
Molecular structures and the states of matter

Key points

- The basic types of bonding are covalent, ionic and metallic.
 - There are weaker, non-covalent, interactions between molecules.
 - Molecular structures are determined using X-ray diffraction.
 - In drawing molecular structures, lines between atoms do not always represent bonds.
 - The shapes of simple molecules can often be predicted using the valence shell electron pair repulsion model.
 - For an ideal gas, the pressure, volume, temperature and amount in moles are related by the ideal gas equation.
 - The Boltzmann distribution predicts that only those molecular energy levels with energies of the order of, or less than, $k_{\text{B}}T$ are occupied.
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This book is concerned with trying to understand why molecules form, what determines their shape, and what it is about a particular molecule which makes it react in a certain way. This is undoubtedly an ambitious task which has already occupied chemists for hundreds of years, and will no doubt keep them employed for many years to come. However, a great deal of progress has been made and, through studying this book, you will see that with the aid of a relatively small number of fundamental principles it is possible to understand much about the chemical world of structures and reactivity.

The idea of a molecular structure – how we describe it, how we represent it on paper, and the different types of structures that occur – is absolutely central to the whole of this book. So this first chapter starts out by considering molecules, and assemblies of molecules, in a fairly general way before we start a detailed discussion of chemical bonding. We will also look at how molecular structures are drawn, and some details about the behaviour of gases which will be very useful to us in the remainder of the book.

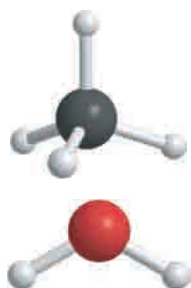


Fig. 1.1 Methane (CH_4 , shown at the top) and water (H_2O , shown at the bottom), are examples of molecules held together by covalent bonds. Each such bond can be thought of as arising from the sharing of a pair of electrons, and is indicated by the grey cylinder joining the atoms. Carbon, oxygen and hydrogen atoms are coloured black, red and grey, respectively.

Weblink 1.1

It is easier to appreciate the details of the structure of SiO_2 shown in Fig. 1.2 if you can rotate it in real time, and view it from different directions. Following the weblink will enable you to do just this.

1.1 Types of bonding

In this section we are going to take a broad over-view of the kinds of bonding seen in chemical compounds and the key characteristics of each type of bonding. At this stage we are not going to be concerned with why particular compounds exhibit certain types of bonding, or give a detailed description of the each type of bonding. These are topics which will be explored extensively throughout the rest of this book.

1.1.1 Covalent bonding

The key feature of covalent bonding is that it arises from the sharing of electrons between atoms, resulting in electron density between the atoms. The simplest examples of this kind of bonding are in molecules such as H_2O and CH_4 , illustrated in Fig. 1.1, in which we equate each bond with a pair of electrons being shared between two atoms. Electrons can be shared between more than two atoms, giving rise to what is called delocalized bonding, as exemplified by the π system of benzene. It is also possible to form multiple covalent bonds in which two or three pairs of electrons are shared between atoms. We may think of a double bond, such as the $\text{C}=\text{C}$ bond in ethene, as resulting from the sharing of two pairs of electrons, and a triple bond, such as the $\text{N}\equiv\text{N}$ bond in N_2 , as resulting from the sharing of three pairs of electrons.

Covalent bonds tend to be directional in the sense that the optimum interaction occurs when the bonds to a given atom have a particular spatial arrangement. For example, when a carbon is attached to four other atoms, the resulting bonds are usually arranged so as to create an approximately tetrahedral geometry around the carbon.

The number of atoms which are covalently bonded together to form a molecule can become very large, as in the case of biomolecules such as proteins, which contain thousands of atoms. It is also possible for the network of covalently bonded atoms to extend throughout a macroscopic *solid* sample: this gives rise to what is called a giant covalent structure. Examples of such systems are diamond (pure carbon) and quartz (SiO_2), shown in Fig. 1.2 on the next page.

The strength of covalent bonds

We can define a bond energy by imagining a process in which a molecule is broken apart into its constituent atoms, and then dividing up the energy needed to achieve this process between the bonds in the molecule. So, for example, the energy needed for the process $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$ can be taken to be four times the C–H bond energy (often called the bond strength).

The strengths of typical covalent single bonds vary between 150 kJ mol^{-1} and 350 kJ mol^{-1} . Double and triple bonds, where they are formed, are stronger. For example, a $\text{C}=\text{C}$ double bond energy is around 600 kJ mol^{-1} , and the $\text{N}\equiv\text{N}$ triple bond is around 950 kJ mol^{-1} .

1.1.2 Ionic bonding

Ionic bonding is essentially confined to solid materials which consist of a regular array of ions extending throughout the macroscopic sample. The most familiar example is solid sodium chloride, NaCl , which consists of a regular array of Na^+ and Cl^- ions, as shown in Fig. 1.3 on the facing page.

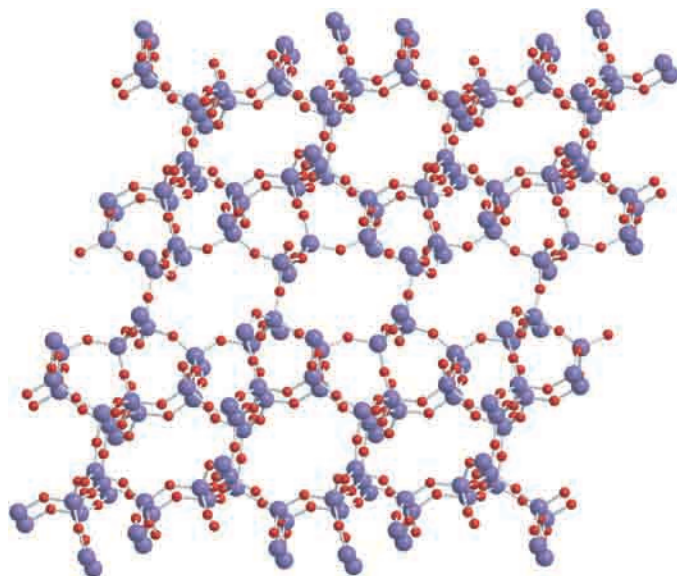


Fig. 1.2 A perspective view of part of the giant covalent structure of SiO_2 . The network of covalent bonds between silicon (shown in blue) and oxygen (shown in red) extends throughout the entire solid.

In such solids there are strong electrostatic interactions between the ions, which are arranged in such a way that the attractive interactions between oppositely charged ions outweigh the repulsive interactions between ions with the same charge. In contrast to covalent bonds, the electrostatic interaction between ions is not directional i.e. all that matters is the distance between two ions, not the orientation.

When ions are present, the electrostatic interaction between them is so strong that it tends to be dominant. However, it is possible for there also to be significant covalent interactions between ions, so pure ionic bonding is best regarded as an idealization.

Sometimes you will see reference being made to an 'ionic bond' between two ions: such terminology is best avoided. The reason for this is that in an ionic solid each ion interacts with many other ions, both of the same and opposite charge to itself. The energy which binds the structure does not come from single interactions between ions (the so-called ionic bonds), but as a result of the interactions between all the ions in the sample.

The strength of ionic bonding

The strength of ionic bonding can be assessed by working out the energy required to take the ions in the solid and then separate them to infinity (in the gas phase), where they will no longer interact: this is often called the *lattice energy*. For NaCl this lattice energy is around 790 kJ mol^{-1} : clearly, the energy of interaction between the ions in an ionic structure is at least as great as that between atoms in a covalently bound molecule.

As well as varying inversely with their separation, the energy of interaction between two ions is also proportional to the product of their charges. This means that two doubly charged ions interact four times more strongly than two singly charged ions at the same separation. As a result, the lattice energy depends strongly on the charges of the ions. For example, MgF_2 , in which the

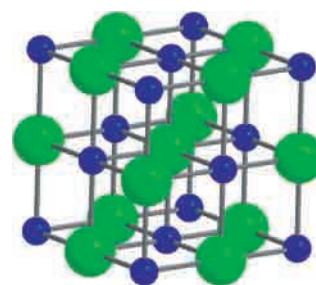


Fig. 1.3 Solid sodium chloride consists of a regular array of Na^+ and Cl^- ions (shown in blue and green, respectively) which are held together by electrostatic interactions. The lines joining the ions do not represent bonds, but are there to guide the eye.

Weblink 1.2

View and rotate in real time the section of the NaCl structure shown in Fig. 1.3.

metal ion is doubly charged, has a lattice energy of 2905 kJ mol^{-1} , which is much greater than that for NaCl. Where both the cation and the anion are doubly charged, the lattice energy is higher again; for example, MgO has a lattice energy of 3850 kJ mol^{-1} . In Chapter 5 we will look in more detail at how lattice energies can be estimated.

1.1.3 Metallic bonding

As its name implies, metallic bonding is the kind of bonding seen in solid (and liquid) metals. In Chapter 5 we will have a great deal more to say about this kind of bonding, but the basic idea is that the structure is held together by electrons which can move freely throughout the macroscopic sample.

The strength of metallic bonding

We can obtain an estimate of the strength of metallic bonding by looking at the energy required to vaporize a metal i.e. turn it from a solid into gaseous atoms. These energies vary very widely, from as little as 100 kJ mol^{-1} for Na, to 330 kJ mol^{-1} for Al and 849 kJ mol^{-1} for tungsten. The values are comparable with those for covalent interactions, but not as strong as those for ionic interactions.

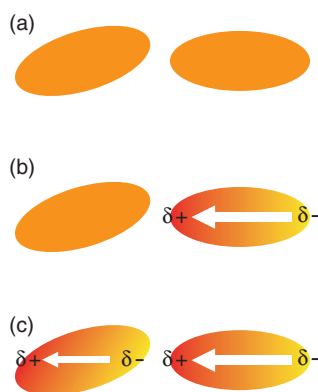


Fig. 1.4 Visualization of the dispersion interaction between two molecules, represented by ellipsoids in (a); the molecules have a symmetrical electron density, and so do not possess dipoles. However, the electron distributions will fluctuate, and this can result in the generation of a dipole, as shown in (b): yellow indicates an increase in electron density, and red a reduction. This dipole will distort the electron distribution of the left-hand molecule in such a way as to induce a dipole in it, as shown in (c). The direction of the induced dipole is always such that there is a favourable interaction between the two dipoles.

1.2 Weaker non-bonded interactions

It is found that between molecules there are a number of interactions which are considerably weaker than typical covalent bonds and so are usually described as *non-bonded interactions*. These interactions are also described as being *intermolecular* as they occur *between* molecules. Despite being weaker than covalent bonds, these intermolecular interactions play an important part in determining the physical and chemical properties of many molecules.

