LEAVING CERTIFICATE CHEMISTRY

Catalytically Cataly

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Atomic Theory Not so Bohr-ing!

| | Can I | ~ |
|--|-----------------|----------|
| Describe (and draw) the nuclear me | del of the stom | |
| State the assumptions and limitations of the nuclear model of the atom | | |
| Describe (and draw) the Bohr model of the atom | | |
| State the assumptions and limitations of the Bohr model of the atom | | |
| Describe the orbital model of the atom | | |
| State the assumptions and limitations of the orbital model of the atom | | |
| Compare all three models of the atom | | |
| Describe (and draw) the shapes of the s and p orbitals | | |
| Bold = HL only | | |

In the Junior Cycle you learnt that atoms are made up of protons, neutrons and electrons. You also learnt that the protons and neutrons are found in the nucleus, and that electrons are found in shells around the nucleus. But how do we know that this is what an atom looks like? And is this really the complete picture of an atom?

Many models of the atom have been put forward by scientists over the centuries. Studying some of these will help us to understand how scientists arrived at the modern structure of the atom and how scientists work (how they draw conclusions based on the experimental data they collect, and how they must be open to altering their ideas as new evidence emerges).

Note: You **don't need** to remember any dates given in this chapter – they're only for context. You also don't need to remember the names of scientists or the details of the experiments they carried out. These are included to aid your understanding, but the only content that can be examined in the LC exam is **the three atomic models and their assumptions and limitations**.

6.1 Nuclear model

Ernest Rutherford (1871–1937), a scientist from New Zealand, was working at the University of Manchester when he accidentally **discovered the existence of the nucleus**.

Rutherford's experiment

In 1909 Rutherford set out to investigate the structure of the atom. At the time scientists believed in what is called the plum-pudding model of the atom: they thought that the atom was essentially a sphere of positive charge with electrons embedded at random. Rutherford and his assistants set up an experiment in which a very thin sheet of gold foil was bombarded with alpha particles. Gold was chosen as it's very malleable and can be beaten into an extremely thin layer.



Alpha particles are a type of radioactive particle, and we now know (although Rutherford did not) that they consist of two protons and two neutrons.

Rutherford knew only that the alpha particles were positively charged, and he wanted to study the path of the positive alpha particles through the gold foil to investigate the structure of the atom.

Figure 6.1 shows the experimental set-up. A screen was set up to detect where the alpha particles hit after passing through the gold atoms.



Figure 6.1

Basing their results on the plum-pudding model of the atom, Rutherford and his team expected the alpha particles to pass straight through the gold foil undeflected or to be slightly deflected when passing near an electron. Most alpha particles did pass straight through the gold foil undeflected (or slightly deflected), but some alpha particles were deflected at large angles and a very few alpha particles deflected straight back along their original paths.



Figure 6.2

The nature of science

Rutherford anticipated that the alpha particles would simply pass straight through the gold foil with little to no deflection. However, being a meticulous scientist, he decided to place the detection screen all around the apparatus rather than just directly behind it, where he expected the alpha particles to be. This thoughtful approach led to unexpected results and serves as a valuable lesson in experimental design: scientists (and students!) must remain open-minded and prepared for unforeseen outcomes.



In 1911 Rutherford published his theory of the atom. It was based on the observations that he and his team made that led them to certain conclusions about the structure of the atom. (Table 6.1)

| Observation | Conclusion | | |
|--|---|--|--|
| Most alpha particles passed straight through the gold foil undeflected | Most of the atom is made of empty space | | |
| Some alpha particles were deflected at large angles | There must be a positive centre, which he called the nucleus (like repels like, and since the alpha particles were positive they must have travelled near to, and been repelled by, something positive) | | |
| A few (as few as one in 20,000) alpha particles deflected straight back along their original paths | The positively charged nucleus must be very small and very dense (it must be small since so few alpha particles deflected back having collided with the nucleus, and it must be dense as it was able to deflect the alpha particles straight back) | | |

Table 6.1

Based on these results, **Rutherford suggested a new model of the atom (the nuclear model)**, which had a very small, dense and positive core he called the nucleus. He suggested that the nucleus was surrounded by empty space within which electrons moved in wide orbits. However,

his theory was unclear on where exactly electrons were to be found and what they were doing. (Figure 6.3)

Assumptions of the nuclear model

- The nucleus contains most of the atom's mass
- Electrons orbit around the nucleus in a relatively empty space

Limitations of the nuclear model

 Lacks detail about electron behaviour and doesn't clearly explain electron arrangement



Figure 6.3 Diagram

Link it

The next atomic model we study is Bohr's model of the atom. Before reading on, can you describe the structure of Bohr's model of the atom? (It is the one you are familiar with from JC).



