States of matter

By the end of this chapter you should be able to:

1. describe, using a kinetic–molecular model, the solid, liquid and gaseous states, melting, vaporisation and vapour pressure;
2. state the basic assumptions of the kinetic theory as applied to an ideal gas;
3. explain qualitatively, in terms of intermolecular forces and molecular size, (i) the conditions necessary for a gas to approach ideal behaviour, and (ii) the limitations of ideality at very high pressures and very low temperatures;
4. state and use the ideal gas equation $PV = nRT$ in calculations, including the determination of the relative molecular mass of a volatile liquid.

The three states of matter

Figure 1.1 shows the Grinnell glacier, at various times in the past. You can see just how much of the glacier has disappeared between 1914 and 1997. Many scientists believe that the increasing rate of melting of glacier ice, and ice at the polar ice caps, is a result of global warming. You may know that, if global warming continues, the sea level on Earth will gradually rise. Mainly the rise will be due to the expansion of sea water; but the melt water from glaciers and the polar ice caps will add to the increase as well. In fact, it has been estimated that, if all the ice over the Earth’s land mass were to melt, sea level would rise by around 20 m. For many Europeans, the retreat of glaciers in mountainous regions and the end of reliable winter snow falls will be the end of skiing holidays. However, there are far more serious consequences world wide; for example, glaciers provide billions of gallons of water for drinking water and the irrigation of crops in lowland regions. In Africa, the end of glaciation will make vast tracts of land uninhabitable owing to the lack of melt water. It has been estimated that a rise of 4 °C in average air temperature will be enough to melt all the glaciers in Europe, and even the Himalayas.

Studying the conditions that cause ice to form, and melt, and the change of water vapour into

- Figure 1.1 Three photographs of the Grinnell glacier, Glacier National Park, USA, taken in a 1914, b 1938 and c 1997.
rain and snow, is part of chemistry. We know how and why water changes between its solid, liquid and gaseous forms; and this knowledge is important in predicting the results of global warming. However, the same processes are at work when any solid, liquid or gas changes from one form to another. This book will introduce you to the main factors that we believe are responsible for the different properties of gases, liquids and solids. However, as in all good stories, we should start at the beginning; and that means you need to know what we mean by states of matter.

The three states of matter are solid, liquid and gas. Whether a substance exists as a solid, liquid or gas mainly depends on two things:

1. **Kinetic energy** – which increases as a substance is heated.
2. **Intermolecular forces** – the forces between the molecules that make up the substance.

The kinetic energy of the molecules in a solid, liquid or gas is a measure of the amount of random movement of molecules. The more kinetic energy the molecules of a substance have, the greater is the tendency for its molecules to be jumbled up, i.e. to be more disordered. The most disorderly arrangement that molecules can achieve is in a gas. At the other extreme, the most orderly arrangement is in a solid. Liquids are somewhere in between. See figure 1.2.

Intermolecular forces tend to hold molecules together. There are intermolecular forces between all molecules; but between some they are very weak, and between others they are quite strong. When the forces are weak, the molecules are not likely to cling together to make a liquid or solid unless they have very little kinetic energy. The noble gases are excellent examples of this. For instance, helium will not liquefy until the temperature is almost as low as –269 °C, or 4 K. On the other hand, the intermolecular forces between water molecules are very strong – strong enough to hold them together up to 100 °C.

To summarise, we can say that:

**Intermolecular forces tend to bring order to the movements of molecules.**
**Kinetic energy brings disorder, and leads in the direction of randomness or chaos.**

Thus, at a given temperature, a substance will exist as a solid, liquid or gas depending on where the balance between these two opposing influences lies. We saw in Chemistry 1, chapter 15, and shall see on page 8 in this book, that an **equilibrium** can be set up when a substance changes state.

### How do we know that gases are disorderly?

One piece of evidence for this comes indirectly from the experiments first performed by Robert Brown in 1827. He observed the movement of pollen on the surface of water, which he found to be completely unpredictable. The random movements of the pollen, known as **Brownian motion**, were finally given a mathematical explanation by Albert Einstein (of relativity fame) in 1905. He showed that a grain of pollen went on a random walk. A **random walk** (figure 1.3) is the sort of walk that a very drunk person would go on if put out in an open space. If we assume that the drunk found it impossible to make a conscious choice, he (or she) would be as likely to walk in one direction as any other. The reason why the grains

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**Figure 1.2** The relation between kinetic energy, disorder and intermolecular forces.

**Figure 1.3** A random walk of a pollen grain.
behave in this way is that they are being bombarded by molecules in the liquid, which are themselves moving in a random way.

Around 1908 Jean Perrin made observations of Brownian motion in gases. He showed that small particles, much larger than individual molecules but still very small (less than $10^{-6}$ m in diameter), also went on random walks. This could only be explained along the same lines as Brownian motion in liquids. The particles were being struck by the randomly moving gas molecules.

**How much order is there in a liquid?**
The particles in a liquid group together, and it is just this tendency that produces some order in their arrangement (figure 1.4). However, the order is over a relatively short range, perhaps over a distance of $10^{-9}$ m (about 10 molecular diameters). Over greater distances, the degree of order diminishes, i.e. the groups themselves are randomly arranged. We can summarise the situation in this way:

> In a liquid there is short-range order, and long-range disorder.