The two most important non-bonded interactions are the *dispersion interaction* (also called the *London interaction*) and *hydrogen bonding*. The latter only occurs in molecules in which a hydrogen atom is attached to a small highly electronegative element, such as nitrogen, oxygen or fluorine. In contrast, the dispersion interaction is a feature of all molecules, so we will describe it first. Collectively, intermolecular interactions (other than hydrogen bonds) are often referred to as *van der Waals forces*.

1.2.1 Dispersion interaction

It is easiest to describe this interaction if we think about the approach of two molecules which do not have dipoles, such as an N_2 molecule, or a cyclohexane molecule. Generally speaking, the reason why a molecule lacks a dipole is that it has certain kinds of symmetry (for example, a *centre of inversion*); however for the present purposes we can just as well imagine that there is no dipole as a result of the electron density being uniform across the molecule. This is represented in Fig. 1.4 (a) by an ellipse with a uniform colour.

It turns out that the electron density fluctuates over time. If at any instant the density becomes unsymmetrical a dipole will be generated, as shown in (b). Here, the electron density on the right has increased, giving a partial negative charge (δ^- , yellow), whereas the electron density on the left has decreased, giving a partial positive charge (δ^+ , red).



Fig. 1.5 Illustration of the arrangement of the dipole and the induced dipole for various orientations of the two molecules. In each pair, the induced dipole is represented by the smaller of the two arrows. Note that the closest contacts are always between red regions (δ^+) and yellow regions (δ^-), which means that the interaction between the two dipoles is always favourable.

The δ^+ end of the dipole is closest to the left-hand molecule, so the electron density of this molecule is pulled to the right, generating an excess of electron density on the right, and a reduction in electron density on the left. The result is the generation of an *induced dipole* on the left-hand molecule, as shown in (c).

As it was the dipole of the right-hand molecule which led to the induction of the dipole of the left-hand molecule, the two dipoles are necessarily arranged so that they have an energetically favourable interaction with one another i.e. the closest approach is between the δ^+ and δ^- ends. It is this favourable interaction which is the origin of the dispersion interaction between molecules.

The key thing to realize is that the induced dipole will be aligned in such a way that it *always* has a favourable interaction with the first dipole. This point is illustrated in Fig. 1.5, in which the orientation of the two dipoles is shown for various different arrangements of the two molecules; in all cases the interaction is favourable.

The fluctuations which lead to the generation of a dipole, and the subsequent induction of a dipole in a nearby molecule, are very rapid processes compared to the rates at which the molecules are moving due to thermal motion. Thus, as the molecules move around, this favourable interaction is always maintained, regardless of the orientation of the two molecules.

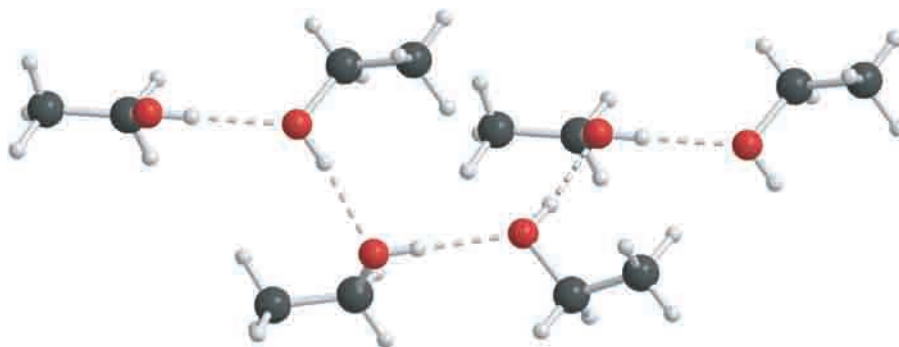
If the molecules have *permanent* dipoles, these will also interact but the problem is that random thermal motion means that the dipoles will *not* always be aligned in such a way as to have a favourable interaction. As a result, when averaged across the sample, the interaction between permanent dipoles is usually much less than the dispersion interaction. Indeed, apart from hydrogen bonding, the dispersion interaction is usually the most significant interaction between molecules.

One of the factors which determines the strength of the dispersion interaction is the *size* of the induced dipole: the larger this dipole, the stronger the interaction. The size of the induced dipole depends on how much a given electric field will distort the electron distribution. The more easily the distribution is distorted, the more *polarizable* the molecule is said to be, and hence the greater the induced dipole.

If the electrons in molecules (and atoms) are held tightly, then the polarizability tends to be low. The most extreme example of this is the fluorine atom in which the high ionization energy reflects the fact that the electrons are tightly held. Thus, compounds containing many fluorine atoms tend to have low polarizabilities, and so the dispersion interaction is weak. This accounts for the fact that many fluoro compounds, such as SF_6 , PF_5 and IF_7 , occur as gases at room temperature. Even uranium hexafluoride UF_6 , despite its high relative molecular mass of 352, sublimes at only 57°C . This property is also exploited in non-stick plastics such as PTFE (polytetrafluoroethylene).

At first glance, it is somewhat counter-intuitive that the interaction between permanent dipoles is weaker than that between induced dipoles. The key point is that induced dipoles are always oriented so that their interaction is favourable; this is not true for permanent dipoles.

Fig. 1.6 Part of the crystal structure of solid ethanol showing, by dashed lines, the hydrogen bonds between different molecules; the molecules at the edge will form further hydrogen bonds with other molecules which are not shown. Note how each of the four molecules in the centre of the picture makes two hydrogen bonds, one to its oxygen and one to the hydrogen attached to the oxygen.



We can obtain an estimate of the strength of the dispersion interaction by looking at the energy needed to vaporize a liquid hydrocarbon, such as ethane. The dispersion interaction is the dominant one which causes such a molecule to liquefy at low temperatures, so the 15 kJ mol^{-1} needed to vaporize the liquid can be taken as an estimate of the size of the interaction. Clearly, this is much weaker than a covalent bond, but by no means insignificant.

1.2.2 Hydrogen bonding

The *hydrogen bond* is a very important non-bonded interaction that occurs between a hydrogen that is attached to a small highly electronegative atom, and a second electronegative atom. Figure 1.6 shows, as dashed lines, the hydrogen bonds which occur in the structure of solid ethanol. In this case, these bonds occur between the hydrogen atom which is attached to oxygen, and an oxygen atom on another molecule. These particular contacts are identified as hydrogen bonds as the O and H are only about 180 pm apart, which is much closer than is usual for atoms in separate molecules, but not as close as a full O–H bond which has a length of around 80 to 85 pm. In the liquid similar bonds are expected to form, although they will of course constantly be made and unmade as the molecules move around due to thermal motion.

There is likely to be a significant dipole in the bond between hydrogen and an electronegative atom, simply because the latter is drawing electron density to itself. The hydrogen therefore has a partial positive charge, which can interact favourably with the partial negative charge appearing on a electronegative atom of a second molecule; this illustrated in Fig. 1.7.

It is thought that this electrostatic interaction between dipoles is a significant contributor to the energy of a hydrogen bond. However, it is observed that such bonds are directional in nature, as is well illustrated in Fig. 1.6. It cannot be, therefore, that the interaction is purely electrostatic. Later on, we will return to a more detailed description of the hydrogen bond which will account for its directional properties.

We can obtain an estimate of the strength of the hydrogen bond by looking at the energy needed to vaporize ethanol, which turns out to be 44 kJ mol^{-1} . Of this, about 15 kJ mol^{-1} can be attributed to van der Waals interactions (mainly dispersion), leaving the remaining 29 kJ mol^{-1} attributable to the hydrogen bonding. Again, the interaction is not as large as for a covalent bond, but

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View and rotate the structure of solid ethanol shown in Fig. 1.6.

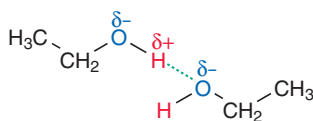


Fig. 1.7 Illustration of the formation of a hydrogen bond, shown in green, between two ethanol molecules. There is a partial positive charge on the hydrogen that is attached to the oxygen, on account of the high electronegativity of the latter. This partial positive charge can interact favourably with the partial negative charge on the oxygen of another molecule.

is certainly significant. As you may know, the three-dimensional structures of biological molecules such as proteins and DNA are maintained largely by an extensive network of hydrogen bonds.

1.2.3 Repulsive interactions

So far we have been talking about the favourable, attractive, interactions between atoms and molecules. Generally, the closer the molecules approach, the more favourable the interaction. This means that the energy due to the attractive interaction decreases as the molecules approach one another, as is illustrated by the blue curve in Fig. 1.8. Thinking of it the other way round, this favourable interaction means that we have to put energy in to break the molecules apart from one another.

It is found that when atoms and molecules approach one another closely there is in addition always a *repulsive* interaction which causes the energy to rise, as shown by the red curve. As the distance between the molecules decreases, the energy due to the repulsive interaction increases more quickly than the decrease due to the attractive interaction. Thus, at some distance, the total energy (shown by the black curve), which is the sum of the attractive and repulsive part, has a minimum value.

This distance at which the energy is a minimum is called the *equilibrium separation*, and is the point at which the attractive and repulsive forces are in balance. On average, we therefore expect to find that the two molecules are separated by this equilibrium separation. We say ‘on average’ as, due to thermal motion, the molecules will actually be moving around in the vicinity of this equilibrium distance.

These repulsive interactions come about when the electron density from one atom overlaps significantly with that of another. We will be in a position to understand why this leads to a repulsion when we have looked in more detail at the electronic structures of atoms and molecules, which is the topic of the next three chapters.

In a molecular solid (section 1.3), the way the molecules are arranged (e.g. the distances between them) is determined by this balance between the attractive and repulsive forces. Similarly, the spacing of the ions in an ionic lattice is determined by the balance between the attractive electrostatic interactions between oppositely charged ions, the repulsive electrostatic interactions between ions of the same charge, and the repulsive interactions between all the ions. Note that even oppositely charged ions, if they approach closely enough, will eventually repel one another.

1.3 Solids

Solid materials can show the whole range of bonding interactions we have been describing above, and not surprisingly the properties of a particular solid reflect the kind of bonding involved.