6.2 The Bohr model

In 1913 Niels Bohr (a Danish scientist) built on Rutherford's work and proposed his **planetary model** of the atom. From his study of the atomic emission spectrum of hydrogen (which we will study in detail in Chapter 7), Bohr proposed that in an atom of hydrogen the single electron orbits the nucleus (similar to how planets orbit the Sun).

However, the crucial difference between Rutherford's model of the atom and Bohr's was that Bohr proposed that **electrons in an atom have a specific, fixed amount of energy** (a quantum of energy), and so can move around the nucleus only in **certain specific orbits** with a fixed radius, depending on the fixed amount of energy they have. This was the first time this had been suggested and it revolutionised the world of science (and contributed to the emerging theory of quantum mechanics).

HL

Bohr's theory states that electrons are found in energy levels. Electrons in the first energy level – the closest to the nucleus – have the same amount of energy as each other, and that amount of energy is less than the energy of electrons in the second energy level (further from the nucleus). Bohr represented energy levels using the letter n: n = 1for the first, n = 2 for the second, n = 3 for the third (more about this in Chapter 7).



An **energy level** is the fixed amount of energy of an electron in an atom.

However, although Bohr's model of the atom worked well for hydrogen, **it didn't work so well for atoms containing more than one electron** (multi-electron atoms). This was due to some limitations of his theory.

Limitations of Bohr's model of the atom

- Bohr's theory didn't take into account wave-particle duality (see Table 6.2)
- We now know that electrons don't travel in fixed orbits, but rather are found in orbitals (due to Heisenberg's uncertainty principle we can refer only to the probability of finding an electron) (see Table 6.2)
- Bohr's theory didn't account for sublevels (you will learn about sublevels on page ??)

Further work on atomic theory

Continued work by Rutherford, and work by many other scientists – Broglie, Schrödinger, Heisenberg and Chadwick among them – led to a new model (the current model) of the atom: the orbital model. It's helpful to have a basic idea of how each of these scientists contributed to developing our understanding of the atom, resulting in our current model.



| Ernest Rutherford | Discovered the existence of the proton and concluded that protons were present in the nucleus of all atoms |
|-------------------|---|
| Louis de Broglie | Proposed that particles have wave-particle duality: they can behave both as particles and waves – see Figure 6.5. (therefore, Bohr's picture of them travelling in a precise orbit at a precise distance from the nucleus is not entirely correct) |
| Erwin Schrödinger | Schrödinger used mathematical equations to predict where electrons are located within the atom. He identified regions of the atom where electrons had a high probability of being found. These regions are called orbitals and are of various shapes – e.g. spherical and dumb-bell shaped. (Again, this conflicted with Bohr's idea of electrons travelling in circular orbits.) |
| Werner Heisenberg | Heisenberg's uncertainty principle states that it is impossible to measure both the velocity and the position of an electron at the same time |
| James Chadwick | Discovered the existence of the neutron |

Table 6.2

6.3 The orbital model

When Schrödinger's wave equations were solved, four kinds of 3-D space were detected (in contrast to Bohr's 2D energy levels), within which there is a very high probability of finding an electron of specific energy. These regions of space were called orbitals, and the four types named s, p, d and f.

An **orbital** is a region of space around the nucleus of an atom within which there is a high probability of finding an electron.

S orbitals are spherical, with the nucleus at their centre. Each energy level has an s orbital – e.g. 1s, 2s – and the size of the orbital is dependent on the energy level to which it belongs.

P orbitals are dumb-bell shaped, arranged around the central nucleus. There are three kinds of p orbitals – p_x , p_y and p_z , oriented at right angles to each other, as shown in Figure 6.7.









PROOFS

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When s and p orbitals are mapped together, an atom that looks like Figure 6.8 is shown. These orbitals surround the nucleus, which is tiny but very dense, and is home to both protons and neutrons. (You will study orbitals in more depth in Chapter 7.)