However, as in a gas, the positions of the particles in a liquid are constantly changing; so membership of the groups is always changing.

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**The arrangement of particles in a solid**
First, a reminder: there are many types of solid, whose properties depend on the particles that they contain. For example, metal crystals consist of lattices of atoms, which are best viewed as positive ions existing in a ‘sea’ of electrons; ionic substances like sodium chloride have lattices built from positively and negatively charged ions (Na$^+$ and Cl$^-$); iodine crystals have a lattice of iodine molecules, I$_2$; graphite crystals contain layers of hexagonal rings of carbon atoms; and diamond is a giant lattice of carbon atoms all bonded in a tetrahedral arrangement. In general, metals and ionic substances have high melting points (although there are exceptions); molecular crystals (like iodine) have low melting points; and giant lattices of interlocked atoms (like diamond) have very high melting points. For the sake of keeping our description of solids fairly simple, we shall use metal crystals as our examples of solids. Much of what we shall say about the structures of metals applies to other types of solids (and when it doesn’t, we shall say why).

When a liquid metal starts to crystallise, the atoms begin to fit together in regular patterns. A particularly simple pattern is shown in figure 1.5. It is clear that this is a very orderly arrangement. However, even at 0 K, the atoms are not completely still; they vibrate about the same average position. The very regular packing of particles in a solid extends over far greater distances than in a liquid. However, eventually the regularity breaks down. This can happen because of impurity atoms getting in the way, and blocking the normal pattern. It can also happen when crystals start to grow in several places and grow towards each other. Where the crystalline regions meet, the two lattices may not meet exactly. We can visualise such situations in the laboratory using bubble rafts, like that in figure 1.6. The study of order and disorder in metal crystals is of huge importance in industry. Variations in a metal lattice can lead to greater strength or, more worryingly, to metal fatigue (figure 1.7).
Differences in properties of solids, liquids and gases

As we have seen, the particles in a gas are, on average, much further apart than they are in a liquid or solid (figure 1.8). There is very little difference between the spacing of atoms in liquids and solids; that is why both liquids and solids are hard to compress. Also, the particles in a gas travel very much faster than those in a liquid. The differences in spacing, and in speed, are the main reason for the different properties of the three states of matter (figure 1.9 and table 1.1). For example, notice that gases are not very good conductors of heat. For heat to be conducted by atoms or molecules, the movement energy of the molecules must be

<table>
<thead>
<tr>
<th>Amount of order of arrangement of particles</th>
<th>Solids</th>
<th>Liquids</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very orderly</td>
<td>Short-range order, longer-range disorder</td>
<td>Almost complete disorder</td>
<td></td>
</tr>
<tr>
<td>Shape</td>
<td>Fixed</td>
<td>Takes shape of container</td>
<td>No shape</td>
</tr>
<tr>
<td>Position of particles</td>
<td>Fixed; no movement from place to place</td>
<td>Some movement from place to place</td>
<td>Always moving rapidly from place to place</td>
</tr>
<tr>
<td>Spacing of particles</td>
<td>Close (10^{-10} m)</td>
<td>Close (10^{-10} m)</td>
<td>Far apart (10^{-8} m)</td>
</tr>
<tr>
<td>Compressibility</td>
<td>Very low</td>
<td>Very low</td>
<td>High</td>
</tr>
<tr>
<td>Conduction of heat</td>
<td>Metals and graphite very good; others poor</td>
<td>Metals very good; others poor</td>
<td>Very poor</td>
</tr>
</tbody>
</table>

*Table 1.1* Comparison of properties of the three states of matter.
passed on from one to another. This requires the molecules to collide, which happens less easily in a gas than in a liquid.

In a solid the particles are held in position by the overall effects of the attractions and repulsions of their neighbours. Even so, the particles do have some movement. They vibrate and fro, although on average they keep the same position. As the temperature increases, they vibrate more violently, and they pass on the energy of their vibrations to their neighbours. However, the only solids that conduct heat very well are those that have electrons that can move from place to place. Especially, metals have many free electrons that can carry their movement energy with them even though the ions themselves are stuck in one place. That is, metals conduct heat well because of their free electrons, not as a result of vibrations of the particles.

Owing to the large amount of empty space in a gas, it is fairly easy to squeeze the molecules into a smaller volume; so gases are easily compressed.

Liquids and solids have their molecules already very close together, so they are very difficult to compress.

### Comparing the melting and boiling points of substances

You will find some representative examples of melting and boiling points in **Table 1.2**. A column showing the relative molecular masses \((M_r)\) of the molecules has been included in the table. If you look carefully, you will see that there is a general rule that governs the values:

The higher the relative molecular mass, the higher the melting point and the higher the boiling point.

One reason why melting and boiling points tend to increase with mass is that, the greater the mass of a molecule, the more electrons it

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**Table 1.2** Melting points and boiling points of some elements and compounds.

