

6 Materials from molecules

6.1 Overview

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6.1.1 Introduction

Water is present in vast amounts on the Earth. It is critical to life and plays an important part in moderating our climate. Within the normal temperature range of our planet, it exists in all three states: liquid, solid and as water vapour in the atmosphere.

Why is it that ice melts easily and other substances do not? Why does ice float on water? Why do ponds freeze over in winter, forming a layer of ice on their surfaces, instead of freezing solid? To answer these questions it is necessary to examine how hydrogen and oxygen atoms join together to make water molecules, and how water molecules then interact with each other.

The properties of many other compounds made from non-metallic elements can be explained in the same way — by examining how the atoms join together to make the molecules, and then how these molecules interact with each other.

This topic explores how to predict the manner in which atoms of non-metals join together to make molecules and the methods that chemists use to represent the molecules that are formed. The important ways that molecules interact with one another will lead to an explanation for many of the observed properties of substances that bond this way — as covalent molecules.

These investigations build upon prior knowledge of electron sharing, chemical naming and formula writing. Of particular importance will be knowledge of electronic structure and noble gas configurations.

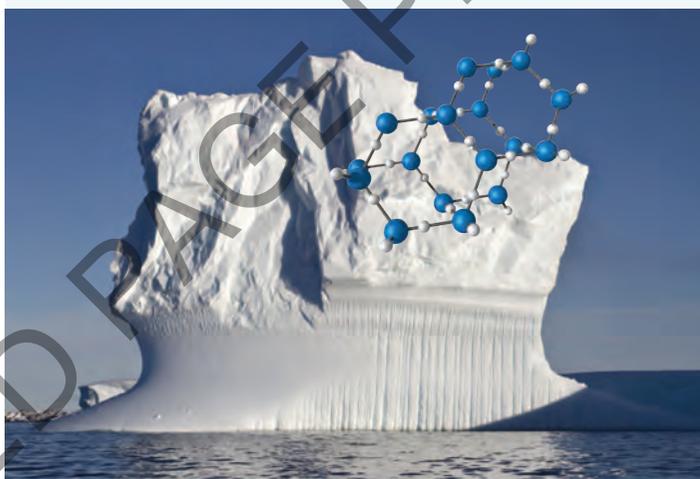
6.1.2 What you will learn

KEY KNOWLEDGE

In this topic, you will investigate:

- representations of molecular substances (electron dot formulas, structural formulas, valence structures, ball-and-stick models, space-filling models), including limitations of these representations
- shapes of molecules and an explanation of their polar or non-polar character with reference to the electronegativities of their atoms and electron-pair repulsion theory
- explanation of properties of molecular substances (including low melting point and boiling point, softness, and non-conduction of electricity), with reference to their structure, intramolecular bonding and intermolecular forces

FIGURE 6.1 Why does solid ice float on liquid water?



- the relative strengths of bonds (covalent bonding, dispersion forces, dipole–dipole attraction and hydrogen bonding) and evidence and factors that determine bond strength, including explanations for the floating of ice and expansion of water at higher temperatures.

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PRACTICAL WORK AND INVESTIGATIONS

Practical work is a central component of learning and assessment. Experiments and investigations, supported by a **Practical investigation logbook** and **Teacher-led videos**, are included in this topic to provide opportunities to undertake investigations and communicate findings.

on Resources

-  **Digital documents** Key science skills (doc-30903)
 Key terms glossary — Topic 6 (doc-30947)
 Practical investigation logbook (doc-30948)

studyon

To access key concept summaries and practice exam questions download and print the **studyON: Revision and practice exam question booklet** (doc-30949).

6.2 Representing molecules

KEY CONCEPT

- Representations of molecular substances (electron dot formulas, structural formulas, valence structures, ball-and-stick models, space-filling models), including limitations of these representations

6.2.1 What is covalent bonding?

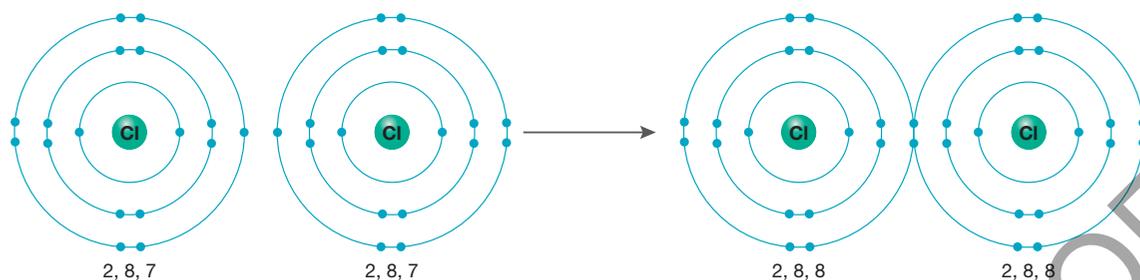
We have observed that atoms of elements with a stable outer shell (or an outer shell that contains eight electrons), such as the noble gases helium, neon and argon, are particularly stable. Other atoms tend to achieve noble gas configuration — that is, eight electrons in the outer shell — by losing or gaining electrons to form ionic bonds, or *sharing* electrons to form **covalent bonds**. The hydrogen atom needs two electrons in its outer shell for stability. Most of the elements in the second and third periods of the periodic table need eight outershell electrons for stability.

Non-metallic atoms generally have high **electronegativities**. This means they can attract electrons easily. Except for hydrogen, non-metals have four or more outershell electrons. When two non-metallic atoms react together, both of them need to gain electrons in order to obtain eight electrons in their outer shells. Since both cannot become negative ions, they share pairs of electrons to achieve eight electrons in the outer shell. This sharing of electron *pairs* between two non-metallic atoms produces the covalent bond. The atoms bond in order to reach a more stable state.

To better understand this process, we can use electron shell diagrams. Consider the two chlorine atoms shown in figure 6.2. Chlorine, as well as all members of group 17, exists in nature as **diatomic molecules** (two atoms covalently bonded together). Each chlorine atom has seven valence electrons. In order to attain a noble gas configuration (an outer shell of eight electrons), each chlorine atom needs one electron.

By sharing the single, unpaired electrons, both atoms can obtain eight in their outer shells, as shown in figure 6.2. A covalent bond results from the simultaneous attraction of the two positive chlorine nuclei to the same shared pair of electrons. This bond holds the two atoms together. A molecule of chlorine forms and is represented by the symbol Cl_2 .

FIGURE 6.2 Two atoms of chlorine sharing a pair of electrons to create a covalent bond and the chlorine molecule Cl_2



Hydrogen – a special case

The hydrogen atom is an exception. This is because each of two hydrogen atoms contains one electron in its first (and outer) shell. They both need another electron to attain the stable electron configuration, 2, of the nearest noble gas, helium. This is achieved by each atom gaining a share in the electron of the other and forming a covalent bond, as shown in figure 6.3. In this way, the diatomic hydrogen molecule, H_2 , is formed.

FIGURE 6.3 The formation of a hydrogen molecule



The molecule

A molecule is a group of non-metallic atoms held together by covalent bonds. The atoms are combined in a fixed ratio and are electrically neutral.

A **covalent molecular element** is made up of identical atoms held together in discrete groups by covalent bonds. Such elements may be found in various arrangements, including diatomic molecules. These molecules are described as **discrete**, because each molecule is separate and distinct from the others.

The noble gases, helium, neon, argon and krypton, all exist as discrete atoms (see figure 6.4). Since they have stable outer shells, they are unreactive and few of their compounds are known.

Diatomic molecules are composed of two atoms of the same element (see figure 6.5). For example, the covalent molecular element hydrogen exists as a gas made up of discrete diatomic molecules. As shown in figure 6.5, each molecule is composed of two hydrogen atoms. This is represented by the symbol H_2 .

Hydrogen is one of several non-metallic elements that are made up of diatomic molecules. Other molecular elements include oxygen, O_2 ; nitrogen, N_2 ; phosphorus, P_4 ; fluorine, F_2 ; and sulfur, S_8 .

In addition to these elements, a large number of compounds also exist as molecules. In a molecular compound, atoms of *different* elements share electrons with each other. These compounds are often called **covalent molecular compounds** because they contain covalent bonds. Water, carbon dioxide and methane are examples of these compounds (see figure 6.6).

A theory for the structure of covalent molecular substances

The major features of the current theory of the structure of covalent molecular substances are as follows:

- The basic units of covalent molecular substances are groups of atoms called **molecules**. All molecules within a pure substance are identical.
- Adjacent atoms within a molecule share electrons in order to achieve a stable outer shell.

FIGURE 6.4 Discrete atoms of helium gas

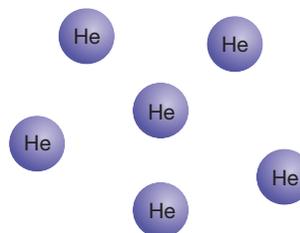


FIGURE 6.5 The molecules of hydrogen gas are diatomic.

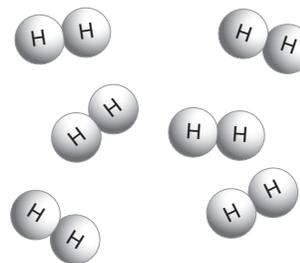
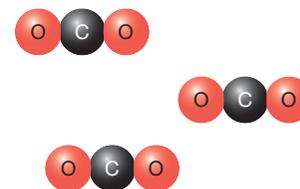


FIGURE 6.6 Carbon dioxide is a covalent molecular compound formed from atoms of carbon and oxygen.



- Electrical attraction between the nuclei of adjacent atoms and the shared electrons causes the atoms in a molecule to be held together. This force of attraction is called covalent bonding.
- The overall charge on each molecule is zero and so adjacent molecules are held together by intermolecular forces, which are weak in comparison to covalent bonds.

The octet rule

As we have already seen, the driving force behind all bonding is to obtain a more stable electron arrangement for the atoms involved. This arrangement in most cases is that of the nearest noble gas. Because all the noble gases have an outer shell of eight electrons, this tendency is often referred to as the **octet rule**. In other words, if an atom does not already have eight electrons in its outer shell, it will bond with other atoms in such a way as to achieve this.

The octet rule should not be confused with a 'full outer shell'. Many of the molecules that you will come across involve period two atoms and, because these atoms have outer shells with a maximum capacity of eight, effectively no difference exists between these terms. However, once period three or higher atoms are involved, outer shells can contain more than eight electrons. In cases such as these, it is inaccurate to state that they are bonding with other atoms 'to obtain a full outer shell'. The alternative, that they bond to 'achieve eight in their outer shell', or they bond to 'achieve a noble gas configuration', is more accurate.

As with many generalisations such as this, exceptions always exist. The most common of these is hydrogen. Because hydrogen's outer shell is stable with only two electrons, the octet rule obviously cannot apply, but the 'stable outer shell' can. In other words, hydrogen atoms will always bond in such a way as to obtain *two* electrons in their outer shell.