The orbital model of the atom is actually much less specific than some of the previous models proposed – we can't state exactly both the position and speed of electrons, and we cannot even state the exact size of an atom.



Figure 6.8

If you find it odd to imagine an electron behaving as both a particle and a wave, and odd that we can talk only about regions where there is a high probability of finding an electron, you are not alone. As Bohr said, 'those who are not shocked when they first come across quantum theory cannot possibly have understood it'.

| Model of the atom | Nuclear model | Bohr model | Orbital model |
|----------------------|--|---|--|
| Diagram | Electron cloud where electrons are located Nucleus containing protons | n = 4 Electron energy levels n = 2 levels n = 1 Electron \bullet Nucleus | 2s orbital 2p orbitals 1s orbital 3s orbital |
| Assumptions | The nucleus contains most of the atom's mass Electrons orbit around the nucleus in a relatively empty space | Bohr assumed that electrons had fixed amounts of energy and could occupy only certain energy levels Bohr assumed that electrons travelled in specific orbits around the nucleus | Electrons are found in orbitals – regions of space where there is a high probability of finding an electron Electrons have wave-particle duality. |
| Limitations | Lacks detail about electron behaviour and does not explain electron arrangement. | Bohr's model worked well for hydrogen, but not for more complex atoms Bohr's model didn't take into account wave-particle duality Bohr mistakenly believed that the exact position of electrons could be known at all times (contrary to Heisenberg's uncertainty principle) Bohr's model didn't account for sublevels | We can predict only the likelihood of where electrons are – we do not know their exact positions |

Table 6.3

HL



The nature of science

How scientific ideas are modified over time

The study of atomic theory is a very good opportunity for us to realise how experimental evidence informs scientific thinking. As a result of experimental evidence, the accepted scientific theory had to change. As we know, this is an important part of science: **the ability to revise theories based on new evidence and the ability to devise experiments that test the work of previous scientists**.

How scientists work

As we trace the path of atomic theory we can see that many scientists lead us to our current understanding of atomic structure. **It's important to note that these scientists worked collaboratively – building on, and learning from, each others' work** – e.g. Bohr and Chadwick worked with Rutherford, and Heisenberg worked with Bohr.

🕑 🛛 Test yourself!

- (a) Draw labelled diagrams of the (i) nuclear model of the atom; (ii) Bohr model of the atom; (iii) orbital model of the atom. (b) Distinguish between these three models in terms of the location of electrons.
- 2. What limitations of the nuclear model of the atom led to the development of Bohr's model?
- 3. Compare the nuclear model to the current atomic model. In what ways does the nuclear model remain relevant today, and what are some of the issues with this model?
- 4. Why is it important for scientists to evaluate and refine atomic models over time?
- 5. In what way is the orbital model less specific than other models of the atom?
- 6. Explain one assumption and one limitation of (a) Bohr's model of the atom; (b) the orbital model of the atom.

For more questions on atomic theory, see Chapter 6 in the accompanying skills book.



Atomic Theory

Molecular Shapes and Intermolecular Forces (The perfect pair!)

| Can I | ~ |
|--|---|
| Use VSEPR theory to predict the shapes of molecules | |
| Visualise these molecules (draw diagrams, build 3D models, create digital models) | |
| Predict the overall polarity of a molecule when given its chemical formula | |
| Predict the overall polarity of a molecule when given a diagram | |
| Explain how molecules containing polar covalent bonds can be non-polar (i.e. link shape to overall polarity) | |
| Distinguish between intramolecular bonds and intermolecular forces | |
| Explain how permanent dipole-dipole forces arise | |
| Explain how hydrogen bonds arise | |
| Explain how London dispersion forces arise | |
| Explain how ion-dipole forces arise | |
| Explain how the type of intermolecular forces present can influence melting and boiling points (and therefore changes of state) | |
| Explain how the type of intermolecular forces present can influence solubility | |
| Interpret secondary data which provides evidence for the effects of intermolecular forces on melting and boiling points, and on solubility, accounting for trends | |
| Explain the effect of the shape and polarity of a molecule on its physical properties | |
| Explain the influence of polarity and symmetry on intermolecular forces, and therefore their | |

influence on the properties of molecules

Bold = HL only

9.1 VSEPR theory

We learnt in Chapter 8 that covalent compounds exist as molecules. Molecules contain different numbers of atoms, different types of bonds (e.g. polar or pure covalent) and exist in many different shapes. We use a theory called VSEPR (pronounced 'vesper') theory to predict the shape of a molecule. **VSEPR** stands for valence-shell electron-pair repulsion theory.