(Values have been measured at standard atmospheric pressure, 100 kPa.)
possesses. It is one of the features of large molecules that their electron clouds are more spread out (diffuse), and it is just this type of molecule that has large forces between instantaneous dipoles. These forces are called instantaneous dipole forces (more correctly 'instantaneous dipole-induced dipole forces', and are also known as van der Waals' forces). Thus, as molecules get heavier, the instantaneous dipole forces become greater, and tend to keep the molecules together.

However, there are many exceptions to the general rule. In particular, you should know that:

Where melting or boiling points are higher than expected, look for very strong intermolecular forces at work, especially hydrogen bonds.

There are two important examples that you should know about:

- **Hydrogen fluoride**, HF, is rather like water in that its boiling point is far above those of the other hydrides of the halogens. The reason is, again, hydrogen bonding. Fluorine is the most electronegative of all the elements, and the hydrogen fluoride molecule is extremely polar. That is, the fluorine atom attracts the pair of electrons in the H–F bond towards itself. The bonding pair spend most of the time nearer the fluorine, thus giving the atom an excess of negative charge. The hydrogen atom has its nucleus (a single proton) only partially surrounded by electrons, and therefore it has an excess positive charge. We show the slight positive and negative charges by the symbols + (‘delta-plus’) and − (‘delta-minus’). The hydrogen bonds are the forces of attraction between the opposite charges and are shown by the dotted lines in figure 1.10.

- **The Group VI hydrides**, especially water, H₂O. Compared to the other hydrides of Group VI, the melting and boiling points of water are remarkably high. (The values are shown in table 1.2, and a graph of the data is included in figure 1.11.) The reason for this lies in hydrogen bonding (figure 1.12). In every one of its states, water molecules can hydrogen bond together. In ice the regular arrangement of the lattice leaves a large amount of free space. Figure 1.13 illustrates the extent of the free space. Because the water molecules in ice are not so close together as in liquid water, ice is less dense than liquid water. In liquid water there is a tremendous amount of order compared to other liquids. Although the pattern of hydrogen bonding is always changing, water molecules are held together much more tightly than are molecules in most other liquids.

- **Figure 1.10** A representation of the structure of solid hydrogen fluoride, where the molecules take up a zig-zag shape. The molecules are held together by hydrogen bonds.

- **Figure 1.11** The boiling points of the Group IV, V and VI hydrides.

- **Figure 1.12** The origin of hydrogen bonding in water.
SAQ 1.1
As shown in figure 1.11, water and ammonia have boiling points much higher than those of the other hydrides of the elements in their Groups. However, the boiling point of methane, CH₄, is lower than those of the other hydrides of Group IV. What is the reason for the difference?

Why gases liquefy, and solids melt
When two molecules are far apart, they move completely independently; neither will feel the presence of the other. However, if they come closer, then intermolecular forces get to work. The two molecules will attract one another. You will have learned about attractive intermolecular forces when you studied instantaneous dipole forces in Chemistry 1, chapter 3. Also, you should have come across hydrogen bonding and dipole–dipole interactions as intermolecular forces that tend to bring molecules together. However, think about molecules coming very close together. The ‘outside’ of a molecule is really a layer of negatively charged electrons: the electron cloud. When molecules approach closely, the electron clouds repel one another. It is the great strength of the repulsion that puts a limit on how close the atoms can get.

If two molecules collide with a great deal of energy, the negatively charged electron clouds get squeezed together and the resulting repulsion pushes them apart. Indeed, in a gas the force is so great that it overcomes the (attractive) intermolecular forces. Thus the molecules return to their life of rushing round at random in the body of the gas.

On the other hand, at lower temperatures the speeds of the molecules are lower and the force of collisions can be much less. There is a better chance of the intermolecular forces equaling, and indeed being greater than, the repulsive forces as the molecules collide. When this happens the molecules will not spring apart. Rather, they will remain close together and we see the gas turning to a liquid.

The molecules of different gases have their own characteristic intermolecular forces, and repulsive forces between their electron clouds. Therefore the temperature at which the forces between colliding molecules become low enough for the instantaneous dipole forces to win is different for every gas; i.e. different gases liquefy at different temperatures.

We can turn this line of argument on its head, and explain the change of liquid to gas by discussing the two opposing forces as the temperature of a liquid increases to its boiling point (see SAQ 1.2).

SAQ 1.2
a Use your knowledge of intermolecular attractions and repulsions to explain why liquids turn into gases as the temperature increases.

b Why does every substance have its own particular boiling point?

Explaining changes of state
Everyone is familiar with the change of liquid water to a vapour. This happens when water evaporates from a puddle, or when washing dries on a windy or sunny day, or when water boils in a kettle. Likewise, most people in industrialised countries convert liquid water into a solid, ice, by
At equilibrium, the space above the liquid has become saturated with the vapour – it contains the maximum amount of vapour possible at the given temperature. (If we were to increase the temperature of the apparatus, more vapour could exist in the space above the liquid, and the vapour pressure would increase.) Make sure you realise that equilibrium is a dynamic process: there is a great deal of change going on with molecules constantly leaving and joining the liquid. However, they do so at the same rate (many millions per second).

Figure 1.14 shows how evaporation of a liquid can take place under equilibrium conditions.