Resources

-  **Weblinks** Ionic and covalent bonding
Covalent bonding

6.2.2 Electron dot diagrams for atoms and molecular elements

In order to simplify drawings of atoms, **electron dot diagrams** (sometimes called Lewis diagrams) may be used to represent the outershell electrons. These can be drawn for atoms and molecules and are a useful way to understand the sharing of electrons in covalent bonds.

Electron dot diagrams for atoms

In an electron dot diagram, the atom's nucleus and all innershell electrons are replaced by its element symbol. The outershell electrons are represented by dots or small crosses around the symbol in a square arrangement. These dots are arranged in pairs if more than four outer electrons are present. (*Note:* the innershell electrons do not participate in the bonding.). For example, nitrogen has five outershell electrons and can be represented by the following electron dot diagram. $\cdot \ddot{\text{N}} \cdot$

The two dots arranged as a pair represent **non-bonding electrons** or lone pairs. The three that appear as single dots (unpaired) are *available for sharing* and are called **bonding electrons**.

Elements of the same group in the periodic table have electron dot diagrams with the same number of dots or crosses. The halogens (group 17), for example, all have seven dots around their element symbols representing seven outershell electrons. Electrons in the outermost shell of an element are called **valence electrons**.

Electron dot diagrams for molecular elements

Earlier in this topic, figure 6.2 showed how, by sharing two electrons, two chlorine atoms can combine to each achieve a noble gas configuration (eight electrons in their outer shells). Electron dot diagrams can be used to represent this process in a simpler and clearer way. As can be seen in figure 6.7, dots (·) and crosses (x) are often used to represent the electrons that come from each atom. This does not mean

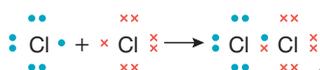
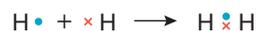
TABLE 6.1 Electron dot diagrams for non-metals in the second period of the periodic table

Group	Element	Valence electrons	Electron dot diagram	Lone pairs	Bonding electrons
14	C	4	$\cdot \overset{\cdot}{\underset{\cdot}{\text{C}}} \cdot$	0	4
15	N	5	$\cdot \overset{\cdot \cdot}{\underset{\cdot}{\text{N}}} \cdot$	1	3
16	O	6	$:\overset{\cdot \cdot}{\underset{\cdot}{\text{O}}}\cdot$	2	2
17	F	7	$:\overset{\cdot \cdot}{\underset{\cdot \cdot}{\text{F}}}\cdot$	3	1
18	Ne	8	$:\overset{\cdot \cdot}{\underset{\cdot \cdot}{\text{Ne}}}:$	4	0

that there are different types of electrons — all electrons are the same. These diagrams are just a convenient way of tracking the origins of the electrons.

In the case of chlorine, each atom shares a pair of electrons to form a single covalent bond. Three pairs of unused electrons remain on each chlorine atom, and these form lone pairs. The electron dot diagram for the formation of a chlorine molecule would, therefore, look as shown in figure 6.7.

The formation of a hydrogen molecule (refer to figure 6.3) may also be simplified using the electron dot method, as shown in figure 6.8. Notice that no unused electrons are present and, therefore, no lone pairs.

FIGURE 6.7 The formation of a chlorine molecule, shown using electron dot representation**FIGURE 6.8** The formation of a hydrogen molecule, shown using the electron dot method**on** Resources

Video eLesson Dot diagrams (eles-2474)

SAMPLE PROBLEM 1

Draw the electron dot diagram for a molecule of fluorine, F_2 .

Teacher-led videos: SP1 (tlvd-0526)

THINK

- Only outershell electrons are to be shown. Fluorine is in group 17 and has 7 outershell electrons.
- Draw the two fluorine atoms with three pairs and a single electron in a square pattern.
- Draw atoms close together so that sharing of single electron is obvious.

TIP: Check that each atom has eight electrons.

WRITE**PRACTICE PROBLEM 1**

Draw an electron dot formula for a molecule of iodine, I_2 .

Multiple covalent bonds

Many molecular substances are held together by **multiple bonds**; that is, bonds formed when two atoms share two or more pairs of electrons. If two atoms share two pairs of electrons, the covalent bond is called a **double bond**. Double bonds are found in molecules such as carbon dioxide, CO_2 , and oxygen, O_2 . When two atoms share three pairs of electrons, a **triple bond** is formed, as in the case of nitrogen, N_2 .

SAMPLE PROBLEM 2

Draw the electron dot formula for a nitrogen molecule, N_2 .

 Teacher-led videos: SP2 (tlvd-0527)

THINK

Nitrogen has five electrons in its outer shell. It needs three more. It will share three of its electrons with three from another N atom. This leaves two unused on each atom.

Draw the diagrams with three electrons on one side and two on the other.

Draw atoms close together so that the sharing of the single electron is obvious.

TIP: Check that each atom has eight electrons.

WRITE



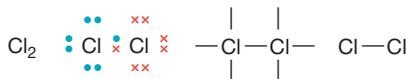
PRACTICE PROBLEM 2

Draw the electron dot formula for an oxygen molecule, O_2 .

6.2.3 Structural formulas and valence structures

Electron dot diagrams themselves may be further simplified by substituting a dash (–) for each pair of electrons. These dashes may represent bonding electron pairs (covalent bonds) or lone pairs (non-bonding electrons), depending on where they are located. Such a representation is called a **valence structure**. If the lone pairs are omitted and only bonds shown, the representation is called a **structural formula**. The structural formula thus shows the way the atoms in a molecule are connected. Although it is not necessary for a structural formula to indicate the shape of a molecule, it is possible to use them for this. This is discussed later in this topic.

FIGURE 6.9 Different ways of representing the chlorine molecule; from left to right: molecular formula, electron dot formula, valence structure and structural formula



Electron dot diagrams, structural formulas and valence structures are, therefore, different ways that molecules may be represented ‘on paper’. Often a combination of these is used. For example, structural formulas are sometimes used with important lone pairs shown by a dash or by dots. The method chosen will often depend on the context in which the diagram is to be used.

6.2.4 Electron dot diagrams for molecular compounds

The procedure for drawing electron dot diagrams for molecular elements is easily extended to molecular compounds. However, these can quickly become complicated as molecular size and the number of different elements increases. For this reason, the electron dot method tends to be used for smaller and simpler molecules. To draw the electron dot formula for a molecular compound, the following steps are often useful:

1. Place the atom with the most bonding electrons (called the **central atom**) in the centre so that the other atoms can be arranged around it.

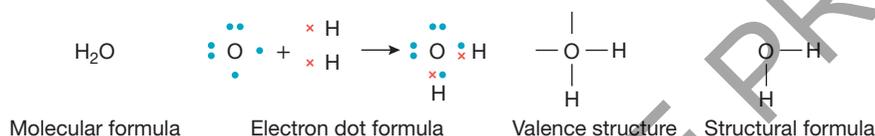
- Draw dot diagrams for each of the atoms in the molecule.
Remember that lone pairs do not participate in the bonding.
- Attach all atoms in such a way that each atom (except hydrogen) is surrounded by eight electrons.
Remember that if you have trouble achieving eight in an outer shell, you might have to consider multiple bonding.

Water

The formula for water is H_2O . In each water molecule, an oxygen atom shares electrons with two hydrogen atoms so that they all achieve complete outer shells.

Notice that the central oxygen atom in a water molecule has two pairs of unbonded electrons. These are called lone pairs. Although they do not participate in the covalent bond, they affect the shape of the molecule, and are shown in the valence structure by the two 'unbonded' dashes.

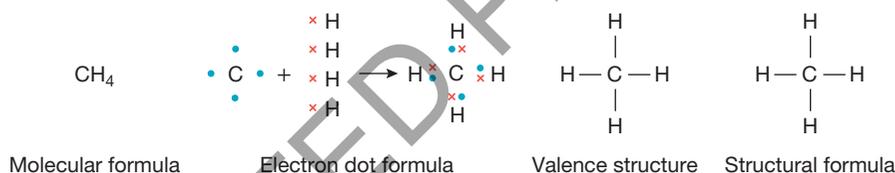
FIGURE 6.10 Different ways of representing the water molecule



Methane

The formula for methane is CH_4 . In each methane molecule, carbon forms a single bond with each of the four hydrogen atoms. All atoms have achieved complete outer shells.

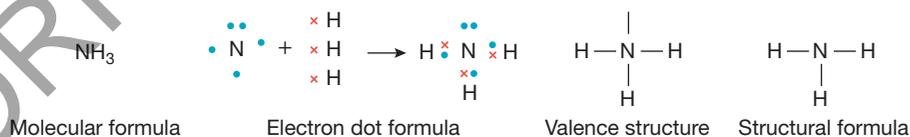
FIGURE 6.11 Different ways of representing the methane molecule



Ammonia

The formula for ammonia is NH_3 . In each ammonia molecule, nitrogen forms a single bond with each of the three hydrogen atoms in addition to having one lone pair. This arrangement achieves a stable outer shell for each atom.

FIGURE 6.12 Different ways of representing the ammonia molecule

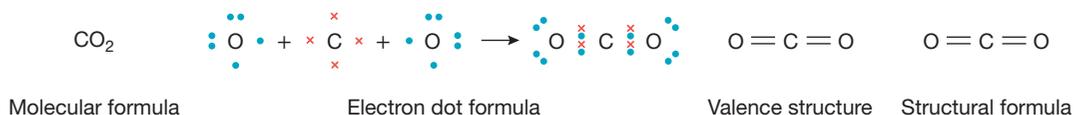


Carbon dioxide

The formula for carbon dioxide is CO_2 . In each carbon dioxide molecule, carbon forms a double bond with each of the oxygen atoms.

The central carbon atom in a carbon dioxide molecule now has eight valence electrons, and so does each oxygen atom.

FIGURE 6.13 Different ways of representing the carbon dioxide molecule



EXCEPTIONS TO THE OCTET RULE

The octet rule is a very useful *rule of thumb* for chemists when working out bonding within molecules and molecular shape.

However, many molecules do not obey this rule. In some instances, molecules bond with fewer than eight electrons in their outer shell, and in many cases have more. Obviously, the latter cannot occur for period two elements due to the capacity of the second shell. However, for periods three and beyond, the outer shell has room for more than eight electrons. Although many compounds involving period three and beyond still obey the octet rule, some don't. Some of these are quite common; for example, sulfuric acid, the structure of which is shown in figure 6.14.

If you count the electrons in the outer shell of the sulfur atom, you will notice that there are 12!

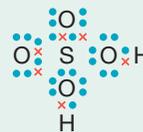
Some other molecules that also exhibit this feature are PCl_5 , SF_6 , IF_5 , SO_3 , H_3PO_4 and HClO_4 .

Look up the structures for these molecules (or even try to work them out first)! Also look for any other examples, and whether you can find some examples of molecules that have fewer than eight outershell electrons around their central atom.

This exercise is a good illustration that many of the tools and techniques used by chemists have their limitations. The bonding models discussed in this topic are a further example of this.

This does not mean that such ideas aren't any good. The main thing to remember is that they serve a purpose and, so long as their limitations are recognised, no reason exists to not keep using them.

FIGURE 6.14 Electron dot diagram of sulfuric acid showing 12 electrons on the sulfur atom



SAMPLE PROBLEM 3

For hydrogen chloride, draw the following.