As we know, atoms share electrons to form molecules. The VSEPR theory is based on the fact that electron pairs in the valence shell (the outermost energy level) repel each other. Since electron pairs repel each other, they'll arrange themselves as far away from each other as possible. For instance, if a molecule has two



Figure 9.1

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electron pairs around its central atom, the electron pairs will position themselves as far apart as possible, resulting in a linear shape, with a bond angle of 180° (Figure 9.1). Note that the bond angle is the geometric angle between two neighbouring bonds (bonds that include a common atom).

However, it's not only the number of electron pairs that determines shape: it's also the type of electron pairs – i.e. are they bond pairs or lone pairs? When two electrons are **shared between atoms**, they're a **bond pair of electrons**. When two electrons aren't shared and aren't involved in a bond (i.e. belong to one atom only), they're a **lone pair of electrons**. Lone pairs have **extra repulsion power** – i.e. they repel other electron pairs to a greater extent than bond pairs do.

Since **lone pairs repel electron pairs to a greater extent, they'll change the shape of the molecule**. For example if one molecule has four bond pairs around the central atom and another molecule has three bond pairs and one lone pair, then the two molecules will be different shapes (even though both molecules have four electron pairs around the central atom).

Study the table below to see the various shapes that result depending on the combination of bond and lone pairs present around the central atom in a molecule.

| Total number of electron pairs around central atom | Number of bond pairs | Number of lone pairs | Shape of molecule | Diagrams | Bond angle |
|--|----------------------------|----------------------------|--------------------|----------|---------------|
| 2 | 2 | 0 | Linear | | 180° |
| 3 | 3 | 0 | Trigonal planar | | 120° |
| 4 | 4 | 0 | Tetrahedral | | 109.5° |
| 4 | 3 | 1 | Pyramidal | | 107° |
| 4 | 2 | 2 | V-shaped/ bent | | 104.5° |

Table 9.1

The following examples will show you how to work out the shape of a molecule when given the molecular formula. For Leaving Certificate we can think of **the central atom in a molecule as the atom of which there is only one**.



Example 1

What shape is BeH₂?

Step 1: Count valence electrons of central atom

Be has four electrons, arranged 2,2. Therefore, it has two valence electrons.

Step 2: Add one electron for each bonding atom

There are two hydrogen atoms bonded to Be, so we add two: 2 + 2 = 4

Step 3: Divide total by 2 to find the number of electron pairs

 $4 \div 2 = 2$ pairs

Step 4: Identify types of electron pairs and predict shape

Be is bonded to two hydrogen atoms – therefore, both pairs of electrons must be bond pairs. We saw in Table 9.1 (page ??) that a molecule with two bond pairs is **linear**, with a bond angle of **180°**.

This makes sense when you remember that the VSPER theory is based on electron-pair repulsion. Since each electron pair repels the other, the two electron pairs will arrange themselves around the beryllium atom in a way that keeps them as far away as possible from each other – hence, the 180° angle.



Step 1: Count valence electrons of central atom

Step 2: Add one electron for each bonding atom

Step 3: Divide total by 2 to find the number of electron pairs

Step 4: Identify types of electron pairs and predict shape. (Use Table 9.1, page ??. This table won't be provided in your exam – you must memorise it, including the bond angles)

Example 2

What shape is BCl₃?

Step 1: Count valence electrons of central atom

Boron has five electrons in total, arranged 2,3. Therefore, it has three valence electrons.

Step 2: Add one electron for each bonding atom

There are three chlorine atoms bonded to boron, so we add 3:3+3=6

Step 3: Divide total by two to find the number of electron pairs

 $6 \div 2 = 3$ electron pairs







Step 4: Identify types of electron pairs and predict shape

B is bonded to three Cl atoms. Therefore, all three electron pairs are bond pairs.

We see in Table 9.1 (page ??) that a molecule with three bond pairs is **trigonal planar**, with a bond angle of **120°**.