However, equilibrium will not always be achieved. For example, on a warm, windy day, wet clothes dry very quickly because the atmosphere is not saturated with water vapour as it would be on a cold, wet day. There are (relatively) so few water molecules in the atmosphere that they have little chance of going back on to the clothes once they have left the surface, or of water molecules already in the air sticking to the clothes. That is, wet clothes drying on a line will not reach equilibrium like the liquid in figure 1.14.

The molecules that escape from the surface of the liquid tend to have higher than average energies – that is why they escape. If a molecule has lower than, or about the same as, the average energy it is unlikely to escape the clutches of the other molecules – the intermolecular forces will hold it back. However, as more molecules escape into the space above the mercury, the chances of them bouncing back into the surface of the liquid increase. Eventually, the chance of a molecule leaving the surface equals the chance of a molecule in the vapour joining the liquid. At that time, equilibrium is reached (see Chemistry 1, page 180):

At equilibrium, the rate at which molecules leave the liquid equals the rate at which molecules join the liquid.

At equilibrium, the space above the liquid has become saturated with the vapour – it contains the maximum amount of vapour possible at the given temperature. (If we were to increase the temperature of the apparatus, more vapour could exist in the space above the liquid, and the vapour pressure would increase.) Make sure you realise that equilibrium is a dynamic process: there is a great deal of change going on with molecules constantly leaving and joining the liquid. However, they do so at the same rate (many millions per second). Figure 1.14 shows how evaporation of a liquid can take place under equilibrium conditions.

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![Figure 1.14](image1.png) - Figure 1.14 Measuring the vapour pressure of a liquid (note that the diagram is not to scale).

![Figure 1.15](image2.png) - Figure 1.15 Water boiling under reduced pressure. Water will boil even at room temperature if the pressure is low enough.
If we heat a liquid we give more energy to the molecules. This increases their chance of leaving the surface, and the liquid will evaporate more quickly. If we continue to heat the liquid, it will eventually boil (figure 1.15). We shall not prove it, but the condition for a liquid to boil is that:

A liquid boils when its vapour pressure equals atmospheric pressure.

We shall return to this point later (see page 19).

**SAQ 1.3**

If you put a little alcohol (ethanol) or propanone on the back of your hand, the liquid will evaporate and you will feel the back of your hand get cold. Why does evaporation lead to cooling? [Hint: Think about the range of energies the molecules possess, and why even the less energetic particles eventually evaporate.]

**SAQ 1.4**

What are clouds made of? Briefly explain why clouds form, and why they often lead to rain falling.

**Some remarkable substances**

In this section we shall briefly consider some substances that are difficult to classify as a solid, liquid or gas.

**Liquid crystals**

It seems a contradiction to call a crystal ‘liquid’. We expect crystals to be solids, and certainly not liquids. Essentially, liquid crystals are liquids that have sufficient long-range order in them to make them behave like a solid. However, they will only behave like a solid over a certain range of temperatures. Usually a liquid crystal is made from molecules that are long, thin and not very symmetrical. You will find some examples in figure 1.16.

The intermolecular forces must be strong enough to hold the molecules together, but not so strong as to restrict their movement too much. The unsymmetrical nature of the molecules leads to an unsymmetrical packing of the molecules. The very useful property of liquid crystals is that the arrangement of the molecules can be upset by very slight changes in their surroundings. Especially, in the liquid crystals used in calculators, digital watches and computer displays (figure 1.17), the molecules rearrange themselves when the crystal is subjected to a small electric field. The rearrangement changes the way the crystal absorbs light.

**Glass**

Glass is a most unusual material. For example, it allows light to pass through it very easily. Also, it melts over a range of temperatures and remains viscous (rather like treacle). This allows glass to be ‘blown into many different shapes (figure 1.19), or to be rolled into sheets for use in windows. The basic building block of ordinary glass is a tetrahedron built from a silicon atom with four oxygen atoms around it (figure 1.18 on page 10). The tetrahedra join to give a three-dimensional interlocking structure that gives glass its high
viscosity. However, unlike a normal solid, glass has no long-range order in its structure.

In 1880 the Irish physicist John Tyndall (who had a 'professional interest' in ice, as he was an extremely keen mountaineer) compared ice and glass in this way: “The ice is music, the glass is noise – the ice is order, the glass is confusion. In the glass, molecular forces constitute an inextricably entangled skein, in the ice they are woven to a symmetrical web.” (Quoted in W. H. Brock et al., John Tyndall, Royal Dublin Society, 1981, page 98.)

Real and ideal gases
Now we shall consider the properties of gases in greater depth. To begin with, you need to know that gases show these properties:
1. They fill all the space open to them.
2. They expand when heated.
3. They exert a pressure on the walls of their containers.
4. The pressure changes as the temperature changes.

Shortly, we shall deal with each of these in more detail; but you will find that we shall spend only part of the time discussing the properties of real gases such as hydrogen, oxygen, methane and so on. Real gases are complicated things, and it can be helpful at first to use a simplified model of a gas. In fact, much of this unit will be about 'gases' that do not exist in the real world – these are gases that we call ideal gases.