Molecular solids are composed of discrete molecules which retain their individual identity, but are held together by non-bonded interactions. Since these interactions are relatively weak, molecular solids tend to have quite low melting points. Many organic compounds form molecular solids, as do elements such as iodine (I_2) and phosphorus. For example, as shown in Fig. 1.9 on the following page, the allotrope white phosphorus contains discrete P_4 molecules,

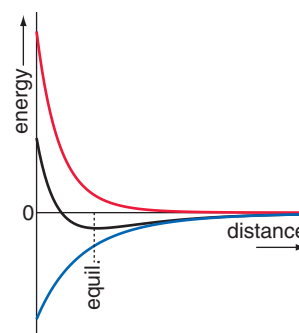
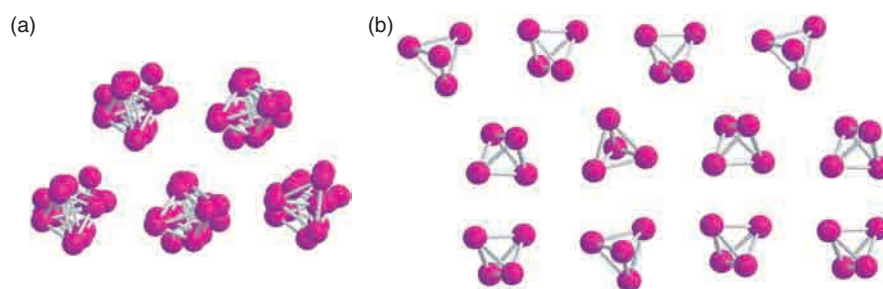


Fig. 1.8 When two molecules approach one another there is a favourable interaction which leads to a reduction in the energy, as shown by the blue curve. If we take the energy zero to be when the molecules are well separated, the energy due to this favourable interaction becomes more negative the closer the molecules approach. There is also a repulsive interaction which eventually leads to an increase in energy as the distance decreases, as shown by the red curve. The repulsive energy increases more quickly than the attractive energy decreases, so that at some point the total energy, shown by the black curve, is a minimum (marked by the dashed line); this is the *equilibrium distance*.

Fig. 1.9 The allotrope of phosphorus known as white phosphorus is a molecular solid, consisting of discrete P_4 molecules arranged in chains and layers. The view shown in (a) is taken looking down the chain of P_4 molecules. View (b) shows how the chains are arranged relative to one another within a layer.



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View and rotate the structure of white phosphorus shown in Fig. 1.9.

arranged in chains and layers. Numerous inorganic compounds, such as P_4O_{10} , also form molecular solids.

Some solids consist not of discrete molecules, but are essentially formed as one giant covalently linked network which extends throughout of the sample. We mentioned this kind of bonding in section 1.1.1 on page 4, and illustrated it with the structure of SiO_2 shown in Fig. 1.2 on page 5. The strength of the covalent bonding tends to give such solids rather high melting points. Similarly, for *ionic solids*, which were described in section 1.1.2 on page 4 and illustrated in Fig. 1.3 on page 5, the strong interactions also lead to high melting points.

The final type of solid we need to distinguish is a *metallic solid*, where the bonding is of the type described in section 1.1.3 on page 6. Such solids are distinguished from all those mentioned so far by being good conductors of electricity on account of the mobile electrons they contain.

1.4 Structure determination by X-ray diffraction

The structure of a molecule is of immense importance to chemists, as so much depends on the way in which the atoms are joined up and the shape the molecule adopts. An enormous amount of effort has therefore been put into developing and refining methods for determining molecular structures. Of these methods, spectroscopy is the one in most common day-to-day use by chemists, and this topic is covered in detail in Chapter 11.

However, spectroscopy is rather a qualitative tool when it comes to structure determination: it can tell us the sorts of groups that are present and possibly how they are connected to one another, but it does not give precise structural information such as bond lengths and bond angles. When it comes to obtaining really detailed and definitive structural information one technique – that of *X-ray diffraction* – reigns supreme.

For an X-ray diffraction experiment we need a small crystal of the compound of interest. In this crystal the ions or molecules are arranged in an orderly way which is the same throughout the solid. We can think of the solid as being composed of the same structural motif (e.g. an array of ions or a molecule) repeated endlessly throughout the solid. This repeating motif is called the *unit cell*.

As a result of the orderly structure, a beam of X-rays which strikes the crystal is reflected in certain specific directions giving rise to what is known as a *diffraction pattern*. Figure 1.10 on the next page shows the key parts of

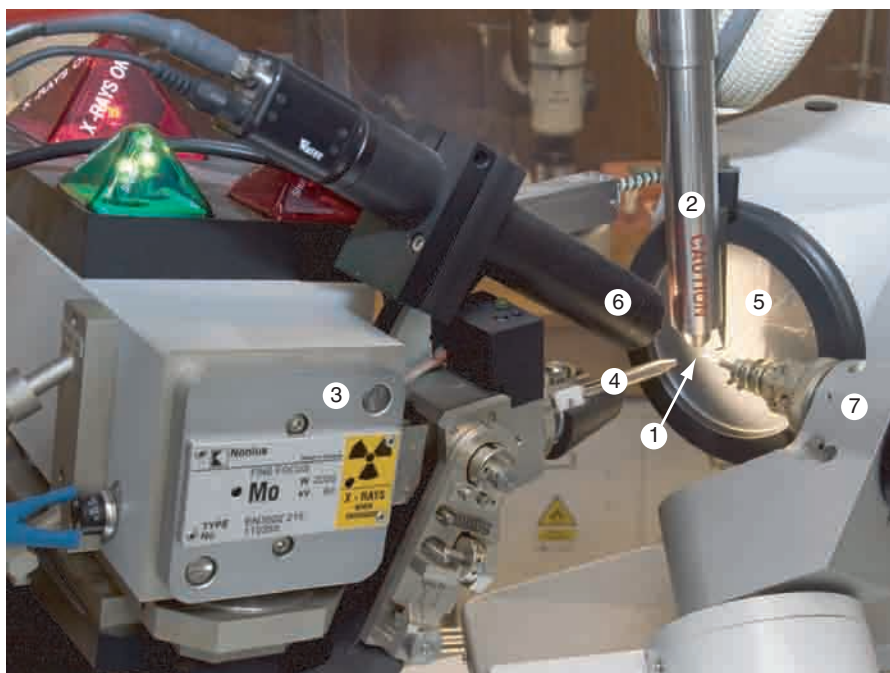


Fig. 1.10 A typical X-ray diffractometer. The crystal is mounted on the end of the fine glass rod 1, and is cooled by a stream of cold nitrogen gas from 2. This cooling helps to prevent the crystal from being damaged by the heat generated when the X-rays are absorbed, and the atmosphere of nitrogen gas also prevents chemical degradation of the crystal. The X-rays are generated in 3 by bombarding a target (here molybdenum) with high-energy electrons. The X-rays are focused along the tip 4 towards the crystal. The detector, 5, is placed behind the crystal, and a small TV camera, 6, is used to aid in the alignment process. The crystal can be rotated, under computer control, into different orientations by the goniometer, 7.

the typical X-ray diffractometer used to measure the diffraction pattern, and an example of such a pattern is shown in Fig. 1.11 on the following page. In fact, the X-rays are diffracted by the electrons, with the strongest diffraction coming from regions of high electron density. In molecules, most of the electron density is clustered around the atomic nuclei (i.e. from the filled shells), and so a diffraction experiment can be used to infer the positions of the atoms.

If the crystal is a molecular solid we will be able to determine from a diffraction experiment not only the precise spatial arrangement of the atoms which form the molecule, but also the way in which the molecules are arranged relative to one another. Similarly, for an ionic solid, we will be able to determine the positions of the ions.

It is not entirely a straightforward matter to go from the measured diffraction pattern to a three-dimensional map of the electron density in the unit cell. However, provided there are not too many atoms in the unit cell (say less than a thousand) it is possible to determine the electron density in a reasonable time using a computational approach known as the *direct method*.

Once we have determined a map of the electron density we can use it to identify where the atoms are. At the simplest level, we can expect there to be atoms at positions which have high electron density, but we have to decide which atom to place at each position. Hydrogen atoms can be difficult to locate as they have much lower electron density than most other atoms.

The usual process is to develop a model of the molecule and then calculate from it the expected electron density – something which is relatively easy to do. In building the model we take account of any other information we have, such as the molecular formula or the expected structure. For example, if the molecule has a benzene ring, we have a good idea where the six carbon atoms are relative

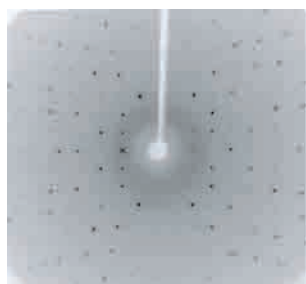


Fig. 1.11 A example of an X-ray diffraction pattern from a small crystal. The crystal is mounted at the centre of the picture and the X-ray beam is coming towards us. To stop the direct beam overloading the detector, a metal ‘beam stop’ is placed between the crystal and the detector; this beam stop, and the wire holding it, appear as the white shadow running from the middle to the top of the picture. X-rays are diffracted from the crystal at certain angles, and each diffracted beam gives rise to one of the black dots. In order to determine a molecular structure, many such diffraction patterns are taken in which the X-rays impinge on the crystal in different directions.

to one another, even though we do not know how to place these six atoms in the unit cell.

The electron density computed from the model is then compared to the experimental electron density; if the two differ at the position of one of the atoms, then that atom needs to be moved. The whole process is repeated over and over again until the best agreement between the experimental and calculated electron densities is obtained. This process is known as *refinement*.

With modern instruments to measure the diffraction pattern in an automatic way, and powerful computers to analyse it, it is possible to determine the structures of small- to medium-sized molecules in a more-or-less routine way. A very large number of structures have been determined, and these are deposited in various databases, as described in Box 1.1 on the next page.

1.4.1 Joining up the atoms in an X-ray structure

The final result of analysing the data from an X-ray diffraction experiment is the location of the atoms, but the experiment does not tell us how these atoms are joined up i.e. where the ‘bonds’ are. Typically the connections are made by assuming that atoms which are closer than some specified distance are bonded to one another. These distances are based on the bond lengths found in a large number of compounds whose structures have already been determined. In other words, we simply use the precedents set by existing, known structures.

The way these precedents are usually expressed is to assign a *covalent radius* to each type of atom i.e. a value for carbon, a different value for nitrogen and so on. If the distance between two atoms is comparable, within certain specified limits, to the sum of the covalent radii, then a bond is considered to exist between the two atoms.

For example, the covalent radius for carbon is usually taken as 68 pm, and that for chlorine as 99 pm. Typically, a tolerance of up to ± 40 pm is permitted on any bond length computed from these values. So, a carbon and a chlorine atom approaching between $68 + 99 - 40 = 129$ pm and $68 + 99 + 40 = 207$ pm would be considered to be bonded, which is rather a wide range.

In joining up the atoms we also take account of the normal rules of valency, for example by making sure that each carbon has a valency of four, and each oxygen a valency of two. This approach works well for organic molecules, where the rules are rarely if ever broken, but becomes harder to apply once we move away from such well behaved molecules.

1.4.2 Caution with X-ray structures

Just about all the molecular structures which are described in this book have been determined by X-ray diffraction. The only exceptions are very small molecules in the gas phase, such as CO_2 and N_2O , for which there are spectroscopic methods capable of giving very detailed structural information. These methods are touched on in Chapter 16.

The information provided by X-ray diffraction is very precise and generally unambiguous. However, we need to be careful about a few things when using these data.