Note that the three electron pairs will arrange themselves as far away as possible from each other – hence, the 120° bond angle.

Example 3

HL

What shape is CH₄?

Step 1: Count valence electrons of central atom

C has six electrons, arranged 2,4. Therefore, it has four valence electrons.

Step 2: Add one electron for each bonding atom

There are four hydrogen atoms bonded to carbon. Therefore, we add four: 4 + 4 = 8

Step 3: Divide total by 2 to find the number of electron pairs

 $8 \div 2 = 4$ electron pairs

Step 4: Identify types of electron pairs and predict shape

The C atom is bonded to four H atoms. Therefore, all four electron pairs must be bond pairs. We saw in Table 9.1 (page ??) that a molecule with four bond pairs is **tetrahedral**, with a bond angle of **109.5**°.

It's very important to remember to draw the tetrahedral shape as shown as it's a 3-D molecule. The wedged line represents H coming out of the page towards you, and the dashed line represents H pointing away from you.



Figure 9.4

Try it!

Blow up four balloons to a similar size. Holding them at a central point, use them to demonstrate linear, trigonal planar and tetrahedral molecules.

Example 4

What shape is H_2O ?

Step 1: Count valence electrons of central atom

O has eight electrons, arranged 2,6. Therefore, it has six valence electrons.

Step 2: Add one electron for each bonding atom

There are two hydrogen atoms bonded to oxygen, so we add two: 6 + 2 = 8

Step 3: Divide total by 2 to find the number of electron pairs

 $8 \div 2 = 4$ electron pairs

Step 4: Identify types of electron pairs and predict shape

The O atom is bonded to two H atoms, so two of these electron pairs must be bond pairs. **Any remaining pairs are lone pairs.** We saw in Table 9.1 (page ??) that a molecule with two bond pairs and two lone pairs is **V-shaped**. We draw H_2O in a V-shaped shape, with a bond angle of **104.5**°.

Note that although there are four electron pairs around the central atom (O), two are bond and two are lone pairs. Therefore, this will not be a tetrahedral shape, but a V-shaped molecule. The extra repulsion of the lone pairs pushes the bond pairs closer together, giving a bond angle of 104.5°, which is smaller than the bond angle in a tetrahedral shape – 109.5°.





Example 5

What shape is NH_3 ?

Step 1: Count valence electrons of central atom

N has seven electrons, arranged 2,5. Therefore, it has five valence electrons.

Step 2: Add one electron for each bonding atom

There are three hydrogen atoms bonded to nitrogen, so we add three: 5 + 3 = 8

Step 3: Divide total by 2 to find the number of electron pairs

 $8 \div 2 = 4$ electron pairs

Step 4: Identify types of electron pairs and predict shape

The N atom is bonded to three H atoms, so three electron pairs must be bond pairs, and therefore the remaining pair must be a lone pair. We saw in Table 9.1 (page ??) that a molecule with three bond pairs and one lone pair is **pyramidal**, with a bond angle of **107**°.



Note that since the lone pair has extra repulsion power, it pushes the three bond pairs further away from the lone pair than they are from each other.



Crack it!

Molecules with a general formula AB_2 (i.e. one of one type of one atom – A – and two of another type of atom – B) will be either linear (e.g. BeH_2) or V-shaped (e.g. H_2O).

The two possible shapes for a molecule with general formula AB_3 are pyramidal (e.g. NH_3) or trigonal planar (e.g. BCI_3).

A molecule with a general formula AB₄ must be tetrahedral (e.g. CH₄).

9.2 Visualising molecules

Although we have already visualised molecules as 2-D diagrams, they are of course 3-D. To help you visualise the actual shapes of molecules, it's helpful to build models yourself, as well as looking at digital simulations.

3-D models

Molymod (molecular modelling) kits are often used by students in the lab to build models of molecules. Each colour in the kit refers to specific atoms. Your kit will come with instructions, but here's a guide to some of the most commonly used elements:

Carbon = black Hydrogen = white Oxygen = red Nitrogen = blue Halogen (group 17 element) = green

Try it!

Use a molymod kit to make models of the following molecules (you may need to use VSEPR theory first to work out their shape!): (a) CCI_4 (b) NH_3 (c) BF_3 .