- Electron dot diagram
- Valence structure

THINK

- Hydrogen has one electron in its shell, and so needs one more. The chlorine atom has seven electrons in its outer shell, so it needs one more.

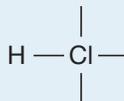
Draw the diagrams together, showing overlap for sharing.

TIP: Check that hydrogen has two electrons in its outer shell and eight electrons for chlorine.

- Draw valence structure by replacing each pair of electrons with a dash.

 **Teacher-led videos:** SP3 (tlvd-0528)

WRITE



PRACTICE PROBLEM 3

For hydrogen fluoride, draw the following.

- Electron dot diagram
- Valence structure

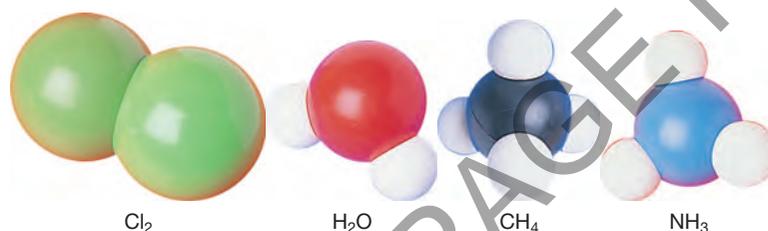
6.2.5 Physical representations

The representations discussed so far have one very obvious disadvantage: they are two-dimensional. Physical models allow us to visualise molecules in three dimensions. As we shall see later in this topic, the three-dimensional shape of a molecule can have a significant effect on its properties. As introduced in topic 4 with reference to ionic compounds, two main types of three-dimensional model are used by chemists to represent molecules. These are **ball-and-stick** models and **space-filling** models. These can be used to inform **computer-generated** models.

Space-filling models

Space-filling models use spheres (usually made of plastic) to represent atoms. These are colour coded to represent different types of atoms. Typical examples are black (carbon), white (hydrogen), red (oxygen), blue (nitrogen) and green (chlorine). The hydrogen spheres are usually smaller than the others to represent the much smaller relative size of the hydrogen atom. These are attached to each other so as to resemble the shape of the molecule as closely as possible.

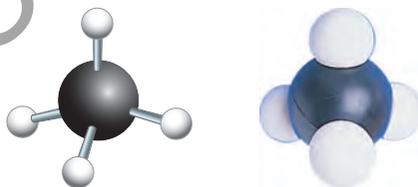
FIGURE 6.15 Space-filling models for (left to right) chlorine, Cl_2 , water, H_2O , methane, CH_4 , and ammonia, NH_3



Ball-and-stick models

Ball-and-stick models are similar to space-filling models except that the spheres are separated and joined by sticks. Each stick represents a covalent bond.

FIGURE 6.16 Methane, CH_4 , represented by a ball-and-stick model (left) and a space-filling model (right)



Ball-and-stick models have the advantage that they can show multiple bonds (see table 6.2).

6.2.6 Limitations of these representations

Why are there different ways to represent molecules? The answer is that chemists use different ways for different purposes. Each representation has its own strengths and limitations. The method chosen will often depend on the context in which it is to be used. If the bonding between atoms is being emphasised, a ball-and-stick model would be better than a space-filling one. While both electron dot and valence structures will also highlight bonding between atoms, the former may lose clarity among a maze of dots representing the electrons. If shape is important, both ball-and-stick and space-filling may be adequate, with both being superior to electron dot and valence structures. In many situations, especially in organic chemistry, a structural formula is an excellent way to represent molecules.

Table 6.2 lists some of the limitations of each of these methods. You may be able to think of more.

TABLE 6.2 Methods of molecular representation with some of their limitations

Method	Limitations
Electron dot (also called Lewis diagrams)	<ul style="list-style-type: none"> • Two-dimensional • Does not indicate shape • Tedious and slow to produce • Can look messy
Valence structure	<ul style="list-style-type: none"> • Two dimensional • Does not necessarily indicate shape* • Can be tedious and slow to write for larger molecules • Important lone pairs may be difficult to distinguish from non-important ones
Structural formula	<ul style="list-style-type: none"> • Two dimensional • Does not necessarily indicate shape* • Can be tedious and slow to write for larger molecules
Space-filling	<ul style="list-style-type: none"> • Does not show the bonding between atoms • Relative sizes of atoms involved are only approximate
Ball-and-stick	<ul style="list-style-type: none"> • Can be physically difficult to produce for larger molecules • Kits to produce are usually expensive

* These methods can be adapted to give an indication of shape by using shape diagrams (see subtopic 6.3).

6.2 EXERCISE

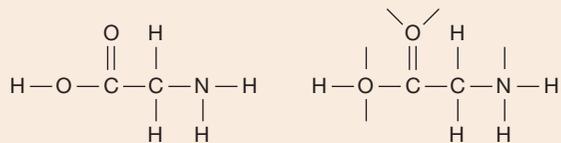
To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

1. Draw an electron dot diagram for an atom of the following.
 - (a) Tellurium (Te)
 - (b) Arsenic (As)
2. Complete the following table.

Group	Element	Valence electrons	Electron dot diagram	Lone pairs	Bonding electrons
	S				
	Si				
	P				
	Cl				
	Br				
	Se				
	Ar				

3. Which of the following substances contain discrete diatomic molecules?
 - (a) Magnesium oxide
 - (b) Iodine
 - (c) Aluminium
 - (d) Neon
 - (e) Phosphorus
 - (f) Carbon dioxide
4. Draw an electron dot formula for a molecule of bromine, Br₂.
5. Although it is not a preferred form of phosphorus, the synthesis of diphosphorus, P₂, has been reported. Draw the electron dot formula for a molecule of diphosphorus.

6. Draw the electron dot diagram and the valence structure for hydrogen iodide, HI.
7. The structural formula and valence structure of the amino acid glycine is shown.
- (a) Draw this structure as an electron dot diagram.
- (b) Give one disadvantage of showing this molecule as an electron dot diagram.



8. Use electron dot diagrams and structural formulas to illustrate the bonds between each of the following pairs of atoms.
- (a) Hydrogen and bromine
- (b) Oxygen and fluorine
9. Draw the electron dot diagram and the structural formula for nitrogen trifluoride, NF_3 , in which all three fluorine atoms are bonded to the nitrogen atom.
10. Draw electron dot diagrams and structural formulas for the following molecules.
- (a) CS_2
- (b) C_2F_4
- (c) C_3H_8
- (d) HCN

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6.3 Predicting molecular shape

KEY CONCEPT

- Shapes of molecules and an explanation of their polar or non-polar character with reference to the electronegativities of their atoms and electron-pair repulsion theory

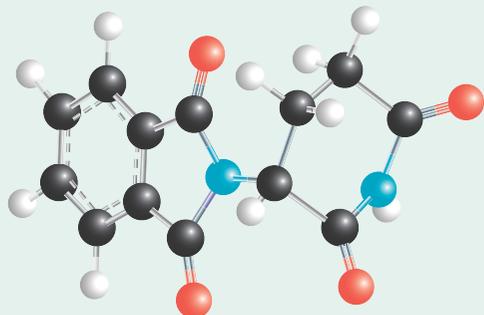
6.3.1 The valence shell electron pair repulsion (VSEPR) theory

The shape of a molecule can have an important effect on its properties and how it behaves. For this reason, it is important to know not only how atoms are joined together to make a molecule, but also in what orientation they are with respect to one another. This is especially important for biological molecules and drugs where a relatively small change in shape can have dramatic differences in effect.

THALIDOMIDE

Thalidomide is a drug that was first produced in the 1950s. It became popular as an over-the-counter drug sold to combat morning sickness in pregnant women. However, it soon became apparent that it was producing a devastating side effect: children were being born with severely deformed limbs. Over 10 000 children were born before the drug was withdrawn. Today the use of the drug is strictly controlled, and prescribed for treating leprosy and certain types of cancers.

Thalidomide has the chemical formula $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4$, shown in the figure.

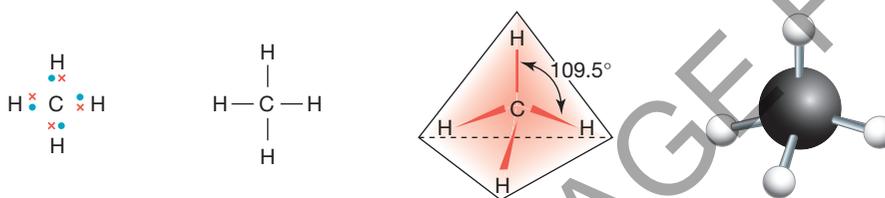


You notice the usual colour convention in the figure: hydrogen atoms are white, oxygen atoms are red, nitrogen atoms are blue and carbon atoms are black.

Thalidomide exists in two forms that are nearly identical. The only difference is a small change in orientation around one of the carbons. One form *did* cure morning sickness. However, the other form caused the birth defects. To make matters worse, the body is able to convert the harmless form into the harmful one, making it almost impossible to prevent the drug's serious side effects.

All discrete molecules have a definite three-dimensional shape. Electron dot diagrams and structural formulas fail to represent the three-dimensional shapes of molecules. For example, the electron dot diagram and structural formula of methane, CH_4 , show the molecule in only two dimensions. In reality, methane molecules exist in three dimensions. The hydrogen atoms are arranged in a tetrahedral shape around the central carbon atom, as shown by the ball-and-stick diagram included in figure 6.17.

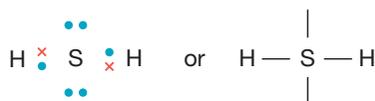
FIGURE 6.17 The electron dot diagram and structural formula of methane do not show its three-dimensional structure, which is tetrahedral. This structure is better represented using a ball-and-stick model.



The **valence shell electron pair repulsion (VSEPR) theory** provides a relatively simple basis for understanding and predicting molecular geometry. The theory requires only that the number of outershell electrons for each atom in the molecule be known. The electron pairs in the molecule repel each other and take up positions as far from one another as possible. When determining the shapes of molecules, the electron pairs of a multiple bond count as only one pair of electrons for prediction purposes. Lone pairs should also be considered, especially when they are on a central atom. Examples of the five most common molecular shapes are given in table 6.3. Note that, in the shape diagrams, a dotted line indicates that the bond is directed into the plane of the paper and the wedge indicates that the bond is directed out of the plane of the paper. The solid lines represent bonds that are in the plane of the paper. The use of ball-and-stick-modelling is an excellent way to understand this theory.

For example, consider hydrogen sulfide, H_2S , and silane, SiH_4 .

To predict the shape of H_2S , first draw either its electron dot diagram or valence structure.



Next, count all the electron pairs (both bonding and non-bonding) around the central atom (in this case, sulfur) and arrange them as far from each other as possible. For four electron pairs in three dimensions (this orientation is a tetrahedral one). The shape diagram may now be drawn.

A similar procedure yields the shape of the SiH_4 molecule. Once again there are four pairs of electrons around the central atom and they therefore adopt a tetrahedral orientation.