The behaviour of ideal gases
Ideal gases have some, but not all, of the properties of real gases. A brief summary of the characteristics of an ideal gas is given in box 1A. An ideal gas is a gas in which there are no intermolecular forces, and in which the molecules don’t take up any space themselves (we regard them as points). Also, we assume that the molecules do not change their total kinetic energy when they bump into each other; this is what we mean if we say that the collisions are 'perfectly elastic'. No real gas is ideal, although some come close to ideal behaviour, e.g. helium. You will find that we can compare real and ideal gases, and from their different characteristics we can learn a great deal about real gases. The key idea is to explain why real gases are different from ideal gases – but more of this later.

Box 1A Key assumptions about ideal gases
In an ideal gas:
- the molecules have mass, but negligible size;
- there are no intermolecular forces;
- the collisions between the molecules are perfectly elastic.

The kinetic theory of gases
You will already know that the molecules in a gas are in a constant state of random motion. This feature of gases is one of the main foundations of the kinetic theory of gases. A statement of the main features of the kinetic theory of gases is given in box 1B. As far as we know, the kinetic theory of gases is an extremely well-supported theory. There is a great deal of evidence to show that, to all intents
and purposes, the motion of gas molecules is random. This means that in any gas, on average, there will be as many molecules moving in one direction as in any other direction.

You might like to know that the average speed of gas molecules is of the order of 500 m s\(^{-1}\) at room temperature. The lighter the molecule, the greater the average speed (and vice versa). For example, hydrogen molecules have an average speed somewhat above 1500 m s\(^{-1}\), and carbon dioxide molecules have an average speed nearer to 350 m s\(^{-1}\).

There is a wide range of energies among the molecules in a gas. Some move very rapidly, and much faster than the average, and some move very much more slowly than the average. When a gas is heated, on average all the molecules increase their kinetic energies (i.e. move faster); but this does not mean that they all increase. Always, some will pick up more energy than others. Indeed, during a collision between two molecules, one of them may move off with a greater speed, and one with a lower speed than before. However, the majority move near to the average speed. The way the kinetic energy of the molecules varies with temperature is shown in figure 1.20. As the temperature goes up, the average energy of all the molecules increases, but the distribution of speeds, and therefore kinetic energies, spreads out. Especially, the proportion of molecules with high kinetic energies increases. If you look carefully at the shapes of the graphs, you will see that they are not quite symmetrical – the curve stretches out more at higher than at lower energies. (This is an important point when explaining how changes in temperature influence the rates of chemical reactions: see Chemistry 1, page 169.)

**Box 1B The kinetic theory of gases**

*Main idea:*
- Gases consist of molecules in a constant state of random motion.

*Related ideas:*
- The pressure of a gas is due to the collisions of the molecules with the walls of the container.
- The molecules travel in straight lines until they collide with one another, or with the walls of the container.
- In these collisions, the total kinetic energy of the molecules does not change.

![Figure 1.20](image-url) How the distribution of the kinetic energy of the molecules in a gas changes with temperature.

**SAQ 1.5**

Use ideas from the kinetic theory of gases to answer these two questions:

a What happens to the average kinetic energy of the molecules in a gas as the temperature increases?

b What might happen to the kinetic energy of any individual molecule in a gas as the temperature increases?

**The pressure and volume of an ideal gas**

The pressure of a gas is caused by the collisions of the molecules with the walls of its container. By doing some mathematics, it is possible to show that the pressure of an ideal gas depends on three factors:

1. the number of molecules per unit volume (i.e. the concentration of the gas);
2. the mass of the molecules;
3. their speed.

This should make sense to you because, if there are more molecules present in a given volume, there should be more collisions with the walls, so the pressure should increase. Likewise, if the molecules have a greater momentum (mass times speed), the harder they will bounce off the walls. Therefore, they exert a greater force on the walls, and cause the pressure to increase.
The ideal gas law

The behaviour of ideal gases is represented by the ideal gas equation:

\[ PV = nRT \]

where \( P \) is the pressure, measured in pascals, \( \text{Pa} \); \( V \) is the volume, measured in metre cubed, \( \text{m}^3 \); \( T \) is the temperature on the Kelvin scale, measured in kelvins, \( \text{K} \) (notice that the degrees sign, °, is not put next to the K of a Kelvin temperature); \( R \) is the gas constant, \( 8.314 \text{ J K}^{-1} \text{mol}^{-1} \); and \( n \) is the number of moles of gas.

If pairs of measurements of \( V \) and \( T \) taken around room temperature are plotted and the lines extended back, they meet at (almost) \(-273 ^\circ \text{C}\). At this temperature, the volume of the gases appears to reduce to zero. Clearly, this is impossible for real gases, but none the less the graphs show that the temperature is of great importance. We can use the \(-273 ^\circ \text{C}\) point on the graph to define the zero of a new scale of temperature. This is the absolute scale or Kelvin scale. We can convert between degrees Celsius and kelvins by adding 273: e.g. \( 100 ^\circ \text{C} = (100 + 273) \text{K} = 373 \text{K} \). Similarly, we convert kelvins to degrees Celsius by subtracting 273: e.g. \( 127 \text{K} = (127 - 273)^\circ \text{C} = -146 ^\circ \text{C} \).