Box 1.1 Structural databases

A very large number of molecular structures have been determined using X-ray diffraction, and these have all been collected together into electronic databases, which are freely available to research scientists. The *Cambridge Structural Database* contains structural information on what are essentially organic molecules i.e. those with a carbon skeleton. At present there are over 360,000 entries in the database. The *Inorganic Crystal Structure Database* contains structural information on inorganic materials, be they molecular, giant covalent or ionic in form; there are presently over 90,000 entries. The structures of biological molecules, such as proteins and nucleic acids, are also collated in separate databases; over 35,000 structures of proteins have been deposited. These databases represent an enormous resource for those interested in patterns and trends in molecular structures.

- A diffraction experiment gives us the structure of the molecule *in the crystal*: when the compound is dissolved in a solvent, or passes into the gas phase, it may not have the same structure. For example, phosphorus pentachloride exists in the solid as an array of PCl_4^+ and PCl_6^- ions, whereas in the gas phase it exists as discrete PCl_5 molecules. More subtle changes of molecular geometry between the solid and solution phases are also commonly found.
- We need to remember that molecules do not necessarily have a single, fixed structure. All molecules are constantly flexing and bending due to vibrations, there may be rotation about (single) bonds, and some molecules readily interconvert between structural isomers. A crystal structure will not necessarily tell us about all of these possibilities, as the crystallization process tends to favour one particular form.
- X-ray diffraction tells us where the *atoms* are located in relation to one another. It does not tell us which atoms are *bonded* to one another; this is something we have to infer based on our chemical intuition and perhaps other experimental data.

We now turn to the important matter of how we represent molecular structures and paper, and what these representations imply.

1.5 Where are the bonds?

As soon as we learn about molecules we start drawing ‘structures’ in an attempt to explain and describe the way in which the atoms are joined up. This whole process becomes so second nature to a chemist that it is all too easy to forget that what we draw is just some representation of the bonding, which may or may not be adequate. In this section we will take a critical view of how we represent molecular structures.

Let us take the water molecule as an example. We know that water has the formula H_2O , and using either spectroscopy or diffraction experiments we can find out the locations of the three atoms relative to one another. Given the arrangement shown in Fig. 1.12 (a), our instinct is to join up the O with the two

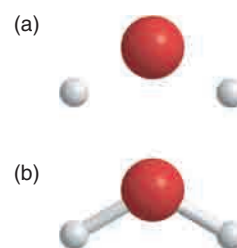


Fig. 1.12 Experiments tell us that the three atoms in water are arranged as in (a). Instinctively we would join these atoms up with two O–H bonds as shown in (b). In the case of water, it is pretty clear that this is the right approach, but for more unusual molecules it is not always clear which atoms are bonded to which.

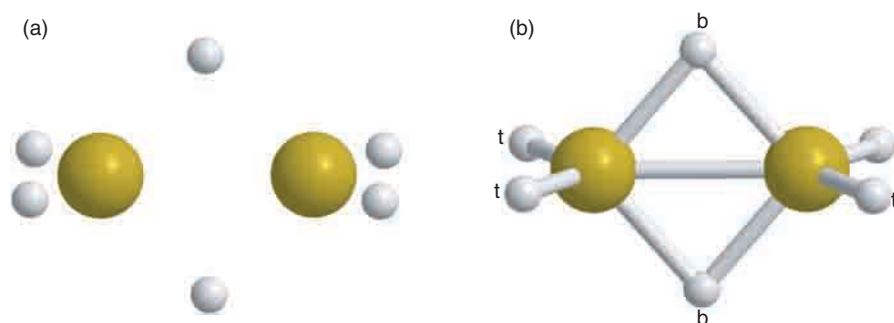


Fig. 1.13 Shown in (a) is the arrangement of the atoms in diborane, B_2H_6 , as determined by X-ray diffraction. Boron atoms are shown in yellow, and hydrogen atoms in grey. Those atoms which are close enough to be considered bonded are joined together to give the structure shown in (b). There are two types of hydrogen atoms: terminal (marked 't') and bridging (marked 'b').

hydrogens, indicating the presence of two O–H bonds, as shown in (b). We do not, however, join up the two H atoms, as we do not expect a bond between them.

In drawing the structure in this way we have used our chemical knowledge that the usual valency of oxygen is two and that of hydrogen is one. Once we have made a covalent bond between the oxygen and each hydrogen, all of the valencies are satisfied so there is no 'need' for a bond between the two hydrogens.

In water, everything is clear cut, but as we look at more complex, and more exotic, molecules we will see that it becomes more and more difficult to say where the bonds are. A very good example of these problems is provided by the case of diborane, B_2H_6 .

The arrangement of atoms in this molecule has been determined by X-ray diffraction, and is shown in the Fig. 1.13 (a). The task is now to join up the atoms in the same way we did for water. The two hydrogens on the left, and the two on the right, are 117 pm from the nearest boron atom, a distance which is certainly short enough to be considered as a bond, so we connect the nearby atoms to represent this. The hydrogen at the top is 132 pm from both boron atoms, which is again a short enough distance for it to be considered a bonded interaction. We therefore attach this hydrogen to both borons, and do the same for the hydrogen at the bottom.

Finally, the two boron atoms are 175 pm apart, which is just about close enough for a bonded interaction between two first-row elements, so we connect these two atoms by a bond, giving the complete structure shown in (b). There are two types of hydrogens in this structure: *terminal*, denoted 't' and *bridging*, denoted 'b'.

We can immediately see that there is a problem with this structure as it has nine bonds, each by implication comprising a pair of electrons giving a total electron count of 18. However, in B_2H_6 there are only 12 valence electrons. Put another way, in the structure the boron atoms have a valency of five, and the bridging hydrogens have a valency of two: both are unexpected.

It is clear from this discussion that the way the atoms are joined up in Fig. 1.13 (b) is inconsistent with both the electron count and the normal rules of valency. There are simply too many bonds.

Weblink 1.5

View and rotate the structure of diborane shown in Fig. 1.13.

The current understanding of the bonding in diborane is that the bonds between the boron atoms and the terminal hydrogens are of a conventional type in which a pair of electrons is shared between the two atoms. The bonding between the borons and the two bridging hydrogens is delocalized, in the sense that the electrons are shared over all four atoms, rather than between pairs of atoms. So, the lines in the figure are correct in that they show bonded interactions, but not all the lines represent simple bonds from the sharing of two electrons.

A second example is the lithium cluster compound, with formula $\text{Li}_4(\text{CH}_3\text{CH}_2)_4$, shown in Fig. 1.14. The core of the structure is four lithium atoms which are placed approximately at the corners of a tetrahedron. Each face of the tetrahedron is bridged by the CH_2 carbon of an ethyl group, such that there are close contacts between the carbon and three lithium atoms. As in the case of diborane, the atoms which are close enough to be considered bonded have been connected by lines. For the ethyl groups we can be sure that the line joining the two carbons does indeed represent a conventional C–C bond. As to the rest of the molecule, it is very much less clear where the bonds are. It is probably best simply to view the lines as a guide for the eye, indicating which atoms are close to one another, and in what spatial arrangement.

Our final example is the structure of solid NaCl, shown in Fig. 1.3 on page 5; here we see the familiar regular arrangement of sodium and chloride ions. Lines have been drawn which connect adjacent ions, but these lines certainly do not represent chemical bonds, as this structure is held together by non-directional electrostatic forces between ions. As in the lithium cluster, the lines are there simply to guide the eye and to help us appreciate the spatial arrangement of the ions.

In summary, we have seen in this section that we need to be careful about how we interpret the representations of molecular structures. For simple compounds, particularly organic-type molecules, there is probably a close correspondence between the lines connecting atoms and the presence of bonds. Once we move away from such structures, although we still connect nearby atoms by lines it is much less clear whether or not these lines are an accurate representation of the bonding in the molecule.

1.6 How to draw molecules

Being able to draw representations of molecules on paper in a straightforward, clear and informative way is going to be very important for us in our study of chemistry. In this section we will look at the particular way in which organic molecules are drawn by practising chemists. It is important to get used to this method of drawing molecules as we will use it extensively throughout this book, and you will find that it is universally employed in more advanced texts.

Even a molecule as simple as methane already represents something of a challenge, as it is three-dimensional; various representations of CH_4 are shown in Fig. 1.15 on the next page. The so-called ‘displayed’ formula shown in (a) certainly represents the bonding correctly, but gives no sense of the three-dimensional shape which is shown in (b).

Although (b) is realistic, it is not convenient to draw by hand, so it is usually represented by the conventional representations shown in (c) and (d). In (c) the C–H bonds which are in the plane of the paper are drawn as single lines,



Fig. 1.14 Crystal structure of the compound $\text{Li}_4(\text{CH}_3\text{CH}_2)_4$, which contains a cluster of four lithium atoms (shown in orange); the faces of this cluster are bridged by carbon atoms (shown in dark grey). To avoid confusion, the hydrogen atoms are not shown.

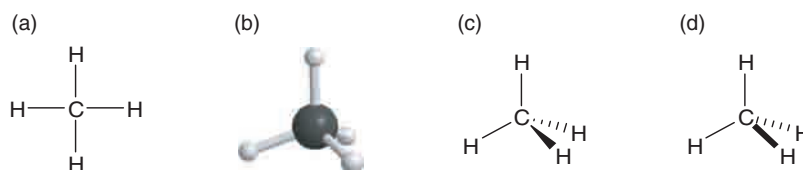
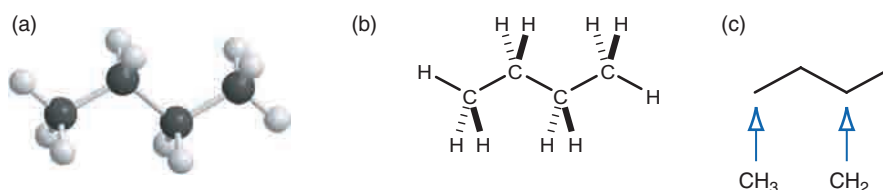


Fig. 1.15 Different representations of CH_4 . The displayed formula shown in (a) does not represent the three-dimensional shape, shown in (b). Representations (c) and (d) are used to convey the three-dimensional shape. The C–H bonds in the plane of the paper are drawn as single lines, the bond coming out of the plane is represented by a solid wedge or thick line, and the bond going into the plane is represented by a dashed wedge or line.

Fig. 1.16 Shown in (a) is the three-dimensional shape of butane, C_4H_{10} ; the conventional representation is given in (b). However, this is rather cluttered so the representation shown in (c) is generally preferred.



whereas the bond coming towards us out of the plane of the paper is shown by a solid wedge. The bond going into the plane of the paper is shown by a dashed wedge; note that the dashing runs across the wedge. Structure (d) is often used as an alternative to (c). Here the bond coming out of the paper is represented by a bold line, and the one going into the paper is represented by a dashed line.