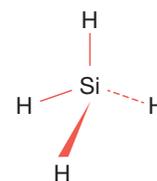
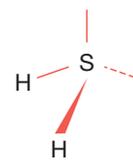
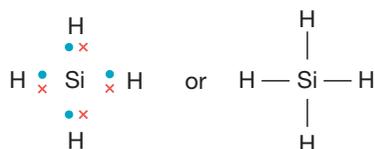


TABLE 6.3 Shapes of some common molecules

Compound	Electron dot diagram	Number of lone pairs around central atom	Number of bonding electron groups (pairs) around central atom	Shape	Ball-and-stick model	Shape diagram
Methane $\text{CH}_4(\text{g})$	<pre> H : H : : : H : C : H : : : H : H </pre>	0	4	Tetrahedral (around C atom)		
Ammonia $\text{NH}_3(\text{g})$	<pre> : : H : : : H : N : H : : : H : H </pre>	1	3	Pyramidal (around N atom)		
Water $\text{H}_2\text{O}(\text{l})$	<pre> : : H : : : : O : H : : : H : H </pre>	2	2	V-shaped (around O atom)		
Ethyne $\text{C}_2\text{H}_2(\text{g})$	<pre> H : C : C : H : : : H : H </pre>	0 for each C atom	2 for each C atom	Linear (around each C atom)		$\text{H}-\text{C}\equiv\text{C}-\text{H}$
Ethene $\text{C}_2\text{H}_4(\text{g})$	<pre> H : H : : : H : C : C : H : : : H : H </pre>	0 for each C atom	3 for each C atom	Planar (around each C atom)		

-  **Video eLessons** Molecular shapes (eles-2475)
VSEPR — Sulfur dioxide (eles-2488)

TIP: To recognise the shape of a molecule:

- determine the arrangement of electron pairs around the central atom (for example, four pairs will be tetrahedral) and ignore the lone pairs
- remember that the distribution of the atoms will help you describe the shape.

SAMPLE PROBLEM 4

Using its electron dot diagram or its valence structure, draw the shape diagram for a molecule of H_2Se .

 **Teacher-led videos:** SP4 (tlvd-0529)

THINK

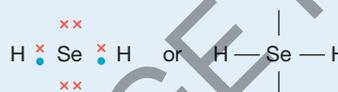
1. Draw the electron dot diagram. H must only show one electron. Se is in group 16 so it must show six electrons in the outer shell.

Arrange H atoms around the Se with an overlap to show sharing.
(Remember that electron sharing may be clearer using a valence structure.)

2. Draw the shape diagram. Count the pairs of electrons around central atom to identify four pairs. Two lone pairs of electrons and two pairs of bonding electrons around the central atom correspond to a V-shaped arrangement. Assign H atoms to the bonding electrons.

TIP: VSEPR theory places electrons as far from each other as possible.

WRITE



PRACTICE PROBLEM 4

Using its electron dot diagram or its valence structure, draw the shape diagram for a molecule of PH_3 .

SAMPLE PROBLEM 5

Using its electron dot diagram or its valence structure, draw the shape diagram for a molecule of C_2H_4 .

 **Teacher-led videos:** SP5 (tlvd-0530)

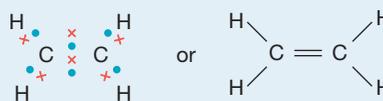
THINK

1. H atoms are always arranged around the outside of the central atom, so the two C atoms must be in the centre.

Draw each H showing one electron and each C showing four electrons.

Arrange H atoms around the C with an overlap to show sharing.

WRITE

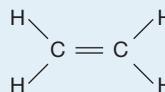


TIP: If sharing is difficult to show with an electron dot diagram, try forming multiple bonds. Electron sharing in this molecule works with a double bond!

2. Draw the molecule showing four electrons between each C as a double bond.

Three areas of electrons are around each C (double bonds count as one) so the shape is planar around each carbon, with bonds 120° apart.

This planar structure makes the whole molecule flat.



PRACTICE PROBLEM 5

Using its electron dot diagram or its valence structure, draw the shape diagram for a molecule of C_2H_2 .

The shape of a molecule is not necessarily the same as the distribution of electron pairs around the central atom. The shape considers the three-dimensional orientation of the atoms in space.

VSEPR theory predicts the shape of molecules.

- A molecule will assume the shape that minimises electron pair repulsions.
- Electron pairs around the central atom will be as far apart as possible.

In general:

- molecules with no lone pairs around the central atom are tetrahedral, unless a double or triple bond creates a linear or planar structure (depending upon the distribution of atoms around the central atom)
- molecules with a single lone pair around the central atom are pyramidal
- molecules with a two lone pairs around the central atom are V-shaped.

on Resources

 **Digital document** Experiment 6.1 Building molecular models (doc-30848)

 **Teacher-led video** Experiment 6.1 Building molecular models (tlvd-0623)

6.3.2 Polar and non-polar molecules

All bonding involves the attractions set up between positive charges and negative charges. It is electrical in nature and electrons play a critical role. Even though molecules are electrically neutral in an overall sense, the possibility exists of regions within a molecule where small localised imbalances may occur. **Polarity** is the term that chemists use to describe this situation. A slight deficiency of electrons in a region (and, therefore, a slight positive charge) is indicated by the symbol $\delta+$ (taken from the lowercase Greek letter for delta). Likewise, a slight excess of electrons is indicated by $\delta-$.

Electronegativity

Covalently bonded atoms usually exhibit unequal attractions for shared electrons. Scientists have found that different atoms have different electron-attracting abilities. The relative attraction that an atom has for shared electrons in a covalent bond is known as its electronegativity. A scale of electronegativities was

developed by Linus Pauling in which the most electronegative atom, fluorine, is assigned a value of 4.0. Fluorine attracts electrons almost twice as well as hydrogen, which is given an electronegativity value of 2.1. No values are assigned for the noble gases. Electronegativity can be likened to a ‘tug of war’, where the two teams are like the atoms on each end of the bond trying to pull the electrons towards them.

The Pauling scale of electronegativities

The following electronegativity trends may be seen in the periodic table.

- Electronegativities increase from left to right within a period.
- Electronegativities decrease from top to bottom within a group.
- Metals generally have lower electronegativities than non-metals.

FIGURE 6.18 The Pauling scale of electronegativities shows electronegativity trends in the periodic table.

		increasing electronegativity →							
		groups							
		1	2	13	14	15	16	17	18
↓ decreasing electronegativity	H								He
	2.1								–
	Li	Be	B	C	N	O	F	Ne	–
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	–	
	Na	Mg	Al	Si	P	S	Cl	Ar	–
	0.9	1.2	1.5	1.8	2.1	2.5	3.0	–	
	K	Ca	Ga	Ge	As	Se	Br	Kr	–
0.8	1.0	1.6	1.8	2.0	2.4	2.8	–		
Rb	Sr	In	Sn	Sb	Te	I	Xe	–	
0.8	1.0	1.7	1.8	1.9	2.1	2.5	–		
Cs	Ba	Tl	Pb	Bi	Po	At	Rn	–	
0.7	0.9	1.8	1.8	1.9	2.0	2.2	–		
Fr	Ra								
0.7	0.9								

LINUS PAULING: CHEMIST AND PEACE ACTIVIST

Linus Carl Pauling (1901–1994) was an American scientist famous for his work on chemical bonding and biochemistry, and his activism for peace. Voted by *New Scientist* as one of the 20th greatest scientists of all time, he was also regarded as one of the two greatest scientists of the 20th century (the other being Einstein). He is widely regarded as the greatest chemist since the founder of the discipline, Antoine Lavoisier, and was the recipient of two Nobel Prizes.

Until the 1930s, chemistry had only been able to describe the properties of substances; it hadn't been able to explain them. Pauling applied the newly developed quantum theory to describe the bonding between atoms and how this explained a substance's properties. In 1931, he published the first of seven papers on the subject; a paper now regarded as one of the most significant works in chemistry. In 1939, following further research, Pauling collated his work to up to that date in the landmark book *The nature of the chemical bond*. This book is still used by chemists across the world today.

During the mid-1930s, Pauling became interested in the field of biomolecules and began to apply his knowledge to the structure of the large molecules that exist in living things. He proposed that molecules such as proteins and DNA have a helical structure and laid the groundwork for the ultimate discovery of DNA's structure by Watson, Crick and Franklin in 1953. He was one of the pioneers of model building. He used data from X-ray diffraction to build scale models of the molecules he was studying.

During World War II, Pauling worked for the United States Government on a number of projects associated with the war. In 1948, he was awarded the Presidential Medal for Merit for his efforts. However, his unease in the postwar period led to him to speak out with several other scientists (including Einstein) against the proliferation of nuclear weapons. He became a tireless campaigner against the testing of nuclear weapons.

Pauling was the winner of two Nobel Prizes. The first, for chemistry in 1953, was for his work on the nature of the chemical bond and his second, for peace in 1962, was for his campaigning against the testing of nuclear weapons. He is the only person to have been awarded two unshared Nobel Prizes, and one of only two people to have won them in different fields. Pauling was a popular personality and was as widely known in the general population as he was in the scientific community. Chemistry students around the world recognise him as the developer of the scale of electronegativities that bears his name.



Non-polar and polar covalent bonds

Covalent bonds in which the bonding electron pair is shared equally and is uniformly distributed between the nuclei of two bonded atoms are called **non-polar covalent bonds**. Such bonds can result only when two atoms of the same element or two atoms of equal electronegativity simultaneously attract a shared pair of electrons.

TABLE 6.4 Non-polar covalent bonding in molecules

Molecule	Electron dot diagram	Structural formula
Hydrogen	H × H	H — H
Chlorine		Cl — Cl
Oxygen		O = O
Carbon disulfide		S = C = S

Covalent bonds in which the bonding electrons are unequally shared, and therefore unsymmetrically distributed between the nuclei of two bonded atoms, are called **polar covalent bonds**. Such bonds occur between atoms of different electronegativities. The shared pair of electrons moves closer to the more electronegative atom. This means that the atom that has greater control of the electron pair becomes slightly negatively charged (δ^-), while the atom that lost some control of the electron pair becomes slightly positively charged (δ^+). Polar covalent bonds can be said to have a charge separation, or a **bond dipole**.

TABLE 6.5 Polar covalent bonding in molecules

Molecule	Electron dot diagram	Structural formula and polarity
Hydrogen chloride		$\delta^+ \quad \delta^-$ H — Cl
Hydrogen bromide		$\delta^+ \quad \delta^-$ H — Br

A polar covalent bond is not purely covalent, since there is not an *equal* sharing of electrons. It has some characteristics of ionic bonding, although the transfer of electrons from one atom to the other is not complete because it is in a purely ionic bond. In fact, if the difference in electronegativity between two atoms is two or greater on the Pauling scale, an ionic bond does form. The relationship between electronegativity and bond type is shown in table 6.6.