PROOES

Digital models

There are many different digital modelling programs available online (so feel free to explore!), but one good option is **molview.org.** Spend some time typing different compounds into the search bar and looking at the digital molecules generated. Compare these to your diagrams and to the 3-D models you made in the lab. What are the pros and cons of each type of model?





Figure 9.7

9.3 How shape affects polarity

Note: For OL, you must be able to determine how shape affects polarity (when given a diagram of a molecule), but not work out the shape of molecules. For HL, you must be able to do both.

At this point we have studied many molecules that contain polar covalent bonds. Now we must distinguish between a molecule containing polar covalent bonds and a polar molecule, since **not all molecules containing polar covalent bonds are polar molecules**.

Link it!

How can we determine if a covalent bond is polar or non-polar? (page ??)

Let's remind ourselves of what the word polar means. Polar indicates that a molecule has two poles of opposite charges. Electron density is focused at one end of the molecule, making it partially negative (δ^{-}) and leaving the other side partially positive (δ^{+}).

If a molecule has non-polar covalent bonds only, the molecule is also non-polar. If a molecule has polar covalent bonds, it may be polar or non-polar.

A polar molecule must have two characteristics:

- 1. It must contain polar covalent bonds.
- **2.** The centres of positive and negative charge must not coincide (the molecule must not be symmetrical).

Let's have a look at some examples to explain this.

Example 6: Water, H₂O

Determine if this molecule is polar or non-polar.

Step 1: Determine if the bonds are polar or non-polar covalent

The O-H bonds in a water molecule are polar covalent (electronegativity difference of 1.24).

Step 2: Determine if the centres of negative and positive charge coincide (if the molecule is symmetrical)





Study Figure 9.10. We can see that the centre of partial negative charge in this water molecule is at the O atom. The centre of partial positive charge is midway between the hydrogen atoms. The centres of partial negative and partial positive charge aren't in

the same place – they don't coincide. (If the centres of partially positive and partially negative charges coincide, they effectively 'cancel' each other out. Here, they don't.) The partial positive and partial negative poles are in different parts of the molecule – therefore, the molecule has two poles – i.e. is polar.

Another way of saying this is that the molecule is not symmetrical. If you fold this in half downwards on the dotted line, both sides of the molecule are not the same.



Example 7: Tetrachloromethane, CCl₄

Step 1: Determine if the bonds are polar or non-polar covalent

Let's look at a molecule of CCI₄. The C-Cl bonds are polar covalent (electronegativity difference of 0.61).

Step 2: Determine if the centres of negative and positive charges coincide (if the molecule is symmetrical)

Study Figure 9.12. We can see that the centre of positive charge is in the centre of the molecule – at the carbon atom. The centre of negative charge is also in the centre of the molecule – midway between all four chlorine atoms. The partial positive and partial negative poles of this molecule coincide and 'cancel' each other out. Therefore, this molecule is not a polar molecule.

Another way of saying this is that the molecule is symmetrical. Even if a symmetrical molecule contains polar bonds, the molecule will still be non-polar.



Figure 9.11



Figure 9.12

A molecule will be non-polar if:

- **1.** It contains only non-polar covalent bonds.
- **2.** It contains polar covalent bonds but the centres of negative and positive charge coincide (the molecule is symmetrical).



For OL students, you must link shape to polarity. Molecules containing polar covalent bonds that are linear, trigonal planar or tetrahedral will be non-polar (as long as the atoms surrounding the central atom are all the same). Molecules containing polar covalent bonds that are pyramidal or V-shaped will always be polar.

Test yourself!

Are the following molecules polar or non-polar?



9.4 Intermolecular forces

We are now moving on from shapes to talk about intermolecular forces. As you should know from Chapter 8, intramolecular bonding refers to bonds inside a molecule (e.g. polar covalent bonds), **whereas intermolecular forces are the forces between molecules**. It's very important that this is very clear in your mind before you continue reading (studying Figure 9.14 will help you).