When you use the equation, do be careful about the units. All the units given above are consistent; but sometimes you may have to use data that are given in other units. Especially, chemists often prefer to work in litres (more properly stated as \( \text{dm}^3 \)) or in \( \text{cm}^3 \). Here is a way to change between these units:

\[ 1 \text{m}^3 = 1 \times 10^3 \text{dm}^3 = 1 \times 10^6 \text{cm}^3 \]

Also, pressure is often quoted in kilopascals, kPa, where \( 1 \text{kPa} = 10^3 \text{Pa} \). An old unit of pressure is the atmosphere, where 1 atmosphere is approximately 100 kPa. You may find that the volumes of gases are often quoted in litres or, more systematically, in \( \text{dm}^3 \). The relationship between the units of volume is as follows:

\[ 1 \text{litre} = 1 \text{dm}^3 = 1000 \text{cm}^3 = 10^{-3} \text{m}^3 \]

**SAQ 1.6**

Look at figure 1.21. Two identical cylinders A and B fitted with pistons are kept in different rooms. Both contain the same number of molecules of gas, but the volume of one (A) is less than that of the other (B). What is the most likely reason for the difference in volume?

**Figure 1.21** Both sets of cylinders and pistons A and B are subject to the same atmospheric pressure, and both contain the same number of molecules of gas.

**Worked example**

What is the volume, given in \( \text{dm}^3 \), of 1 mol of an ideal gas at \( 20 ^\circ \text{C} \) and \( 100 \text{kPa} \)? (This combination of temperature and pressure is often called ‘room temperature and pressure’.)

We have to convert the pressure to pascals and the temperature to kelvins: so we have \( P = 100 \times 10^3 \text{Pa} \), \( T = (20 + 273) \text{K} = 293 \text{K} \), \( R = 8.314 \text{ J K}^{-1} \text{mol}^{-1} \), and \( n = 1 \text{ mol} \). Putting these values into the ideal gas equation gives

\[ V = \frac{1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{mol}^{-1} \times 293 \text{K}}{100 \times 10^3 \text{Pa}} = 0.024 \text{ m}^3 \]

Converting this to \( \text{dm}^3 \) gives \( V = 24.4 \text{ dm}^3 \). We usually make the approximation that 1 mol of gas occupies 24 \( \text{dm}^3 \) at room temperature and pressure.

**SAQ 1.7**

If a balloon contained 1 \( \text{dm}^3 \) of helium at \( 20 ^\circ \text{C} \) and \( 100 \text{kPa} \) pressure, how many moles of helium would be present?

**SAQ 1.8**

A weather balloon (figure 1.22) may have an ‘envelope’ of material that may contain a total volume of, say, 1000 \( \text{dm}^3 \) when it is fully expanded. However, the volume of helium put in the balloon when it is released into the atmosphere is only a fraction of this volume. Why is the balloon not fully inflated before it is released?
The behaviour of real gases

One of the obvious ways that real gases differ from ideal gases is that they liquefy when the temperature is low enough and the pressure is high enough. Lowering the temperature of real gases allows the intermolecular forces to overcome the motion of the molecules. Squeezing the molecules together has a similar effect: bringing molecules closer together allows the intermolecular forces to be more effective (just as bringing the north and south poles of magnets close together increases the effects of their attractive forces).

Only ideal gases would strictly obey the ideal gas equation. All real gases show deviations from ideal behaviour for two reasons:

1. The molecules in real gases take up space.
2. Real gases have intermolecular forces between the molecules.

We shall consider each of these factors in more detail now.

Real molecules occupy space

In an ideal gas, it is assumed that the molecules do not occupy space (see box 1A), so the volume in which they exist is (literally) the volume of the container. However, for real gases, each molecule takes up a very small volume (of the order of $10^{-30} \text{ m}^3$), which is then not available for another molecule to move in. There are so many molecules that the total volume they occupy cannot be ignored. Figure 1.23 illustrates this idea.

SAQ 1.9

Assume that the effective volume of an oxygen molecule is $64 \times 10^{-30} \text{ m}^3$.

a Estimate the volume occupied by 1 mol of oxygen molecules. Avagadro’s number = $6.02 \times 10^{23} \text{ mol}^{-1}$

b What percentage of the volume of 1 mol of oxygen gas is this at room temperature and pressure?

The influence of intermolecular forces

Intermolecular forces bring molecules together. These forces are always present in gases, even though a gas is only a gas because the intermolecular forces are not strong enough to prevent the molecules bouncing apart when they collide.

Think about what happens if a molecule is moving out of the main body of a gas towards the walls of the container (see figure 1.24 overleaf). The vast majority of molecules will be attracting it from behind, or from its sides. This tends to slow the molecule and prevent it colliding with the walls of the container with as much force as it would do if there were no intermolecular forces. In other words, the pressure exerted by a real gas is less than it would be if the gas were ideal.
Molecules in an ideal gas feel an overall force attracting them inwards.

**Summary table**

<table>
<thead>
<tr>
<th>Occupation of space by molecules</th>
<th>Molecules in an ideal gas</th>
<th>Molecules in a real gas</th>
<th>Effect in real gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Occupied space</td>
<td>Reduces volume from ideal value</td>
<td></td>
</tr>
<tr>
<td>Intermolecular forces</td>
<td>None</td>
<td>Present, and can be strong</td>
<td>Reduces pressure from ideal value</td>
</tr>
</tbody>
</table>

**Real gases can approach ideal behaviour**

Remember that two of the conditions for ideal behaviour were that the molecules were of negligible size and that there were no intermolecular forces. We can sometimes come close to these conditions for real gases if:

1. we use gases that have very small intermolecular forces between the molecules;
2. we use gases at very low pressures.