TABLE 6.6 Relationship between electronegativity and bond type

Difference in electronegativity between bonding atoms	Type of bond formed
Zero; e.g. H (2.1) and H (2.1)	Non-Polar covalent
Medium; e.g. H (2.1) and Cl (3.0)	Polar covalent
Large; e.g. Na (0.9) and F (4.0)	Ionic

SAMPLE PROBLEM 6

State whether the following bonds are polar or non-polar.

- Oxygen to oxygen bonds
- Hydrogen to phosphorus bonds
- Oxygen to chlorine bonds

 Teacher-led videos: SP6 (tlvd-0531)

THINK

A bond will be polar if a difference in electronegativity exists between the two atoms on each end.

- No difference exists for O to O.
- No difference exists for H to P.
- A difference does exist for O to Cl.

WRITE

Oxygen to oxygen bonds are non-polar.
Hydrogen to phosphorus bonds are non-polar.
Oxygen to chlorine bonds are polar.

PRACTICE PROBLEM 6

State whether the following bonds are polar or non-polar.

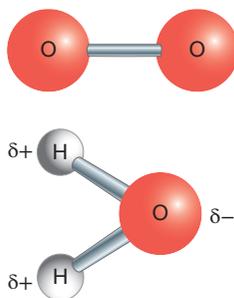
- Chlorine to chlorine bonds
- Phosphorus to chlorine bonds

Non-polar and polar molecules

Molecules containing only non-polar bonds are **non-polar molecules**, such as O_2 .

In a **polar molecule**, one end of the molecule is slightly negative and one end is slightly positive. Such a molecule is sometimes called a dipolar molecule, or molecular dipole. All polar molecules contain polar bonds. However, some molecules with polar bonds are non-polar. This occurs when the individual dipoles are arranged in such a way that they cancel each other out. So having polar bonds in a molecule does not necessarily mean that the molecule is polar overall. The polarity or non-polarity of the molecule depends, rather, on the *direction* of the bond dipoles in the molecule, which is determined by the molecule's *shape*. Figure 6.19 shows examples of both a non-polar and polar molecule.

FIGURE 6.19 In the non-polar oxygen molecule, O_2 , the oxygen atoms have equal electronegativity and share electrons equally (left). Water molecules are polar because the oxygen atom has greater electronegativity than the hydrogen atoms, so it becomes the more negatively charged end of the molecular dipole (right).



Determining the polarity of a molecule

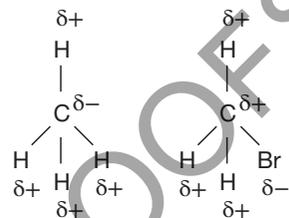
To determine the polarity of a molecule the following steps should be followed:

1. Draw an electron dot diagram of the molecule.
2. Apply the VSEPR rules to draw a shape diagram of the molecule.
3. Use electronegativities to determine bond dipoles.
4. Use the shape diagram along with bond dipoles to determine whether the molecule is polar or non-polar. If bond dipoles cancel each other out, the molecule is non-polar. If bond dipoles do not cancel each other out, one side of the molecule attracts electrons more than another side and the molecule is polar.

The following guidelines are often useful.

- Linear, planar and tetrahedral molecules with equal polar bonds that cancel each other out are non-polar. If the bond dipoles are not equal or do not cancel each other out, the molecule is polar. For example, CH_4 is non-polar whereas CH_3Br is polar because the C—Br bond dipole is not cancelled by the C—H bond dipoles.
- V-shaped or pyramidal molecules are polar because their polar bonds do not cancel.

FIGURE 6.20 CH_4 is non-polar because the bond dipoles cancel each other out. CH_3Br , however, is polar.



SAMPLE PROBLEM 7

Predict the polarity of the following molecules.

- a. Water
- b. Carbon dioxide

Teacher-led videos: SP7 (tlvd-0532)

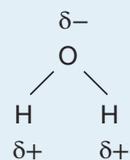
THINK

Recall that a molecule being polar requires two things: it must have polar bonds and its shape must be such that the dipoles from these bonds do not cancel out (that is, it must be asymmetrical).

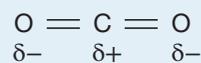
Therefore, check electronegativities first and then draw the shape diagrams.

- a. Water, H_2O , is a V-shaped molecule due to the effect of the two lone pairs. The two O—H bond dipoles are equal but since they are not at an angle of 180° to one another (that is, aligned in opposite directions) they do not cancel each other out. A water molecule is, therefore, polar.
- b. Carbon dioxide, CO_2 , is a linear molecule with two polar bonds. However, the bond polarities cancel each other out because they are in opposite directions. Electrons are not attracted preferentially to one side or the other of the molecule. Carbon dioxide is, therefore, a non-polar molecule.

WRITE



Water is polar.



Carbon dioxide is non-polar

PRACTICE PROBLEM 7

Predict the polarity of the following molecules.

- a. Iodine
- b. Hydrogen bromide

6.3 EXERCISE

To answer questions online and to receive **immediate feedback** and **sample responses** for every question, go to your learnON title at www.jacplus.com.au.

- Using its electron dot diagram or its valence structure, draw the shape diagram for a molecule of AsH_3 .
- State whether the following bonds are polar or non-polar. Justify your answer.
 - Sulfur to oxygen bonds
 - Bromine to bromine bonds
- Explain whether the following molecules are polar or non-polar.
 - Chlorine (Cl_2)
 - Ammonia
- Use the electronegativity trends in the periodic table (shown in figure 6.18 in section 6.3.2) to predict whether the following bonds are polar or non-polar. Show the bond dipoles where they are present using $\delta+$ and $\delta-$.
 - H—F
 - O—H
 - C—H
 - N—H
 - C—C
- Classify the following bonds as ionic, polar covalent or non-polar covalent. Justify your answers.
 - HI
 - KCl
 - F_2
- Arrange the following bonds in order from non-polar covalent to ionic. F—N, N—N, Cl—N.
- Explain why compounds with a large electronegativity difference between their atoms are likely to show ionic bonding, whereas atoms with only a small difference will display covalent bonding.
- A molecule has a tetrahedral shape. Does this mean that it is non-polar? Explain.
- Sketch the shapes of the following molecules and use your knowledge of electronegativity to draw bond dipoles for each to predict whether it is polar or non-polar.
 - CH_4
 - CH_3Cl
 - CH_2Cl_2
 - CHCl_3
 - CCl_4
- ICl_3 and ICl_5 are two compounds that form between iodine and chlorine and do not obey the octet rule. These two compounds have ten (ICl_3) and twelve (ICl_5) electrons in the outer shells of the central atom.
 - Draw electron dot diagrams and valence structures for each of these compounds.
 - Why is it possible to have more than eight electrons in the outer shell for iodine?

studyon

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Fully worked solutions and sample responses are available in your digital formats.

6.4 Explaining the properties of molecular substances

KEY CONCEPT

- Explanation of properties of molecular substances (including low melting point and boiling point, softness, and non-conduction of electricity), with reference to their structure, intramolecular bonding and intermolecular forces

6.4.1 Inter-molecular attractions

The existence of molecular crystals indicates that molecules can be held together in an orderly array. How do these molecules ‘stick’ together?

In addition to covalent bonds *within* molecules, called **intramolecular** bonding, attractions exist *between* molecules, called **intermolecular** forces of attraction, which hold molecules to each other. These attractive forces are weaker than either covalent or ionic bonds, but they determine whether a molecular compound exists in the solid, liquid or gaseous states. The temperature at which a molecular substance melts or boils, therefore, depends on the strength of the intermolecular forces. The stronger the intermolecular forces, the higher the melting or boiling point.

Three types of intermolecular forces are possible. In some molecular substances, more than one force may be operating between the molecules. The weakest attractions between molecules are **dispersion forces** followed by **dipole–dipole interactions**. The third and strongest intermolecular force is called **hydrogen bonding**.

Dispersion forces

In a sample of molecules, the nuclei of atoms in one molecule are able to attract the electrons of atoms in neighbouring molecules (in addition to attracting their own electrons in forming a covalent bond). All electrons are attracted by all neighbouring nuclei.

Dispersion forces are the weakest of the intermolecular forces. To be condensed to a liquid, the noble gas helium must be cooled to $-269\text{ }^{\circ}\text{C}$ so that the atoms are travelling slowly enough for the dispersion forces to have a better chance of pulling these two atoms together. The helium nucleus in one atom attracts the electrons in a neighbouring atom. If further cooled to $-272\text{ }^{\circ}\text{C}$, the liquid helium solidifies.

Dispersion forces can also occur between instantaneous dipoles. Electrons are moving constantly. At any point in time, a chance exists that the electrons may be found on one side of an atom or molecule, and it can develop an ‘instantaneous dipole’ (frame 3 in figure 6.22). This temporary dipole can cause a shift in the distribution of electrons in neighbouring atoms or molecules, resulting in ‘induced dipoles’. Very small forces of attraction result between the particles.

FIGURE 6.21 When sufficiently cooled, helium atoms are very weakly attracted to each other by the electrostatic attraction of one nucleus to the electrons of other atoms.

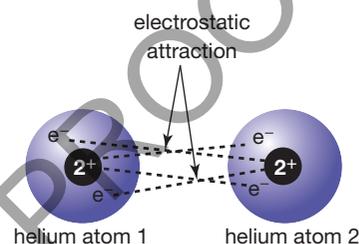
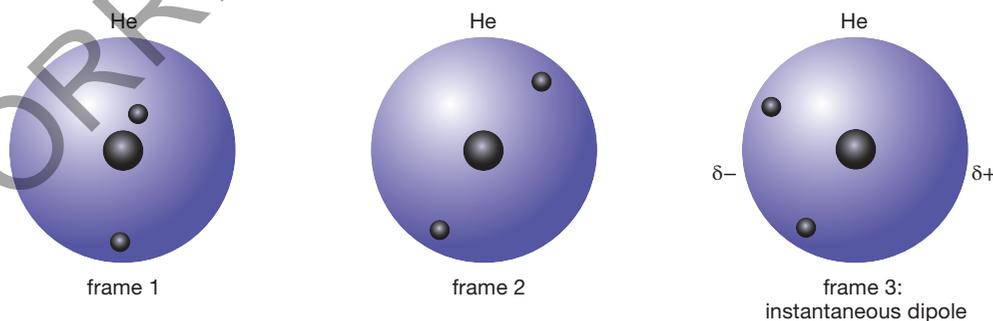


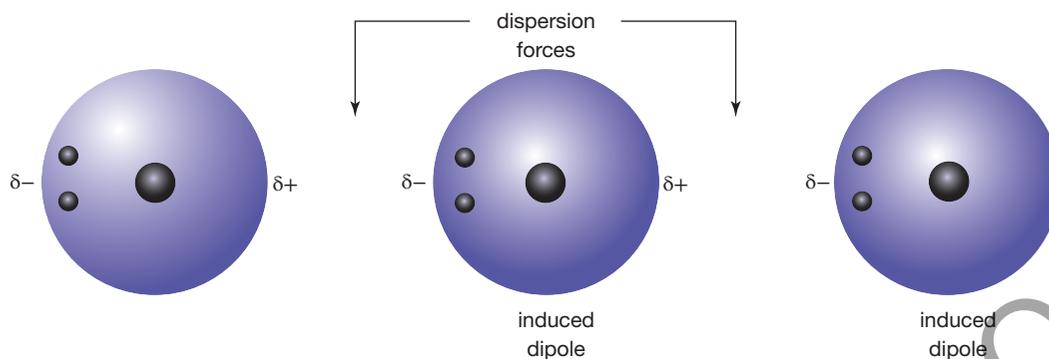
FIGURE 6.22 The electrons in this helium atom are moving all the time; sometimes they create an instantaneous dipole.



