = \frac{mc^2}{l}$$



- (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:

$$\text{pressure} = \frac{\text{force}}{\text{area}} = \frac{mc^2 / l}{l^2} = \frac{mc^2}{l^3}$$

- 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  $\langle c^2 \rangle$ , and multiply by  $N$  to find the total pressure:

$$\text{pressure } p = \frac{Nm\langle c^2 \rangle}{l^3}$$

- 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, so we need to divide by 3 to find the pressure exerted.

$$\text{pressure } p = \frac{1}{3} \frac{Nm\langle c^2 \rangle}{l^3}$$

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

$$p = \frac{1}{3} \frac{Nm}{V} \langle c^2 \rangle \quad \text{or} \quad pV = \frac{1}{3} Nm\langle c^2 \rangle$$

- (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.)
- 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  $\rho$  of the gas, and we can write:

$$p = \frac{1}{3} \rho \langle c^2 \rangle$$

- 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  $pV = \frac{1}{3}Nm\langle c^2 \rangle$  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 molecules will spend more time in the bulk of the gas, and less time colliding with the walls.
- So, the pressure will be lower.
- These arguments should serve to convince you that the equation is plausible; this sort of argument cannot prove the equation.

### Temperature and molecular kinetic energy:

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

$$\frac{1}{3}Nm\langle c^2 \rangle = nRT$$

- 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:

$$m\langle c^2 \rangle = \frac{3nRT}{N}$$

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

$$m\langle c^2 \rangle = \frac{3RT}{N_A}$$

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

$$\frac{1}{2}m\langle c^2 \rangle = \frac{3RT}{2N_A}$$

- The quantity  $R/N_A$  is defined as the **Boltzmann constant**,  $k$ .
- Its value is  $1.38 \times 10^{-23} \text{ J K}^{-1}$ .
- Substituting  $k$  in place of  $R/N_A$  gives

$$\frac{1}{2}m\langle c^2 \rangle = \frac{3kT}{2}$$

- The quantity  $\frac{1}{2}m\langle c^2 \rangle$  is the average kinetic energy  $E$  of a molecule in the gas, and  $k$  is a constant.

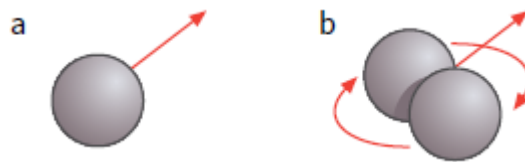
- Hence the thermodynamic temperature  $T$  is proportional to the average kinetic energy of a molecule.

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:

mean translational kinetic energy of atom  $\propto T$

- We need to consider two of the terms in this statement.
- Firstly, we talk about translational kinetic energy.
- This is the energy that the molecule has because it is moving along; 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](#)
- Secondly, we talk about mean (or average) translational kinetic energy.
- There are two ways to find the average translational 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 ( $\text{J K}^{-1}$ ).
- Its value is very small ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ ) 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  $kT$ ’.



### **Mass, kinetic energy and temperature:**

- Since mean k.e.  $\propto T$ , it follows that if we double the thermodynamic temperature of an ideal gas (e.g. 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.  $\propto v^2$ , 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.