Gases like hydrogen and helium fulfil the first condition; and by using very low pressures, the molecules of a gas spend a great deal of their time far apart from each other. This results in the intermolecular forces not having a chance to work effectively. It also means that because there are very few molecules in a given space at low pressures, the volume that the molecules do occupy is a very small proportion of the total; i.e. their own volume does become nearly negligible.

**SAQ 1.10**

In your own words, explain why, at low pressures, real gases begin to behave more like ideal gases.

**Measuring the relative molecular mass of a volatile liquid**

We shall now use the ideal gas equation to calculate the relative molecular mass of a volatile liquid. This may, at first sight, seem rather an odd statement given that the ideal gas equation plainly applies to gases and not to liquids. However, the key to the puzzle is that the method relies on turning the liquid into a gas. Before you go on, you should remind yourself about the mole as a measure of the quantity of matter in chemistry (see Chemistry 1, page 19).

**SAQ 1.11**

What is the approximate volume of:

- **a** 2 mol and
- **b** 0.25 mol of carbon dioxide at room temperature and pressure?

**The method**

There are several ways of performing this experiment. The method we shall choose is to use the apparatus shown in figure 1.25.

The outline of the method is as follows:

1. Take a known mass of the volatile liquid.
2. Introduce the liquid into a gas syringe in an oven.
3. Turn the liquid to vapour and measure its volume.

**Figure 1.25** One method of measuring the volume of a volatile liquid using a gas syringe and an oven.
Knowing the gas volume and its temperature, we can use the ideal gas equation to work out how many moles of gas are present. Then, because we know the mass of this number of moles, we can work out the relative molecular mass of the gas, and hence of the liquid.

The nozzle of the gas syringe is covered with a rubber cap (a septum), and the gas syringe is put in the oven or steam jacket. Once the reading on the gas syringe shows no further change, the initial reading on the gas syringe is taken, and a sample of the liquid is taken up into a small syringe. Here, we shall assume that we are using ethoxyethane (ether) as the liquid. The small syringe is weighed and the ethoxyethane injected into the gas syringe. Then the small syringe is immediately reweighed. Once the ethoxyethane is in the gas syringe, the liquid quickly vaporises and the plunger is driven outwards. Eventually equilibrium is achieved and there is no further change in the volume recorded on the gas syringe. Provided the temperature of the steam jacket and the atmospheric pressure are known we can calculate the relative molecular mass.

**Some sample results**

Here are some sample readings:

- **Mass of small syringe and ethoxyethane**
  - before injection into gas syringe = 20.476 g
  - after injection into gas syringe = 20.252 g
- **Initial reading on gas syringe** = 1.4 cm³
- **Final reading on gas syringe** = 96.8 cm³
- **Temperature of steam jacket (oven)** = 99.6 °C = 372.6 K
- **Atmospheric pressure** = 100 kPa

From these results we have

- **Mass of ethoxyethane used** = 0.224 g
- **Volume of vapour** = 95.4 cm³ = 95.4 × 10⁻⁶ m³

We can use the ideal gas equation to work out the number of moles, \( n \), of ethoxyethane that this volume represents. We have

\[
PV = nRT
\]

or

\[
\frac{PV}{RT} = n
\]

\[
\begin{align*}
n & = \frac{100 \times 10³ \text{Pa} \times 95.4 \times 10⁻⁶ \text{m}³}{8.314 \text{J K}⁻¹ \text{mol}⁻¹ \times 372.6 \text{K}} \\
& = 0.003 \text{ mol}
\end{align*}
\]

Relative molecular mass = \[
\frac{0.224 \text{ g}}{0.003 \text{ mol}} = 74.7 \text{ g mol}⁻¹
\]

**Experimental error**

The formula of ethoxyethane is \((\text{C}_2\text{H}_5)_2\text{O}\), so its true relative molecular mass is 74 g mol⁻¹. It is quite common for results in this experiment to overestimate relative molecular masses. The most important reason for this is that, before the liquid can be injected into the gas syringe, some if it evaporates from the needle of the small syringe. This means that we over-estimate the mass of liquid that turns into gas in the gas syringe. For example, in our calculation above, the actual mass of liquid injected into the gas syringe may have been only 0.223 g. Then the relative molecular mass would have been calculated as 0.223 g/0.003 mol = 74.33 g mol⁻¹. (If the true mass injected were 0.222 g, the result would have been exactly 74 g mol⁻¹, the true relative molecular mass.)

**SAQ 1.12**

The gas syringe experiment only works with liquids that are highly volatile, i.e. those which evaporate easily.

a. Explain why the mass of liquid injected into the gas syringe is often less than that given by the weighings.

b. How, and why, does this affect the calculation?