Figure 1.16 (a) shows the three-dimensional structure of butane (C_4H_{10}). Note that the carbon chain lies in a plane and forms a zig-zag. In fact, there is plenty of experimental evidence that hydrocarbon chains often adopt this conformation, so the conventional representation shown in (b) is quite realistic. However, the problem with representation (b) is that it is very cluttered, and would take quite a long while to draw out.

To get round this problem, chemists use an abbreviated form of this structure, as shown in (c). In this representation all of the hydrogens attached to the carbons are left out, as are the letters 'C' representing the carbons themselves. Where two lines join, there is assumed to be a carbon, and in addition there is a carbon at the free end of a line. For a given carbon, it is simply assumed that there are sufficient hydrogens attached such that the valency of four is satisfied. So, the carbons on the far right and left are methyl groups, CH_3 , and the two carbons on the middle are CH_2 groups.

This *framework* representation of molecules can be extended to other molecules by using the following rules:

1. Draw chains of atoms as zig-zags with approximately 120° angles.
2. Do not indicate carbon atoms by a 'C'.
3. Do not include any hydrogens, or bonds to hydrogens, which are *attached to carbon*.
4. Draw in all other atoms together with all of their bonds, and all the atoms to which they are attached
5. If a carbon atom is drawn in, include all the other atoms attached to it.

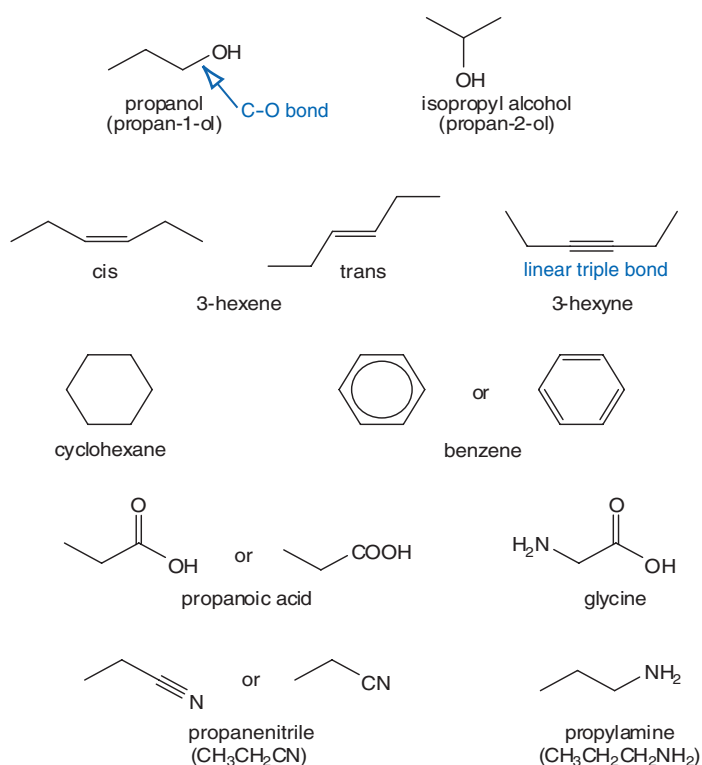


Fig. 1.17 Examples of organic molecules drawn as framework structures. There is often more than one way of drawing a structure, and which you choose depends on personal taste or on what part of the molecule you want to emphasise. For example, in the case of propanoic acid, if we are going to discuss the reactions of the carbonyl group, then the left-hand of the two representations is preferred.




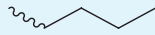


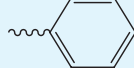
Several examples of the applications of these rules are shown in Fig. 1.17. It is important not to be too rigid, though, about applying these rules, and to realise that often there are alternative ways of drawing the same structure. The key thing is to make sure that the structure is clear and unambiguous.

1.7 Common names and abbreviations

When drawing and talking about chemical structures there are quite a few abbreviations which are in common use for particular groups. The most important of these are given in Table 1.1 on the next page. For the more complex groups, framework structures are also given. In these, the wavy line indicates the point of attachment of the group.

As you will have learnt, there is a systematic way of naming chemical compounds. On the whole, most practising chemists will understand these names but they are also likely to use older, historical, names for some common compounds. A selection of these ‘trivial names’ are listed in Table 1.2 on page 19. You will simply have to get used to these as part of the everyday language of chemistry.

Table 1.1 Common abbreviations

abbreviation	name	formula	framework structure
Me	methyl	-CH ₃	
Et	ethyl	-CH ₂ CH ₃	
<i>n</i> -Pr	normal propyl	-CH ₂ CH ₂ CH ₃	
<i>i</i> -Pr	iso propyl	-CH(CH ₃) ₂	
<i>n</i> -Bu	normal butyl	-CH ₂ CH ₂ CH ₂ CH ₃	
<i>t</i> -Bu	tertiary butyl	-C(CH ₃) ₃	
Ac	acetyl	-COCH ₃	
Ph	phenyl	-C ₆ H ₅	
Ar	aryl	any aryl group (a substituted benzene ring)	
R	alkyl	any alkyl group	

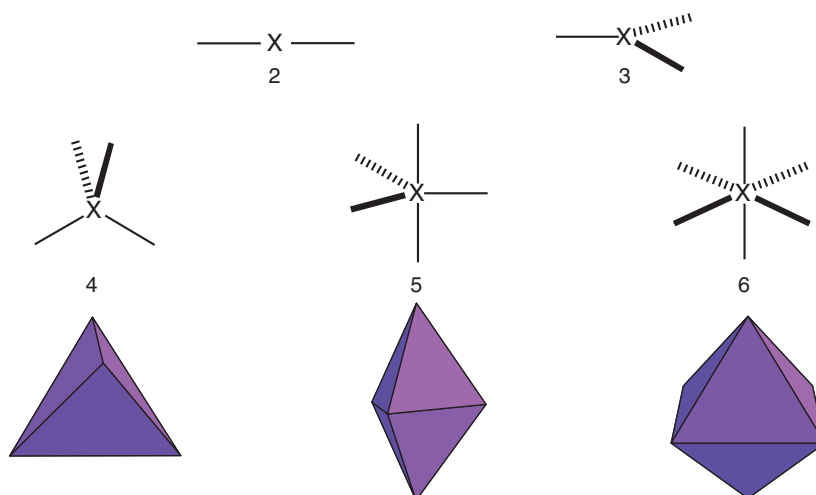
1.8 Predicting the shapes of molecules using VSEPR

With modern theories and the aid of powerful computers we can predict, with quite good accuracy, the shapes of small- to medium-sized molecules. Often, however, we do not need to know all of the details of the molecular geometry (i.e. every bond length and bond angle), but simply require a general idea of the shape. The *valence shell electron pair repulsion* (VSEPR) model is a useful, non-computational, way of predicting the general shape of small molecules. We will look briefly at how this theory can be applied, its successes and its limitations.

The basic idea behind the VSEPR model is rather simple, and is best illustrated by considering the series of hydrides AH_{*n*}, where A is an element from the second period. All we do is count the number of *electron pairs* in the valence shell of A and then assume that these electron pairs will arrange themselves in such a way as to be as far apart from one another as possible. The process is illustrated in Fig. 1.18 on the next page

For example, in CH₄ the carbon contributes four electrons and each hydrogen contributes one, making eight in all. There are thus four pairs of electrons, one associated with each C–H bond. The idea is that these electron pairs, and

Fig. 1.19 Illustration of the geometrical arrangements of two to six electron pairs which minimize the repulsion between the pairs. The arrangement for three pairs is trigonal planar, four is tetrahedral, five is trigonal bipyramidal and six is an octahedral. For these last three arrangements, a picture of the solid from which the arrangement of ligands is derived is also shown. In a given shape, the positions occupied by the ligands are all equivalent, with the exception of the trigonal bipyramid; in this, the two *axial* positions at the top and bottom are different from the other three *equatorial* positions.



In fact experiment shows that the H–N–H bond angle in ammonia is 107° , somewhat less than the tetrahedral angle of 109.5° . We can refine the model to accommodate this by proposing that the repulsion between a bonded pair and a lone pair is greater than the repulsion between two bonded pairs. This difference in the repulsion would mean that N–H bonded pairs could get closer together, resulting in the required reduction in the H–N–H bond angle.

A similar argument applies to OH_2 where there are again four electron pairs, this time two bonded pairs and two lone pairs, resulting in a tetrahedral arrangement and hence a ‘bent’ geometry for water. The H–O–H bond angle in water is 104.5° , even smaller than the H–N–H bond angle in ammonia; this observation can be accommodated by supposing that the lone pairs repel one another even more than they repel bonded pairs.

A similar argument can be used for other numbers of electron pairs, and the optimum arrangements for between two and six lone pairs is shown in Fig. 1.19. For example, BeH_2 has just two pairs of electrons in its valence shell, and according to the figure these should be arranged at 180° to one another to give a linear geometry, which is exactly what is found experimentally.

BF_3 and the ion CH_3^+ (which is known in the gas phase) both have three electron pairs, which are arranged at 120° to one another, giving a trigonal planar geometry, again in agreement with experiment. The fluorides PF_5 and SF_6 have five and six bonded pairs, respectively, and their geometries are found to conform to the predictions of Fig. 1.19.

Multiply bonded species

The VSEPR model can also deal with multiply bonded species, such as CO_2 in which there are double bonds between each oxygen and the carbon. The valence shell of the carbon has eight electrons, four contributed by the carbon and, on account of the double bonds, *two* contributed by each oxygen. There are thus four electron pairs in the carbon valence shell, grouped into two ‘pairs of pairs’ of electrons associated with each C–O bond. By arranging the two bonds at 180° to one another, the repulsion between the two pairs of pairs of electrons is minimized, thus accounting for the linear geometry of CO_2 .

A second example is sulfur trioxide, SO_3 , which has six valence electrons contributed from the sulfur, and six in total from the three oxygens. These form three S–O double bonds, each comprising two electron pairs. Minimizing the repulsion between these ‘pairs of pairs’ gives a trigonal planar geometry, which is what is observed for SO_3 .

A more complex example is the sulfate ion, SO_4^{2-} . Recognizing that the oxidation state of the sulfur is VI, we would normally draw the structure as having a double bond to two of the oxygens, and a single bond to the other two, as shown in Fig. 1.20 (a). The problem with this structure is that it is inconsistent with the known equivalence of the four oxygen atoms. The structure shown in (b), although rather less familiar, makes the four oxygens equivalent and, by giving the sulfur a 2+ charge, has the overall correct charge.

In structure (b) the electron count is six from the sulfur, less two for the 2+ charge, and a total of four from the oxygens. The total number of electrons is thus eight, giving four pairs which arrange themselves tetrahedrally. This is in accord with the known structure of the sulfate ion.