Two factors influence the strength of dispersion forces:

1. The number of electrons in the molecules. In general, the more electrons the molecules of a substance have, the stronger the dispersion forces between them.
2. The shapes of the molecules. Shape affects how closely the molecules may approach each other in the solid and liquid states. The closer the molecules can get, the stronger the attraction is. All covalent molecular substances have dispersion forces between their molecules.

FIGURE 6.23 The atom on the left has caused a temporary induced dipole in the middle atom, which in turn has caused another temporary induced dipole in the atom on the right.



Consider the noble gases He and Ne, or small molecules such as F_2 , H_2 and CH_4 . These atoms or molecules have relatively few electrons and so have very weak dispersion forces. Such substances have low boiling points and exist as gases at room temperature. Larger compounds, such as octane, C_8H_{18} (a component of petrol), exist as liquids. However, candle wax, $C_{25}H_{52}$, is a solid with a low melting point.

This trend can be illustrated using the halogens, as shown in table 6.7. As we go down the group, the molecules become larger and a progression occurs from a gaseous to liquid and ultimately solid state. Boiling and melting points of halogens show a corresponding increase.

TABLE 6.7 Properties of group 17 elements

Name	Formula	State	Melting point (°C)	Boiling point (°C)
Fluorine	F_2	Gas	-220.3	-188
Chlorine	Cl_2	Gas	-101	-34
Bromine	Br_2	Liquid	-7.3	59
Iodine	I_2	Solid	113	184

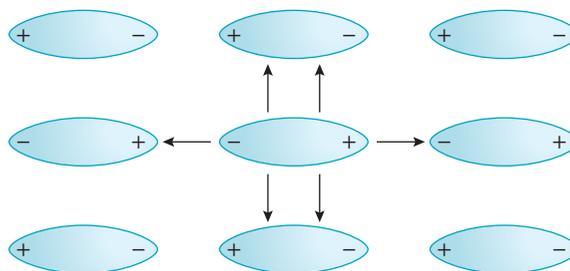
Dipole–dipole interactions

If the molecules in a sample are polar, the presence of molecular dipoles causes simultaneous intermolecular attraction. The positive side of one molecule attracts the negative side of another molecule, which attracts the next, and so on to the limits of the sample.

Polar molecules have two forces of attraction operating between their molecules. If two molecules are of similar size — that is, have a similar number of electrons — the dispersion forces acting on them are similar. However, if one of the molecules is polar, it will also be affected by dipole–dipole attractions.

This results in a stronger overall intermolecular force and a higher boiling point. Consider Ar (boiling point $-186\text{ }^\circ\text{C}$) and HCl (boiling point $-83.7\text{ }^\circ\text{C}$). Both substances have 18 electrons, yet HCl has a much higher boiling point. This is because HCl is a polar molecule and so has an extra intermolecular force of dipole–dipole interactions. Such a compound is generally more likely to exist as a liquid or solid at room temperature than a non-polar compound of similar size.

FIGURE 6.24 In dipole–dipole interactions, the central polar molecule is attracted to other polar molecules around it. They, in turn, are attracted by their neighbours.



Hydrogen bonding

Hydrogen bonding is a special case of dipole–dipole attraction. Hydrogen is an atom containing one proton in the nucleus and one electron revolving around it.

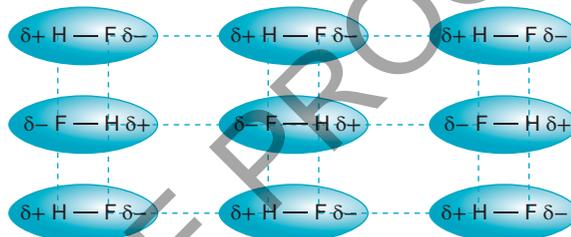
When hydrogen bonds to a more electronegative atom such as nitrogen, oxygen or fluorine, its electrons move slightly toward that atom. This causes the hydrogen nucleus to be exposed or unshielded. The molecule that forms is a dipole.

The negative end of one of these dipoles is attracted to the positive end of another.

Because the hydrogen (positive end) is unshielded, the other dipole can approach far more closely. The closer the dipoles get, the stronger the bond that forms. The bond between the dipoles is called a hydrogen bond. These bonds are represented in figure 6.25 by dotted lines, indicating that they are a weaker bond type than a covalent bond. Hydrogen bonds form only *between* molecules and only when hydrogen has been bonded to fluorine, oxygen or nitrogen.

Hydrogen bonds are stronger than other dipole–dipole bonds and result in materials with higher melting and boiling points than would otherwise be expected.

FIGURE 6.25 The negative ends of the dipoles are attracted to the positive ends, causing a hydrogen bond to form.



6.4.2 Properties of molecular substances in relation to structure

Although the covalent bonding holding the atoms together in a molecule is strong, the forces between molecules are usually weak. The physical properties of a compound depend on the type of bonding it displays. Ionic compounds are crystalline solids, but molecular substances may exist as solids, liquids or gases. A great variety of physical properties occurs among molecular substances due largely to the differences in strength of the intermolecular attractions. Even so, a few generalisations can be made.

- Molecular substances do not conduct electricity in the solid or molten form because the molecules are electrically neutral.
- If dissolved in water without reacting with it, molecular substances do not conduct electricity, again because the molecules are electrically neutral.
- Some molecules dissolve in water to produce ions. These molecules are said to ionise when they are dissolved in water, and can conduct electricity owing to the movement of the ions produced.
- Molecular substances vary in their solubility in water and other solvents. Generally, polar compounds are soluble in polar solvents such as water but insoluble in non-polar solvents such as tetrachloromethane. Non-polar solutes tend to be more soluble in non-polar solvents than polar solvents. This is sometimes described as the ‘like-dissolves-like’ rule.
- Molecular compounds have low melting and boiling points since the forces between the molecules are weak, and relatively little energy is required to break them. Many molecular substances are gases or liquids at room temperature.
- Most molecular substances are soft and easily scratched. Once again this is due to the weak forces of attraction between the molecules that mean molecules can be easily removed from the surface.

FIGURE 6.26 The softness of wax, together with its insolubility in water, make it ideal to apply to surfboards.



Note that in all of these cases (except for the third point above), the molecules themselves remain unchanged. Although they may be separated from other molecules by processes such as boiling, dissolving and scratching, the molecules themselves remain intact. This is because the *intramolecular* force of covalent bonding is very strong.

SAMPLE PROBLEM 8

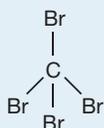
Name the type(s) of intermolecular forces that exist between molecules in the following substances.

- CBr_4
- CH_3OH

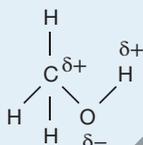
 Teacher-led videos: SP8 (tlvd-0533)

THINK

- CBr_4 is a non-polar tetrahedral molecule.



- CH_3OH has a tetrahedral shape around the carbon atom and a V-shape around the second central atom, oxygen, resulting in a polar molecule. It also has a highly electronegative atom (oxygen) bonded to a hydrogen atom.



WRITE

Only dispersion forces exist between these molecules.

Dispersion forces and hydrogen bonding exist between these molecules.

PRACTICE PROBLEM 8

Explain the type(s) of intermolecular forces that exist between molecules in the following substances.

- Cl_4
- CH_3NH_2

Resources

 Weblink Intermolecular forces

6.4 EXERCISE

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- Explain the type(s) of intermolecular forces that exist between molecules in the following substances.
 - CCl_4
 - $\text{CH}_3\text{CH}_2\text{NH}_2$
 - Cl_2
 - CH_3OH
 - CH_3Cl

- Explain why water, H_2O , has a higher boiling point than hydrogen sulphide, H_2S , despite it being a smaller molecule with fewer electrons.
- The boiling points of HCl , HBr and HI are, respectively, $-85\text{ }^\circ\text{C}$, $-67\text{ }^\circ\text{C}$ and $-35\text{ }^\circ\text{C}$. Explain the difference in these boiling points with reference to the forces that exist between the molecules of each substance.
- Br_2 and ICl have the same number of electrons, yet Br_2 melts at $-7.2\text{ }^\circ\text{C}$, and ICl melts at $27.2\text{ }^\circ\text{C}$. Explain this in terms of intermolecular forces.
- N_2 has 14 electrons and Cl_2 has 34 electrons. Predict which of these substances would have the higher boiling point. Justify your answer in terms of intermolecular forces.
- Two noble gases, helium and argon, have boiling points of $-269\text{ }^\circ\text{C}$ and $-186\text{ }^\circ\text{C}$ respectively. Explain the large difference in their boiling points.
- Kr (boiling point $-152\text{ }^\circ\text{C}$) and HBr (boiling point $-67\text{ }^\circ\text{C}$) have the same number of electrons. Explain what factors could affect intermolecular forces to cause the difference in boiling points between Kr and HBr .
- HCl has more electrons than HF so we would expect it to have the higher boiling point. However, this is not the case; the boiling points of HCl and HF are $-83.7\text{ }^\circ\text{C}$ and $19.4\text{ }^\circ\text{C}$ respectively. Explain what factors could account for this reversal in trend.
- Explain why F_2 , O_2 and N_2 are all gases at room temperature.
- Predict whether I_2 dissolves more readily in non-polar tetrachloromethane or in polar water. Explain your answer.
- Would you expect candle wax, $\text{C}_{25}\text{H}_{52}$, to be
 - soft or hard?
 - soluble in water?
 - an electrical conductor?
 Explain your predictions using your knowledge of structure and bonding.
- Only certain substances display hydrogen bonding.
 - Is hydrogen bonding an intramolecular force or an intermolecular force?
 - The causes of hydrogen bonding are within a molecule but its effect is felt between molecules. Explain this statement.
 - State the requirements for hydrogen bonding.

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6.5 The relative strengths of bond types in molecular substances

KEY CONCEPT

- The relative strengths of bonds (covalent bonding, dispersion forces, dipole–dipole attraction and hydrogen bonding) and evidence and factors that determine bond strength, including explanations for the floating of ice and expansion of water at higher temperatures

6.5.1 Factors that determine bond strength

Table 6.8 lists some properties of the hydrogen halides (compounds between hydrogen and an element from group 17). The patterns and trends within this table illustrate some of the factors that determine bond strengths.

TABLE 6.8 Some physical properties of the hydrogen halides

Hydride	Formula	Melting temperature (°C)	Boiling temperature (°C)	Bond dissociation energy* (kJ mol ⁻¹)	Bond length (picometres) (pm)
Hydrogen fluoride	HF	+19.5	-83	568	92
Hydrogen chloride	HCl	-85	-115	432	127
Hydrogen bromide	HBr	-67	-87	366	141
Hydrogen iodide	HI	-35	-51	298	161

* Bond dissociation energy measures how difficult it is to break the bonds within a molecule and separate it into its component atoms. The higher the value, the stronger the bonds.