There are different types of intermolecular forces between molecules depending on the type of compound. The forces you will study are:

- 1. Permanent dipole-dipole forces (including hydrogen bonding)
- 2. London dispersion forces
- 3. Ion-dipole forces

1. Permanent dipole-dipole forces

Imagine a molecule of HCI. The intramolecular bond between the hydrogen atom and chlorine atom is covalent. As we have already learnt, this bond is polar covalent since the two electrons are not equally shared. Since the Cl atom is more electronegative (3.16), the shared pair of electrons is more attracted to it than to H (electronegativity = 2.20). This leaves the Cl atom slightly negative (δ^{-}) and the H atom slightly positive (δ^{+}). This separation of charge results in a **dipole** – i.e. there are two poles of charge in the molecule: one partially positive, one partially negative.

positive, one partially negative. The slightly positively charged end of one molecule is attracted to the slightly negatively charged end of the other. This force of attraction between molecules is called a permanent dipole-dipole force.

Since the δ^+ and δ^- charged poles are permanent (due to electronegativity differences between the atoms), these intermolecular forces are also permanent.

δ⁺ δ⁻ H Cl-Figure 9.15



Permanent dipole-dipole forces exist between the negative pole of one polar molecule and the positive pole of another polar molecule.

Permanent dipole-dipole forces: hydrogen bonding

Hydrogen bonds are a special type of permanent dipole-dipole intermolecular force that occurs between **the hydrogen of one molecule and the nitrogen, oxygen or fluorine of another.**



Figure 9.17

From the diagram you'll notice that this looks very similar to permanent dipole-dipole forces. However, atoms of nitrogen, oxygen and fluorine are all **very small and highly electronegative**. The large difference in electronegativity between **H and N**, **O or F** causes a **very strong dipole**. Essentially, hydrogen bonds are a **stronger type** of permanent dipole-dipole force.

Hydrogen bonds are a specific type of permanent dipole-dipole attraction between a hydrogen atom of one molecule and a small, highly electronegative atom (nitrogen, oxygen or fluorine) of a neighbouring molecule.

PROOFS

Note that for a compound to have hydrogen bonding between its molecules it must contain a hydrogen atom directly bonded to a nitrogen, oxygen or fluorine molecule. It's not just the presence of these atoms in a molecule - they must be directly bonded to each other.

δ 81 H H Hydrogen Bond

Figure 9.18

(Don't be confused by the word 'bond' here: hydrogen bonds are still a type of intermolecular force.)

2. London dispersion forces

London dispersion forces are similar to permanent dipole-dipole forces except that they're temporary. They're named after Fritz London, who first explained this phenomenon. They're still a force of attraction between the partially positive end of a molecule and the partially negative end of a neighbouring molecule, except that those partial charges are very short-lived, and therefore the attraction between them is also short-lived.

So how do they occur?

Let's imagine a molecule of hydrogen. The intramolecular bond between the two hydrogen atoms is non-polar covalent, so electrons are shared equally between the two atoms (i.e. the two hydrogen atoms have an equal 'pull' over the shared pair of electrons in the covalent bond).

However, although it's true that neither atom is more electronegative than the other, at a specific moment in time both electrons can be closer to one end of the molecule than the other. This is because electrons are not fixed in position but instead move around (within orbitals, as we know from Chapters 6 and 7).

Link it!

What is an atomic orbital? What are the shapes of an s orbital and a p orbital? (page ??)

PROOFS

For this moment in time, one side of the molecule would be partially positive (δ^+) and the other partially negative (δ^-). When these temporary dipoles (δ^+ and δ^-) are set up, they can induce a dipole in a neighbouring hydrogen molecule.

Study Figure 9.19. Since one end of the H₂ molecule is slightly negative, it will repel the electrons in the neighbouring molecule (like repels like). This will cause the electrons in that molecule to shift, resulting in δ^+ and δ^- charges in that molecule also.

It's important to realise that **temporary** dipoles are set up, not permanent ones. Temporary dipoles don't last because electrons constantly move around at high speed, changing the partial charges in the molecule, so the attractions occur only for an instant. In fact, the next moment the molecules may look like Figure 9.20.



Figure 9.19







London dispersion forces are weak, temporary forces of attraction between neighbouring molecules as a result of temporary dipoles (caused by the movement of electrons within a molecule).

All molecules have London dispersion forces between them. For non-polar molecules – e.g. H_2 , O_2 , Cl_2 – they're the only type of intermolecular forces between molecules.



London dispersion forces are weaker than permanent dipole-dipole forces (when compared to comparable substances with the same or a similar number of electrons). This is because they're temporary.