In more complex molecules, we can use the VSEPR approach to predict the spatial arrangement of bonds around a particular atom. For example, in organic molecules the four single bonds around a carbon are expected to be arranged tetrahedrally, and the two single bonds to an oxygen are expected to have an angle somewhat less than the tetrahedral angle between them. Similarly, the three single bonds to a nitrogen are expected to be arranged in a trigonal pyramid. This kind of approach is very useful for giving a rough idea of the arrangement of bonds around a particular atom.

1.8.1 Limitations of the VSEPR approach

The VSEPR approach is reasonably successful when applied to organic molecules and to other compounds consisting mainly of non-metallic elements. However, it is too simplistic a model for us to expect it to apply universally, and there are many cases where the predictions of the VSEPR theory are simply wrong.

For example, as shown in Fig. 1.21, in *amines* the three bonds around the nitrogen are found to be arranged in a trigonal pyramid, in accordance with the predictions of VSEPR. However, in *amides* the three bonds around the nitrogen are found to be arranged in a planar geometry, which is not what is expected from VSEPR. As we will see in later on, this planar geometry is associated with the bond between the nitrogen and the carbonyl carbon having partial double-bond character.

A further example is provided by the (gaseous) molecular fluorides of the Group 2 metals. As we have seen, the prediction is that these should be linear, but although this is so for BeF_2 and MgF_2 , the bond angles in CaF_2 , SrF_2 and BaF_2 are 145° , 120° and 108° , respectively. VSEPR can offer no explanation for this trend.

A final example of the failure of VSEPR is given by transition metal complexes. There are a large number of these of the type ML_6 , all of which have an octahedral arrangement of ligands L, despite varying numbers of electrons in the valence shell of the metal.

It is important to realise that molecules do not necessarily adopt the shapes they do *because* of the repulsion between valence electrons, as implied by the VSEPR model. The real reasons why a shape is preferred are surely more

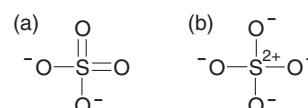


Fig. 1.20 Two different representations of the bonding in the sulfate anion. Representation (a) is more familiar, but is not consistent with the equivalence of all four oxygen atoms. In (b) these atoms are clearly equivalent, but note the 2+ charge on the sulfur.

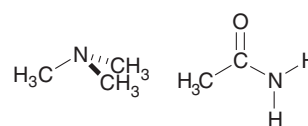
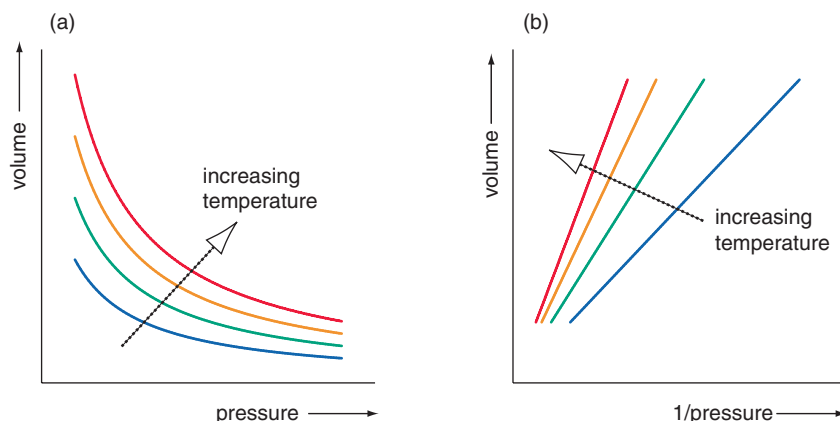


Fig. 1.21 In an amine, shown on the left, the bonds around the nitrogen are found to be arranged in a trigonal pyramidal fashion, as predicted by VSEPR. However, in an amide, shown on the right, the three bonds to nitrogen lie in a plane, contrary to the predictions of VSEPR.

Fig. 1.22 Illustration of the pressure–volume relationship for a fixed quantity of an ideal gas at various temperatures. In (a) volume is plotted against pressure for various temperatures. The inverse relationship between these two quantities is best seen by plotting, for example, volume against the reciprocal of pressure, as shown in (b). The resulting straight lines are in accord with Boyle’s Law.



complex than the repulsion between electron pairs. The fact that the model sometimes predicts the correct shape does not mean that the model is correct – it might just be fortuitously giving the right answer. All in all, we need to approach the VSEPR model with a fair dose of scepticism. It does provide us with a useful guide, but we should not be too surprised if its predictions turn out to be incorrect.

1.9 The ideal gas

In the subsequent chapters we are quite often going to make use of the properties of gases, so this is a convenient moment to review these and introduce how they can be described in a quantitative way. Experimental work has shown that the pressure, volume and temperature of a fixed amount of a gaseous substance are related. For example, at a fixed temperature it is found that the volume is inversely proportional to the pressure applied i.e. the higher the pressure, the smaller the volume. This relationship is often known as *Boyle’s Law*.

Similarly, for a fixed volume of gas, it is found that the pressure is proportional to the temperature i.e. the higher the temperature, the greater the pressure (known as *Charles’ Law*). In fact these relationships are not followed precisely, with especially large deviations being seen for gases under high pressures or with higher densities. However, at sufficiently low pressures and densities, all gases follow Boyle’s and Charles’ Laws.

These observations led to the idea of an *ideal gas* (also called a *perfect gas*), which is one which obeys the *ideal gas equation*:

$$pV = nRT. \quad (1.1)$$

In this equation, p is the pressure, V is the volume, T is the (absolute) temperature, n is the amount of gas in moles, and R is a universal constant known as the *gas constant*. In SI, the pressure is in N m^{-2} , the volume is in m^3 and R has the value $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$.

If the amount of gas (i.e. n) and temperature are fixed, then the terms on the right-hand side of Eq. 1.1 are constant and so

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

It is important to realize that the units of n are moles. n is often described as the ‘number of moles’; although this usage is common, it is somewhat imprecise as n is not a number, but an amount.

Thus the volume is inversely proportional to the pressure, which is Boyle's Law. In fact from Eq. 1.1 on the preceding page we can see that the exact relationship is $V = nRT/p$, so if we plot V against $1/p$ we will obtain a straight line whose slope is proportional to the temperature. This relationship is illustrated in Fig. 1.22 on the facing page.

Similarly, if we rearrange Eq. 1.1 to give

$$p = \frac{nRT}{V},$$

and then imagine keeping the amount of gas and the volume fixed, we have $p \propto T$, as illustrated in Fig. 1.23; this is Charles' Law. The last equation also tells us that, at fixed temperature and volume, the pressure is directly proportional to the amount of gas (i.e. n), which is also illustrated in the figure.

Equation 1.1 is called an *equation of state*, since it connects the variables p , V , n and T which describe the physical state of the system. To a good approximation, real gases obey the ideal gas equation provided that the pressure and density are not too high. For example, the behaviour of gases such as helium, nitrogen and methane at normal pressures and temperatures are well-approximated by the ideal gas equation. However, a dense gas, such as the vapour above a volatile liquid, or a gas such as ammonia at several atmospheres pressure, show significant deviations from ideal behaviour. Such gases are said to be *non-ideal*.

We will often need a relationship between the pressure, volume and temperature of a gas, such as that provided by the ideal gas law. For simplicity, we will simply *assume* that the gases we are dealing with obey the ideal gas law to a reasonable approximation. There are more complex laws which describe the behaviour of real gases to a better approximation (such as the van der Waals equation of state), but using such laws will make our calculations much more difficult, and so we will not go down this route.

At a molecular level, it can be shown that a gas in which there are negligible interactions between the molecules, and in which the molecules occupy a negligible part of the total volume, will obey the ideal gas law. It thus makes sense that ideal gas behaviour is seen at low pressures and densities, as this means that the molecules are far apart relative to their size. Similarly such an interpretation makes sense of the observation that helium, in which there are very weak interatomic interactions, behaves as an ideal gas over a much wider range of pressures than does ammonia, in which there are stronger intermolecular interactions.

1.9.1 Using the ideal gas equation

Equation 1.1 can be rearranged in the following way

$$\begin{aligned} pV &= nRT \\ \frac{p}{RT} &= \frac{n}{V}. \end{aligned}$$

The quantity n/V is the moles per unit volume, in other words the *concentration*, which we will give the symbol c : $c = p/(RT)$. This shows that, at fixed temperature, the concentration of molecules in a gas is proportional to the pressure. So, in effect, the pressure of a gas is a measure of the concentration.

☞ If you are unfamiliar with the use of SI units, refer to section 20.2 on page 882.

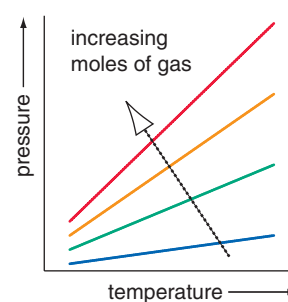


Fig. 1.23 Illustration of the pressure–temperature relationship for a fixed volume of an ideal gas; lines are plotted for amounts of gas in moles. These plots are in accord with Charles' Law.

Example 1.1 Using the ideal gas equation

Use the ideal gas equation to calculate the volume occupied by one mole of gas at atmospheric pressure ($1.013 \times 10^5 \text{ N m}^{-2}$) and 0°C .

All we need to do is rearrange Eq. 1.1 on page 22 and then substitute in the values for n , p and T . We use SI units for all of the quantities (see section 20.2 on page 882), and are careful to use the absolute temperature, 273.15 K.

$$\begin{aligned} V &= \frac{nRT}{p} \\ &= \frac{1 \times 8.3145 \times 273.15}{1.013 \times 10^5} \\ &= 0.0224 \text{ m}^3. \end{aligned}$$

As we have used SI throughout, the answer comes out in m^3 . This value may be familiar to you, as it is the molar volume at STP (standard temperature and pressure), often quoted as 22.4 dm^3 .

The second example is to calculate the concentration, in molecules per cubic metre, of an ideal gas at STP. All we need to do is use Eq. 1.2 which gives the required concentration, N/V :

$$\begin{aligned} \frac{N}{V} &= \frac{pN_A}{RT} \\ &= \frac{1.013 \times 10^5 \times 6.022 \times 10^{23}}{8.3145 \times 273.15} \\ &= 2.69 \times 10^{25} \text{ molecules m}^{-3}. \end{aligned}$$

The amount in moles, n , is given by N/N_A , where N is the number of molecules (or atoms) and N_A is Avogadro's constant, which is the number of molecules (or atoms) per mole. Substituting this expression for n into the ideal gas equation gives

$$pV = \frac{N}{N_A}RT.$$

A simple rearrangement gives

$$\frac{N}{V} = \frac{pN_A}{RT}. \quad (1.2)$$

In this expression N/V is also the concentration, but this time in molecules (or atoms), rather than moles, per unit volume. As before, this measure of concentration is related to the pressure; we will find good use for both of these expressions for concentration later on.