**SAQ 1.13**

The volatile liquid propanone was used in an experiment to measure its relative molecular mass, like the one we have discussed above. The following data were collected:

- **Mass of syringe and propanone**
  - before injection into gas syringe = 20.374 g
  - after injection into gas syringe = 20.193 g
- **Initial reading on gas syringe** = 1.6 cm³
- **Final reading on gas syringe** = 97.1 cm³
- **Temperature of steam jacket (oven)** = 99.3 °C
- **Atmospheric pressure** = 100.2 kPa

Calculate the relative molecular mass of propanone.
The three states of matter are solid, liquid and gas. The state a substance exists in depends on the kinetic energy of the particles and the strength of the intermolecular forces between its particles.

The particles in a solid have orderly arrangements; liquids have short-range order but long-range disorder; gases have completely disorderly arrangements of their particles.

The space between gas particles is very much greater than the spaces between the particles in a solid or liquid. The spacing of particles in a liquid and solid is about the same.

As the kinetic energy of particles increases, the temperature increases, intermolecular forces are overcome and solids tend to melt, and liquids turn to gas.

Substances that have hydrogen bonds between their molecules often have unusually high melting and boiling points, e.g. H₂O, HF.

Liquids have a characteristic vapour pressure at a given temperature and pressure. In a closed system, an equilibrium is set up such that the rate at which molecules leave the liquid equals the rate at which gaseous molecules return to the liquid.

A liquid boils when its vapour pressure equals the atmospheric pressure.

The key assumptions about ideal gases are:
- The molecules have mass, but negligible size.
- There are no intermolecular forces.

The kinetic theory of gases claims that:
- Gases consist of molecules in a constant state of random motion.
- The pressure of a gas is due to the collisions of the molecules with the walls of the container.
- The molecules travel in straight lines until they collide with one another, or with the walls of the container.
- In these collisions the total kinetic energy of the molecules does not change.

Ideal gases obey the ideal gas equation, \( PV = nRT \).

Real gases show deviations from ideal behaviour because:
- the particles in a real gas occupy space;
- real gases have intermolecular forces between their particles.

Real gases approach ideal behaviour at (i) high temperature and (ii) low pressure.

At low temperature and/or high pressure the intermolecular forces in real gases have a large effect and the behaviour of the gases are far from ideal.

The relative molecular mass of a volatile liquid can be measured by: (i) weighing a sample; (ii) injecting the sample into a gas syringe held at a temperature greater than the liquid's boiling point; (iii) allowing equilibrium to be reached; (iv) measuring the temperature and volume of the vapour; and (v) using the ideal gas equation to calculate the number of moles of vapour present.
Questions

1. Table 1.2 (page 5) and figure 1.11 (page 6) provide information that you will need in order to answer this set of questions.
   a. Why does carbon (as diamond) have such a high melting point?
   b. What might be the reason for ammonia, \( \text{NH}_3 \), having an anomalous boiling point compared to other hydrides of Group V? [Hint: What is special about the structure of an ammonia molecule?]
   c. What is the main type of bonding that holds the alkanes together in their solid or liquid states?
   d. What is the main type of bonding that holds the alcohols together in their solid or liquid states?
   e. How do the boiling points of the alkanes, methane to butane, compare with those of the corresponding alcohols, methanol to butan-1-ol?

2. Use the data in table 1.2 to sketch a diagram showing how the boiling points of the Group VII hydrides (HF, HCl, HBr and HI) vary. Explain the trend that you observe.

3. When water (or any liquid) boils, you can see bubbles appear in the liquid. What are the bubbles in boiling water?

4. Check back: What is the connection between vapour pressure, atmospheric pressure and the boiling point of a liquid? Now explain why it takes longer to cook vegetables in water at high altitudes (e.g., on the side of a high mountain) than at sea level.

5. Here is a question that will make you think about the repercussions of the idea that the particles in a gas are in a constant random motion. It will also bring home to you the relevance of the small scale of atoms and molecules compared to our everyday experience.

   The diagram represents a container filled with nitrogen gas. The container is connected to a vacuum pump by a small tube fitted with a tap. Please remember that the diagram is not to scale!
   a. What, if anything, is in the space between the nitrogen molecules?
   b. Suppose the tube connecting the container to the vacuum pump has a diameter of 1 cm. The diameter of a nitrogen molecule is approximately \( 4 \times 10^{-10} \) m. How many nitrogen molecules could fit across the diameter of the tube?
   c. Would a nitrogen molecule find it hard to find its way down the tube?
   d. Using a rough value, assume you are about 1 m wide. If the tube were of the same scale to you as it is to a nitrogen molecule, how wide would it be? How does this distance compare to, say, the diameter of the Earth (about \( 3 \times 10^6 \) m)?
   e. Now imagine that the tap to the vacuum pump is opened very briefly so that some, but not all, of the nitrogen molecules escape. Draw a diagram like the one above to show what you think the arrangement of the molecules would be at the very instant the tap was closed.
   f. Briefly explain why some of the gas would go into the vacuum pump when the tap was opened.

6. Trichloromethane (chloroform) has a boiling point of about 62 °C. On the face of it, this liquid should be a suitable candidate for using in the gas syringe experiment. Why might you expect its measured relative molecular mass not to be accurate? [Hint: Think about intermolecular forces.]