When we examine the bond dissociation energies, a trend appears. Going down the table (which corresponds to going down group 17), the values decrease, meaning the covalent bond between the hydrogen and the halide atom is becoming weaker. This is because the electrons involved from the halide atom are one electron shell further out each time. This makes the length of the bond longer (as shown in the last column in table 6.8). The bond is weaker because the two electrons in it are more spread out and also further away from the nucleus. This trend is obvious in nearly all other molecules — the longer the length of the bond, the weaker it is.

Another trend is that double bonds are stronger than single bonds, and triple bonds are stronger yet again. Table 6.9 illustrates this for carbon to carbon bonds.

TABLE 6.9 Bond lengths and strengths for carbon-carbon bonds

Bond type	Bond dissociation energy (kJ mol ⁻¹)	Bond length (pm)
C—C	348	154
C=C	614	134
C≡C	839	120

Returning to table 6.8, trends are also apparent in melting and boiling temperatures, although not quite as perfect. Descending down a group, both these increase, except for hydrogen fluoride. This means that the forces between the molecules are getting stronger. This is because the molecules are getting larger and contain more electrons, increasing the strength of the dispersion forces that hold the molecules together.

But why is hydrogen fluoride an exception? It is because hydrogen fluoride has an additional type of bonding between its molecules: hydrogen bonding. This makes the forces between hydrogen fluoride molecules stronger and the molecules harder to separate from each other when melting and boiling take place. The influence of hydrogen bonding also occurs in water, and it is explored below and in greater detail in topic 11.

SAMPLE PROBLEM 9

Consider the following hydrides from group 16: H₂O, H₂S, H₂Se.

- Which will have the strongest bonding within its molecules?
- Which will have the strongest dispersion forces between its molecules?
- Which will have the overall strongest bonding between its molecules?
- Which will have the highest boiling point?

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THINK

- Recall that bond length gets longer down a group, and that the longer the bond, the weaker it is. H_2O has the shortest bonds and, therefore, the strongest intramolecular bonding.
- Recall that dispersion forces depend on the number of electrons in the molecule — the more electrons, the stronger the dispersion forces. H_2Se is the largest molecule and has the greatest number of electrons. It will, therefore, have the strongest dispersion forces between its molecules.
- Recognise that hydrogen bonding exists in H_2O but in none of the others. This is stronger than the dispersion forces that are (always) present. H_2O , therefore, has the strongest overall intermolecular bonding.
- Recall that the stronger the forces between molecules, the higher the boiling point. H_2O , therefore, has the highest boiling point.

WRITE

H_2O has the strongest bonding within its molecules.

H_2Se has the strongest dispersion forces between its molecules.

H_2O has the strongest overall bonding between its molecules.

H_2O has the highest boiling point.

PRACTICE PROBLEM 9

Consider the following hydrides from group 17: HF, HCl, HBr, HI.

- Which will have the strongest bonding within its molecules?
- Which will have the strongest dispersion forces between its molecules?
- Which will have the overall strongest bonding between its molecules?
- Which will have the highest boiling point?

Relative strengths of bond types

Molecular substances may experience up to four different types of bonding. *All* molecules are held together by covalent bonding. Because this acts *within* a molecule, it is classified as an *intramolecular* force. It is a very strong force and considerably greater than any of the other forces that may be experienced. *All* molecules also experience attraction to other molecules from dispersion forces. These are the very weak forces that originate due to the movement of electrons within the molecule. Other forces that may be experienced *between* molecules are dipole–dipole attractions and hydrogen bonding. These two are due to the polarity that exists within *some* molecules. All forces *between* molecules may be classified as *intermolecular* forces.

The decreasing order of strength between the four types of bonding is as follows, starting with strongest.

Covalent bonding >>>> hydrogen bonding >> dipole–dipole attraction > dispersion forces

6.5.2 The effect of hydrogen bonding on the properties of water

Hydrogen bonding significantly affects the physical properties of water. The existence of hydrogen bonding between water molecules results in:

- the relatively high melting and boiling points of water compared with other substances. More heat is required to enable the molecules to gain sufficient kinetic energy to break free of the hydrogen bonds, which are stronger than dispersion forces alone. For example, H_2O is a liquid at room temperature with a boiling point of $100\text{ }^\circ\text{C}$, whereas H_2S , which has more electrons, is a gas at room temperature and boils at $-61\text{ }^\circ\text{C}$. The behaviour of H_2O as it changes state between liquid water and solid ice is also governed by the hydrogen bond.

- the expansion of water upon freezing. Generally, as substances are heated, they expand. However, water behaves a little differently. The density of water is greatest at 4 °C. (Density refers to how much mass is in a given volume; for example, oil is less dense than water so it floats on top of water.) Water does expand when heated from 4 °C but, unusually, it also expands as the temperature decreases from 4 °C. As the temperature continues to decrease, water at 4 °C sinks and eventually the temperature at the surface becomes 0 °C and freezes. Ice forms in an open, hexagonal crystalline lattice that places the water molecules further apart than occurs in the liquid state. Because water expands on freezing, it is less dense as a solid. Ice, therefore, floats on water.

If ice were denser than water, some bodies of water would freeze solid during winter and the aquatic life would die. Icebergs form when sections of the frozen icecap break off and float in the sea. When ice forms on the surface of water, it acts as an insulator, preventing the water below from freezing. This means that aquatic life can survive, even in sub-zero conditions.

FIGURE 6.27 The hexagonal structure of ice. The molecules in liquid water are hydrogen bonded but free to move about. In ice molecules are held further apart and in a more orderly arrangement, owing to the extensive hydrogen bonding.

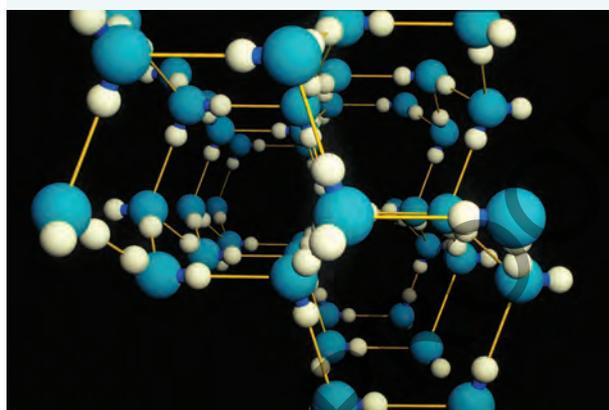


FIGURE 6.28 The density of water is greatest at 4 °C

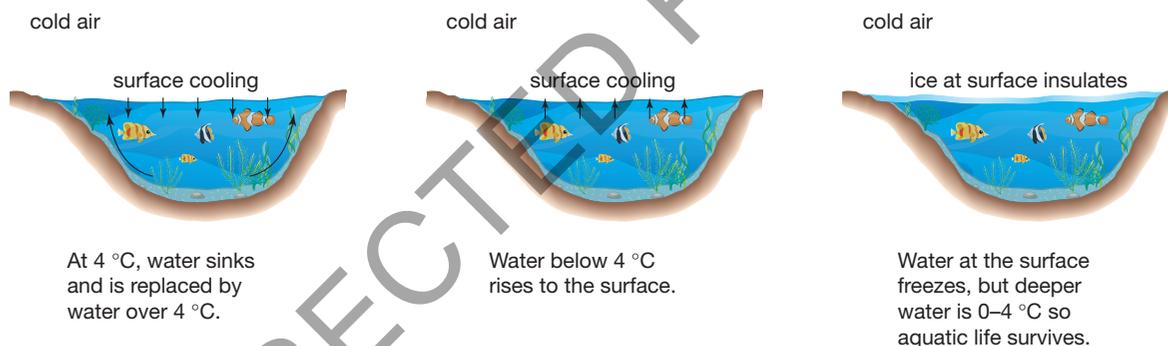
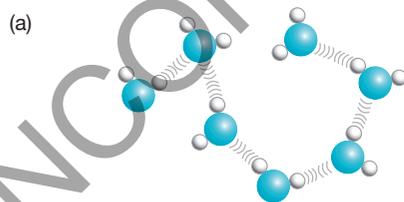
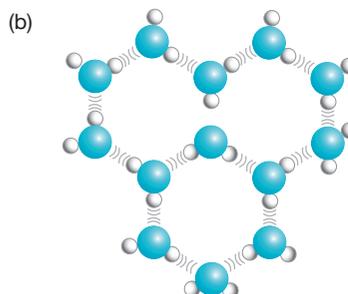


FIGURE 6.29 Hydrogen bonding in water when (a) water molecules are in liquid form and (b) water molecules in solid form (ice)



Water molecules move too quickly when in liquid form to form regular structures; however, they still remain attached.



When in solid form (ice), water molecules join together to form hexagonal structures.

6.5 EXERCISE

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- Place the following list of bonding types in order, from weakest to strongest.
covalent bonding, hydrogen bonding, dispersion forces, dipole–dipole attractions
- Consider the following list of compounds: CF_4 , CCl_4 , CBr_4 .
 - Does hydrogen bonding exist in any of these substances?
 - Which has the strongest bonding within its molecules?
 - Which has the strongest dispersion forces between its molecules?
 - Which has the highest boiling point?
- Consider the following list of compounds: CH_3F , CH_3Cl , CH_3Br .
 - Does hydrogen bonding exist in any of these substances?
 - Which substance has the weakest intramolecular bond(s)?
 - Which substance has the strongest dispersion forces between its molecules?
- How would you expect the boiling points of argon (Ar) and fluorine (F_2) to compare? Explain.
- Write the structural formulas for the following and name the shape of each molecule.
 - O_2
 - CHCl_3
 - Br_2
 - OF_2
 - CCl_4
 - C_2H_2
- Draw and name the shape diagrams of the following compounds.
 - CF_4
 - PH_3
 - HCl
- Predict whether the following molecules are polar or non-polar.
 - HI
 - SiH_4
 - CS_2
 - SF_2
 - CH_3Cl
 - C_2H_4
- CH_3F has a boiling point of -78°C , whereas CH_3OH has a boiling point of 65°C . Explain this difference.
- Which of the following exhibits hydrogen bonding? Why?
 - H_2O
 - C_2H_6
 - CH_3OH
 - $\text{CH}_3\text{CH}_2\text{OH}$
- Explain why a full, sealed glass bottle of water will crack when left in a freezer.

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6.6 Review

6.6.1 Summary

Representing molecules

- Covalent molecular substances are substances held together by covalent bonds and include elements and compounds. These substances are made up of molecules.