Example 1.1 illustrates two typical calculations using the ideal gas equation.

1.9.2 Mixtures of gases: partial pressures

So far we have been talking about a single substance in the gas phase. However, it is fairly straightforward to extend the discussion to a mixture of gases by introducing the concept of the *partial pressure* of a gas. We will find this very useful later on when we discuss chemical equilibrium.

The concept of the partial pressure of a gas can be understood in the following way. Imagine that we have a mixture of gases, in a container of a particular volume and at a given temperature; the gas mixture exerts a pressure p_{tot} . Now imagine a thought experiment in which we remove all but one of the gases in the mixture. The pressure exerted by this remaining gas on its own is called its *partial pressure*.

Put another way, the partial pressure of a gas in a mixture is the pressure which that gas would exert *if* it occupied the whole volume on its own. This idea is illustrated in Fig. 1.24.

The total pressure exerted by the mixture is the sum of the partial pressures of the components of the mixture

$$p_{\text{tot}} = p_1 + p_2 + p_3 + \dots,$$

where p_1 is the partial pressure of substance one in the mixture, p_2 that of substance two and so on. This relationship is sometimes referred to as *Dalton's Law*.

For a mixture of ideal gases, the partial pressure of component one is given by

$$p_1 = x_1 p_{\text{tot}},$$

where x_1 is the *mole fraction* of that substance. This mole fraction is defined as

$$x_1 = \frac{n_1}{n_{\text{tot}}},$$

where n_1 is the amount in moles of substance 1, and n_{tot} is the total amount (in moles) of all components in the mixture: $n_{\text{tot}} = n_1 + n_2 + n_3 + \dots$

Due to the way it is defined, the mole fraction of each component in a mixture is less than one, and the sum of the mole fractions of all the components is = 1

$$\begin{aligned} x_1 + x_2 + x_3 + \dots &= \frac{n_1}{n_{\text{tot}}} + \frac{n_2}{n_{\text{tot}}} + \frac{n_3}{n_{\text{tot}}} + \dots \\ &= \frac{n_1 + n_2 + n_3 + \dots}{n_{\text{tot}}} \\ &= \frac{n_{\text{tot}}}{n_{\text{tot}}} = 1. \end{aligned}$$

If each gas in the mixture is ideal, we can work out the partial pressures by applying the ideal gas equation to each component. For example, for component one:

$$p_1 V = n_1 RT \quad \text{hence} \quad p_1 = \frac{n_1 RT}{V}. \quad (1.3)$$

Since $x_1 = n_1/n_{\text{tot}}$, it follows that $n_1 = x_1 n_{\text{tot}}$, and so equation above for p_1 can be written

$$p_1 = \frac{x_1 n_{\text{tot}} RT}{V}.$$

Example 1.2 demonstrates the practical application of these relationships.

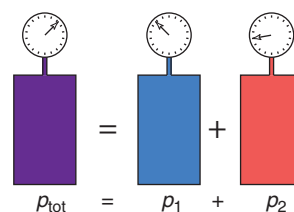


Fig. 1.24 Illustration of the concept of the partial pressure of a gas. The container on the left contains a mixture of two gases which together exert a total pressure p_{tot} . If the first gas occupied the total volume on its own, the pressure it would exert is called its partial pressure, p_1 . Similarly, if the second gas occupied the total volume on its own, the pressure would be its partial pressure, p_2 . The sum of the partial pressures is the total pressure.

Example 1.2 Partial pressures

A container of volume 100 cm^3 is filled with $\text{N}_2(\text{g})$ to a pressure of 10^5 N m^{-2} at a temperature of 298 K ; a second container of volume 200 cm^3 is filled with $\text{O}_2(\text{g})$ to a pressure of $2 \times 10^5 \text{ N m}^{-2}$, also at 298 K . The two containers are then connected so that the gases can mix. Calculate the partial pressure of the two gases in the mixture, assuming that the temperature is held constant at 298 K and that both gases are ideal.

All we need to know is the amount in moles of the two gases, then we can simply use Eq. 1.3 on the previous page to find the partial pressures. As we know the volume, temperature and pressure of each of the separate gases, the amount in moles of each is found by rearranging the ideal gas equation, $pV = nRT$, to give $n = pV/RT$

$$\begin{aligned} n(\text{N}_2) &= \frac{10^5 \times 100 \times 10^{-6}}{8.3145 \times 298} \\ &= 4.036 \times 10^{-3} \text{ mol.} \end{aligned}$$

Note that we had to convert the volume from cm^3 to m^3 : $1 \text{ cm}^3 = 10^{-6} \text{ m}^3$. Using this value in Eq. 1.3 on the preceding page we have

$$\begin{aligned} p(\text{N}_2) &= \frac{n(\text{N}_2)RT}{V} = \frac{4.036 \times 10^{-3} \times 8.3145 \times 298}{300 \times 10^{-6}} \\ &= 3.33 \times 10^4 \text{ N m}^{-2}. \end{aligned}$$

Note that this time, for the mixed gases, we had to use the volume of the mixture, which is 300 cm^3 .

A similar calculation gives $n(\text{O}_2) = 1.614 \times 10^{-2} \text{ mol}$, and hence $p(\text{O}_2) = 1.33 \times 10^5 \text{ N m}^{-2}$. In fact, the partial pressure of O_2 is *four* times that of N_2 as there are four times as many moles of O_2 as there are of N_2 (twice the initial volume, twice the initial pressure).

1.10 Molecular energy levels

One of the key ideas which underlies our understanding of chemistry at the molecular level is that atoms and molecules have available to them a set of *energy levels*. We will have a lot more to say about these energy levels throughout this book, and indeed in the next three chapters there is a lot of discussion of the energy levels available to the electrons in atoms and molecules. However, at this point it is useful just to have a quick overview of this very important topic.

When we say that molecules have energy levels available to them, what we mean is that the molecule cannot have any energy, but can only have an energy corresponding to one of these levels: we say that the molecule *occupies* a particular energy level. This rather strange result arises from *quantum mechanics*, which is the theory needed to describe the behaviour of microscopic objects, such as electrons, atoms and molecules. The following chapter, and Chapter 16, go into more detail about this theory.

It turns out that each kind of motion that an atom or molecule might undergo has associated with it a set of energy levels. These kinds of energy levels are:

translational energy levels: these are associated with the movement (‘translation’) of atoms and molecules through space. The separation between these energy levels is extremely small.

rotational energy levels: these are associated with the overall rotation of molecules (atoms do not rotate). The separation of these energy levels is very much greater than those for translation.

vibrational energy levels: these are associated with the vibration of the bonds in a molecule. The separation of these levels is typically two to three orders of magnitude greater than those for rotation.

electronic energy levels: these are associated with the electrons in atoms and molecules. The separation of these levels is usually much greater than for vibrational levels.

1.10.1 The Boltzmann distribution

Any one molecule, at any point in time, will occupy just one of the translational levels, one of the rotational levels, one of the vibrational levels and one of the electronic levels. As the molecules bump into one another, they exchange energy and so move between the different energy levels. Since collisions are very frequent, there is an incessant and relentless rearrangement of the molecules amongst the energy levels.

In any sample of material that we might handle in the laboratory (a *macroscopic* sample) there are an enormous number of molecules, so there is no way in which we can know which energy level each molecule is occupying. However, as a result of there being very many molecules, it turns out that we can specify the *average* number of molecules in any particular energy level: this average is called the *population* of the energy level.

At equilibrium, the populations of the levels are given by the *Boltzmann distribution*. This states that the population n_i of the energy level with energy ε_i is given by

$$n_i = n_0 \exp\left(\frac{-\varepsilon_i}{k_B T}\right), \quad (1.4)$$

where k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), T is the absolute temperature, and n_0 is the population of the lowest level (which has energy $\varepsilon_0 = 0$).

As a result of the properties of the exponential function, the Boltzmann distribution says that the population of a level decreases as the energy of that level increases. Furthermore, the population of the higher energy levels increases as the temperature increases. This last point comes about because as T increases, $1/T$ decreases, and so $-\varepsilon/k_B T$ becomes less negative.

The predictions of the Boltzmann distribution are all summed up in the graph shown in Fig. 1.25. The vertical axis shows n_i/n_0 , which is the population of the i th level, n_i , expressed as a fraction of the population of the lowest energy level, n_0 ; n_i/n_0 is called the fractional population. The maximum value that the fractional population can take is therefore one, and this occurs when all of the molecules are in the lowest level.

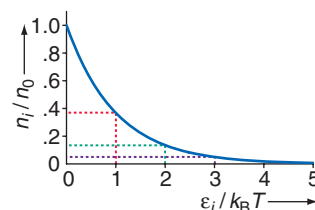


Fig. 1.25 Graph showing how the fractional population of the i th level, n_i/n_0 , varies as a function of the energy of that level, expressed as a fraction of $k_B T$. The red, green and purple dashed lines show the fractional populations for $\varepsilon_i/k_B T = 1, 2$ and 3, respectively. The population is only significant if ε_i is of the order of, or less than, $k_B T$.

➤ The properties of the exponential function are reviewed in section 20.4 on page 895.

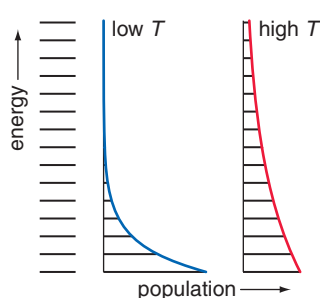


Fig. 1.26 Illustration of how the populations of a set of energy levels changes with temperature. The energy levels are shown on the left. In the two graphs on the right the population of each level is indicated by the *length* of the line, with the smooth curve showing the overall trend. At low temperatures, only the first few levels are occupied, but at high temperatures many more of the higher levels are occupied. Note that at the higher temperature the population of the lower levels decreases relative to what they were at the lower temperature.

Weblink 1.6

This link takes you to real-time version of Fig. 1.26 using which you can explore the effect of changing the energy level spacing and the temperature on the populations of the energy levels predicted by the Boltzmann distribution.

The horizontal axis is the energy of the level, expressed as a ratio of $k_B T$. Since the units of k_B are J K^{-1} and those of T are K , the product $k_B T$ has units of joules i.e. it is an energy. The ratio $\epsilon_i/k_B T$ is therefore an energy divided by an energy, so it has no units and is said to be *dimensionless*. The graph illustrates what has already been explained: as the energy ϵ_i increases, the population decreases, and as the temperature increases the population of the levels above the ground state increases.

If the energy of the level is equal to $k_B T$, then $\epsilon_i/k_B T = 1$, and from the graph the fractional population of this level is 0.37. Doubling the energy so that $\epsilon_i/k_B T = 2$ reduces the fractional population to 0.13, and making $\epsilon_i/k_B T = 3$ reduces the population still further to 0.05.