- A molecule is a discrete (separate) group of non-metallic atoms held together by covalent bonds. The atoms are combined in a fixed ratio and are electrically neutral.
- A covalent molecular element is made up of molecules of the *same* element. The molecules may contain varying numbers of atoms. These include diatomic molecules, which are composed of two atoms that share electrons (e.g. Cl₂).
- A covalent molecular compound is made up of atoms of *different* elements (e.g. CH₄).
- Atoms tend to lose, gain or share electrons in order to achieve a stable noble gas configuration of eight electrons in the valence shell. The exception to this rule is the hydrogen atom, which needs only two electrons to complete its outer shell.
- Covalent bonds are produced when non-metallic atoms react together, *sharing* pairs of electrons so that each may get eight outershell electrons. These bonds are the result of the force of attraction between shared electrons and the nuclei of the non-metal atoms in the bond.
- Covalent bonds may be single bonds (formed by one shared pair of electrons) or multiple bonds.
 - In a double bond, two electron pairs are shared by two atoms.
 - In a triple bond, three electron pairs are shared by two atoms.
- Molecules can be represented in several ways to better understand their structures. Ball-and-stick, space-filling and computer-generated models are used to represent the three-dimensional structure of molecules. Two-dimensional models include:
 - electron dot diagrams
 - valence structures, which replace each pair of electrons (bonding and non-bonding) with a dash (–)
 - structural formulas, where dashes are used for bonding electron pairs and non-bonding pairs are often omitted
 - combinations of these representations.
- Though electrons are identical, when representing a covalent bond using an electron dot diagram they may be thought of as either bonding or non-bonding electrons.
 - Bonding electrons are the single electrons available for sharing, and they determine the number of bonds an atom can form with other non-metals.
 - Non-bonding electrons or lone pairs are paired electrons that are not available for sharing.
- The atom with the most bonding electrons is known as the central atom.

Predicting molecular shape

- Molecule shapes can be determined using electron dot diagrams and VSEPR theory, which allows us to determine the best shape for minimum repulsion between the electron pairs around the central atom.
- In general, the molecule shape is:
 - linear if the central atom has *one* bonding pair or one pair on either side (e.g. H₂, CO₂)
 - V-shaped if the central atom has *two* bonding pairs and *two* lone pairs (e.g. H₂O)
 - planar if the central atom has *three* bonding pairs and no lone pairs (e.g. C₂H₄).
 - pyramidal if the central atom has *three* bonding pairs and *one* lone pair (e.g. NH₃)
 - tetrahedral if the central atom has *four* bonding pairs and *no* lone pairs (e.g. CH₄).
- Non-metallic atoms have high electronegativities, which means that they have a strong attraction for the shared electrons in a covalent bond. Differing electronegativities cause electrons to be unequally shared, and can affect the polarity of the bond.
 - Bonds across which no difference exists in electronegativity will share electrons equally and are non-polar.
 - Bonds across which a difference in electronegativity does exist will share electrons unequally and are polar.
- Molecules can be polar or non-polar. This depends on whether their bonds are polar and on their shape.
 - If all bonds are non-polar, the molecule will be non-polar.
 - If the molecule contains polar bonds but the effects of all of these cancel out due to the molecule's shape, the molecule will be non-polar.

- If the molecule contains polar bonds but the effects of all of these do not cancel out due to the molecule's shape (i.e. the molecule is asymmetric), the molecule will be polar.

Explaining the properties of molecular substances

- In addition to the intramolecular forces that work within molecules to hold them together, weak bonds exist between molecules and are called intermolecular forces.
 - Dispersion forces are found in all atoms or discrete molecules and increase with the size of the atom or molecule and the corresponding number of electrons.
 - Dipole–dipole interactions are found only in polar discrete molecules.
- Hydrogen bonding is a special case of dipole–dipole interaction. It is found only in molecules where a hydrogen atom is directly bonded to a more electronegative fluorine, oxygen or nitrogen atom. These bonds are stronger than other dipole–dipole bonds and result in higher melting and boiling points.
- Discrete covalent molecular substances have similar properties. Molecular substances:
 - have low melting and boiling points due to weak intermolecular forces
 - are usually liquid or gaseous at room temperature due to weak intermolecular forces
 - do not conduct electricity because the molecules are electrically neutral
 - are soluble in water if polar, and soluble in non-polar solvents if non-polar (the 'like-dissolves-like' rule)
 - are soft.

The relative strengths of bond types in molecular substances

- The forces existing within and between the molecules of a covalently bonded substance have different strengths. In order of decreasing strength, these are:

Covalent bonding >>>>> hydrogen bonding >> dipole–dipole attraction > dispersion forces.
- Hydrogen bonding between water molecules explains some of its unusual properties, including its expansion on freezing and the floating of ice on water. It also explains the relatively high melting and boiling points for water.

6.6.2 Key terms

ball-and-stick model representation of a molecule in which the atoms are shown as balls and the bonds as sticks

bond dipole separation of charge in a polar covalent bond

bonding electrons the pairs of electrons involved in forming a covalent bond

central atom the atom in a molecule with the most bonding electrons

computer-generated model representation of a molecule that is produced by a computer

covalent bond sharing of electrons between nuclei that bonds them together in a molecule

covalent molecular compound a molecular compound in which atoms of different elements share electrons with each other

covalent molecular element element made up of identical atoms held together by covalent bonds

diatomic molecule substance containing two atoms only

dipole–dipole interactions weak bonding caused by the positive end of one dipole attracting the negative end of another dipole

discrete separate, distinct; not in an infinite array or lattice

dispersion force the bond between adjacent molecules formed by instantaneous dipoles; this weak non-directional bonding is also known as van der Waals force

double bond strong bond between two atoms formed by two pairs of electrons that are shared by the two nuclei

electron dot diagram representation where the atom's nucleus and all innershell electrons are replaced by its element symbol and the outershell electrons are represented by dots around the symbol in a square arrangement

electronegativity the electron-attracting power of an atom

hydrogen bonding the bond between a hydrogen atom covalently bonded to an atom of F, O or N and another molecule that also contains an atom of H, F, O or N

intermolecular bonding bonding that occurs between molecules
intramolecular bonding internal bonds within a molecule
molecule group of atoms bonded together covalently
multiple bond bond formed when two atoms share two or more pairs of electrons
non-bonding electrons electrons that are not involved in bonding
non-polar covalent bond bond formed between atoms with the same electronegativity
non-polar molecule molecule that does not have permanent dipoles or is symmetrical
octet rule a generalisation that works for many (but not all) atoms, stating that atoms will donate or share electrons in order to achieve eight electrons in their outer shells
polar covalent bond bond formed when two atoms that have different electronegativities share electrons
polar molecule a molecule which, due to its polar bonds *and* its asymmetric shape, has an overall imbalance in the distribution of its electrons.
polarity localised imbalances in electric charges within a molecule resulting in a negatively charged end and positively charged end
space-filing model three-dimensional representation of a molecule that shows the relative sizes of atoms within the molecule and the distances between them
structural formula a diagrammatic representation of a molecule showing every bond
triple bond strong bond between two atoms formed by three pairs of electrons that are shared by the two nuclei
valence electrons outershell electrons
valence structure a diagrammatic representation of the outershell electrons in a molecule; Similar to an electron dot diagram but replaces each pair of electrons with a dash (-)
valence shell electron pair repulsion (VSEPR) theory a model with the main point that the structure around a given atom in a molecule is determined principally by minimising electron repulsions

on Resources

 **Digital document** Key terms glossary — Topic 6 (doc-30947)

6.6.3 Practical investigations

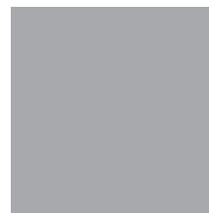
Experiment 6.1

Building molecular models

Aim: To construct molecular models of H_2 , Cl_2 , HCl , H_2O , NH_3 , CH_4 , CH_2F_2 , H_2S , C_2H_6 , C_2H_5Cl and CH_3CH_2OH and then use these to determine molecular shapes

Digital document: doc-30848

Teacher-led video: tlvd-0623



6.6 Exercises

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6.6 Exercise 1: Multiple choice questions

1. The best model to illustrate the shape of a molecule is which of the following?
 - A. Electron dot
 - B. Space-filling
 - C. Valence structure
 - D. Ball-and-stick

2. A molecule has four bonding pairs of electrons around its central atom. What would the shape of this molecule be described as?
- Tetrahedral
 - Pyramidal
 - V-shaped
 - Linear
3. A molecule has three bonding pairs of electrons and a lone pair around its central atom. What would the shape of this molecule be described as?
- Tetrahedral
 - Pyramidal
 - V-shaped
 - Linear
4. What does the sharing of electrons in bond formation *always* involve?
- The formation of positive and negative ions
 - The formation of polar molecules
 - Shared electrons being attracted more by one atom than another
 - The bonded atoms having greater stability than the unbonded atoms
5. Which one of the following electron dot diagrams best represents the bonding in the nitrogen molecule?
- :N::N:
 - :N::N
 - $\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}$
 - $\text{:}\ddot{\text{N}}\text{:}$
6. Which of the following is a characteristic property of a covalent molecular compound?
- Relatively low melting point
 - Malleable and ductile
 - High melting point
 - Conducts electricity when molten but not when solid
7. What is the structure of C_2H_2 ?
- Linear
 - V-shaped
 - Planar
 - Pyramidal
8. Which of the following best describes the molecular shape, polarity of bond and molecular polarity of the H_2S molecule?
- Linear, polar covalent, non-polar
 - Linear, polar covalent, polar
 - V-shaped, ionic, polar
 - V-shaped, polar covalent, polar
9. Which of the following substances might one expect to exhibit the weakest intermolecular forces?
- HCl
 - He
 - NH_3
 - H_2O
10. At room temperature, methane is a gas while tetrachloromethane is a liquid. Choose the statement that best explains this.
- There is appreciable hydrogen bonding in tetrachloromethane but not in methane.
 - The tetrachloromethane molecule is polar, while the methane molecule is non-polar.
 - Tetrachloromethane has an appreciably higher molecular mass than methane.
 - The bonds in tetrachloromethane are polar covalent.

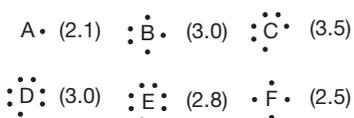
Question 4 (9 marks)

Water has some unique properties and we cannot live without it.

- a. Use a labelled diagram to explain why the water molecule is V-shaped. **3 marks**
- b. Explain the intramolecular and intermolecular forces in water. **2 marks**
- c. Why is the density of ice less than the density of water? **2 marks**
- d. Describe an experiment to show the difference in density between water and ice. **2 marks**

Question 5 (10 marks)

The electron dot diagrams for six elements are shown with their corresponding electronegativities in brackets. The usual symbols have been replaced by the letters A to F.



- a. Describe the position of D and E relative to each other on the periodic table. **1 mark**
- b. Name a possible element that C might represent. **1 mark**
- c. Element A forms covalent bonds with B, C, D, E and F. Which bonds will be the most polar? **1 mark**
- d. Draw electron dot diagrams for the following. **3 marks**
 - i. A bonding with B
 - ii. A bonding with D
 - iii. A bonding with F
- e. Which of the molecule(s) from part (d) will be **3 marks**
 - i. polar?
 - ii. non-polar?
- f. What is the shape of the molecule formed between A and B? **1 mark**

6.6 Exercise 4: studyON Topic Test

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