What this illustrates is that, as a result of the exponential function, the only levels which have significant populations are those whose energies are of the *order of or less than* $k_B T$. This is an exceptionally important result, which we will use frequently.

Figure 1.26 illustrates in a slightly different way how the populations change with temperature. This diagram shows in the *actual* values of the populations, rather than the fractional populations n_i/n_0 shown in Fig. 1.25 on the previous page. As the temperature increases, the higher energy levels become more populated, but since the number of molecules is fixed, this means that the population of the lower levels has to decrease. The overall effect of increasing the temperature is that the molecules are spread out more evenly, rather than being concentrated in the lower levels.

The thermal energy

The quantity $k_B T$ is often thought of as a measure of the thermal energy, as it is the size of this quantity which determines which energy levels will be populated at thermal equilibrium. At 298 K, $k_B T = 4.1 \times 10^{-21}$ J, which is rather a small number to comprehend. It can be made more tangible by multiplying by Avogadro's constant, so that we have an energy per mole; doing this gives the value 2.5 kJ mol^{-1} . We see that the thermal energy is a lot less than the energies associated with chemical reactions.

The spacing of translational energy levels is of the order of 10^{-41} J, which is incredibly much smaller than $k_B T$ at room temperature. There are therefore an extremely large number of translational energy levels which have significant populations.

Rotational energy levels are spaced by around 10^{-23} J, which is significantly smaller than $k_B T$, so typically there are hundreds of such energy levels which have significant populations. In contrast, vibrational energy levels are spaced by around 10^{-21} J, so only the first one or two levels above the ground state are populated to a significant extent. Finally, electronic energy levels are even more widely spaced, so it is unusual for any other than the ground state to be occupied.

Relation between the Boltzmann constant and the gas constant

In section 1.9 on page 22 the ideal gas equation, which relates pressure, volume and temperature, was introduced: $pV = nRT$. In this equation, the gas constant, R , is in fact related to the Boltzmann constant in the following way:

$$R = k_B N_A,$$

where N_A is Avogadro's constant i.e. the number of molecules (or atoms) per mole. It is because of this relationship between R and k_B that the gas constant appears in many expressions which, on the face of it, appear to have little to do with gases.

1.11 Moving on

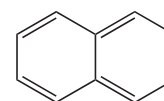
We now need to move on to develop our understanding of bonding so that we can answer the question as to why it is that one compound consists of molecules held together by covalent bonds, whereas another exhibits ionic bonding. We will start by describing covalent bonding, which, as you know, is all about the 'sharing' of electrons.

The behaviour of small particles such as electrons is described using a theory known as quantum mechanics. We will introduce this theory by first using it to describe the behaviour of electrons in atoms, and then develop the theory further to describe the behaviour of electrons in molecules, and hence in chemical bonds.

You are already familiar to some extent with the quantum mechanical description of atoms, as the familiar atomic orbitals ($1s$, $2s$, $2p$ etc.) are a consequence of this theory. In the following chapter we will say much more about where these orbitals come from, and what they actually represent.

QUESTIONS

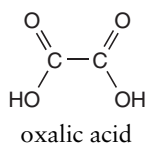
- 1.1 The energy released by the complete combustion of gaseous methane to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ is 803 kJ mol^{-1} . Given that the $\text{O}-\text{O}$ bond energy in O_2 is 498 kJ mol^{-1} , the $\text{C}-\text{O}$ bond energy in CO_2 is 805 kJ mol^{-1} and the $\text{O}-\text{H}$ bond energy in H_2O is 497 kJ mol^{-1} , estimate the $\text{C}-\text{H}$ bond energy in methane. (Hint: write a balanced chemical equation for the combustion of methane and then think about the number and type of bonds broken or made as the reaction proceeds).
- 1.2 What is the distinction between a *molecular* solid and an *ionic* solid? Account for the following observations:
- Solid PbBr_2 does not conduct electricity, but when molten the salt is a good conductor.
 - Neither solid naphthalene nor molten naphthalene conduct electricity.
 - Metallic gold, both when solid and molten, conducts electricity.
- 1.3 As we go down Group 18, the noble gases, the atoms become more polarizable. Explain what you understand by this statement. Also explain how this trend in polarizability can be used to explain the observation that the boiling points of the liquefied noble gases increase as you go down the group.



naphthalene

- 1.4 Explain the following trends in the boiling points of the following two sets of hydrides:

set (a)	boiling point / °C	set (b)	boiling point / °C
H ₂ O	100.0	CH ₄	-161.5
H ₂ S	-59.6	NH ₃	-33.3
H ₂ Se	-41.3	H ₂ O	100.0
H ₂ Te	-2		

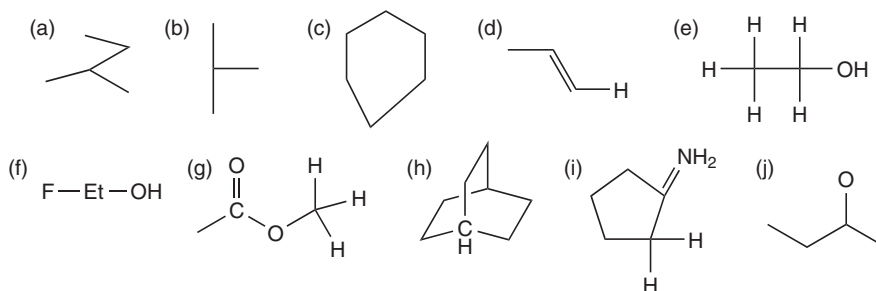


- 1.5 What types of intermolecular forces are present in the following molecules: (a) butane C₄H₁₀; (b) CH₃F; (c) CH₃OH; (d) CF₄?

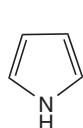
- 1.6 In the gas phase, ethanoic acid is thought to exist as a dimer, held together by *two* hydrogen bonds. Suggest a structure for the dimer.

In the solid, oxalic acid, (COOH)₂, forms extended chains, also held together by hydrogen bonds. Sketch a likely structure for such a chain.

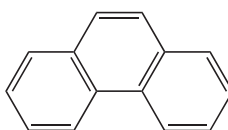
- 1.7 The following framework structures are poorly drawn or simply implausible. Point out the errors in each, and re-draw them correctly.



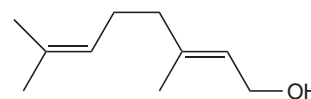
- 1.8 Find the molecular formula (i.e. C_aH_b...) of each of the following framework structures:



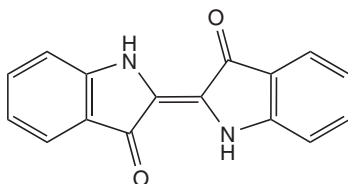
pyrrole



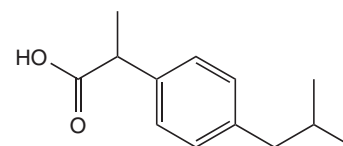
phenanthrene



geraniol

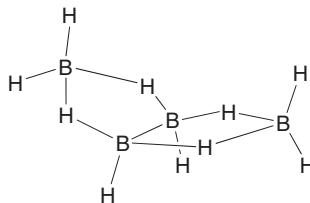


indigo

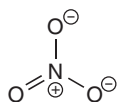


ibuprofen

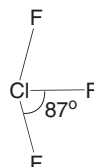
1.11 The boron hydride with formula B_4H_{10} is often drawn as



- If each line represents a conventional bond in which two electrons are shared between two atoms, how many electrons are indicated by this structure?
- Assuming that each boron contributes three electrons, and each hydrogen contributes one, how many valence electrons are there in B_4H_{10} ?
- How can you reconcile your answers to (a) and (b)?



- 1.12 Use the VSEPR model to predict approximate structures for the following species: (i) BH_3 , (ii) BH_4^- , (iii) H_3O^+ , (iv) CH_5^+ , (v) PCl_5 , (vi) PCl_4^+ , (vii) PCl_6^- , (viii) NO_3^- (see opposite). (Hint: for the charged species, first work out the number of electrons in the valence shell ignoring the charge, and then reduce this total by one for a positive overall charge, or increase it by one for an overall negative charge).
- 1.13 ClF_3 is a highly reactive but nevertheless well-characterized volatile liquid used (among other things) to produce UF_6 in the processing of nuclear fuels. It has the following T-shaped structure



- Use the VSEPR theory to show that the structure of ClF_3 can be expected to be based on a trigonal bipyramid.
 - The T-shaped structure can be considered to be a distorted trigonal bipyramid in which two 'equatorial' positions are occupied by lone pairs. Draw a diagram to illustrate this, and suggest why the bond angle in ClF_3 is not 90° as it would be in a regular trigonal bipyramid.
- 1.14 Explain why, at normal pressures and temperatures, $MgCl_2$ is a solid, SiO_2 is a solid, CO_2 is a gas and Ar is a gas.
- 1.15 Calculate the concentration, in moles m^{-3} and molecules m^{-3} , of nitrogen gas at a pressure of 0.1 atmospheres and a temperature of 298 K. You may assume that the gas behaves ideally. (1 atmosphere is $1.013 \times 10^5 \text{ N m}^{-2}$)
- 1.16 What pressure will one mole of an ideal gas exert at 298 K if it is confined to a volume of (i) 1 m^3 , (ii) 1 dm^3 , and (iii) 1 cm^3 ?
- 1.17 A container of volume 100 cm^3 contains 1.0×10^{-4} moles of H_2 and 2.0×10^{-4} moles of N_2 , such that the total pressure is 0.1 atmospheres. Calculate the mole fraction and partial pressure of each species. Also, calculate the temperature of the mixture.

- 1.18 Two containers of equal volume, and held at the same temperature, each contain the same amount in moles of an ideal gas. Explain why the pressure in each container is the same.

Suppose that one of these containers is filled with gas A and one with an equal amount in moles of gas B. Now, we connect the two containers such that the gases A and B mix. On mixing, what happens to the total pressure? How are the partial pressures of A and B related to the total pressure?

- 1.19 Suppose we take a container of fixed volume and maintain it at a constant temperature. In the container there is a mixture of three gases, which can be considered to be ideal. Suppose that the amount in moles of one of the gases is now increased. What happens to: (i) the total pressure and (ii) the partial pressures of each gas?

If the amount in moles of each gas is doubled, what happens to (i) the total pressure, (ii) the mole fraction of each gas?

- 1.20 Calculate the fractional population (i.e. n_i/n_0) of the following energy levels of carbon monoxide, at 298 K and at 2000 K:
- A rotational level at energy 8.0×10^{-23} J above the ground level.
 - A vibrational level at energy 4.3×10^{-20} J above the ground level.
 - An electronic level 1.3×10^{-18} J above the ground level.

Comment on your answers.