3. Ion-dipole forces

Link it!

lon-dipole forces are forces of attraction between an ion and a molecule with a dipole.



What is a cation? What is an anion? (See pages ?? and ??)

Opposites attract - cations will be attracted to the partially

negative end of a polar molecule, while anions will be attracted to the partially positive end of a polar molecule (Figure 9.22). This force of attraction is an **ion-dipole force.**

lon-dipole forces play a key role in dissolving ionic compounds in polar solvents – e.g. a solution of sodium chloride (NaCl) in water. (More on this on page ??.)

The strength of ion-dipole attractions depends on (1) the size of the charge on the ion; (2) the strength of the dipole on the molecule; (3) the distance between the ion and the dipole.

9.5 Intermolecular forces and physical properties: melting and boiling points

Intermolecular forces have a significant effect on physical properties, such as the melting or boiling point of the substance. This is because **attractive forces between molecules make molecules more difficult to separate**. Think of what we discussed in Chapter 3 – the process of melting and vaporisation. Particles must gain energy in order to change from a closely packed arrangement in a solid to the more widely spaced arrangement in a liquid (and they must gain even more energy to separate far apart enough to become a gas).



If the particles have strong attractive forces between them – i.e. **strong intermolecular forces** – then molecules must gain a significant amount of heat energy in order to weaken those forces and change state. This means the compound would have **high melting and boiling points**.

If the particles have weak intermolecular forces between them, a smaller amount of energy is required. Therefore, these substances would have lower melting and boiling points.

Crack it!

The stronger the intermolecular force, the higher the boiling point.

Two key factors affect the strength of intermolecular forces:

- 1. The type of intermolecular force
- 2. The molecular mass

1. Type of intermolecular force

Hydrogen bonds are the strongest. Permanent dipole-dipole forces are next in terms of strength. London dispersion forces are the weakest. (Also, remember that intermolecular forces are found between molecules of covalent compounds, but ionic compounds have the highest boiling points of all.)



2. Molecular mass

The strength of intermolecular forces increases as the size of the molecule increases. This is because larger molecules have more electrons and can form stronger dipoles (dipoles with a greater imbalance of electrons). Stronger dipoles can induce stronger dipoles in neighbouring molecules. This increases the attraction between molecules – i.e. increases the strength of the intermolecular forces.



Example 8

List the following substances in order of increasing boiling point and justify your answer: H_2O , H_2 , HCI, O_2 .

 $List = H_2, O_2, HCI, H_2O$

Justify = the stronger the intermolecular force (IMF) = the higher the boiling point.

The strongest IMF between molecules of H₂O is hydrogen bonds.

The strongest IMF between molecules of HCl is permanent dipole-dipole forces.

The strongest IMF between molecules of H₂ and O₂ is London dispersion forces.

Hydrogen bonds are stronger than permanent dipole-dipole forces and London dispersion forces, meaning that H_2O has the highest boiling point. Permanent dipole-dipole forces are stronger than London dispersion forces, meaning that HCl has the next highest boiling point.

Both H_2 and O_2 have only London dispersion forces between their molecules. However, oxygen has a larger molecular mass than hydrogen. This allows stronger temporary dipoles to form. This leads to stronger London dispersion forces between molecules of oxygen than between molecules of hydrogen. More energy is required to overcome stronger intermolecular forces and therefore oxygen has a higher boiling point.

Test yourself!

- 1. Ammonia (NH₃), nitrogen (N₂) and hydrogen chloride (HCl) have boiling points of −85.1°C, −33.34°C and −195.8°C. Which boiling point belongs to which compound? Justify your answer.
- HL
- 2. Study Table 9.2. Explain the trend in boiling points.

| Compound | <i>M</i> _r | Boiling point (°C) |
|---------------------------|-----------------------|--------------------|
| Hydrogen, H ₂ | 2.016 | -252.9 |
| Oxygen, O ₂ | 32 | -183 |
| Chlorine, Cl ₂ | 70.9 | -34.04 |
| Bromine, Br ₂ | 159.8 | 58.8 |
| Iodine, I ₂ | 253.8 | 184.3 |

Table 9.2



Crack it!



For any two compounds that have the same IMFs between their molecules, compare the size of the molecules (larger molecule = stronger IMF = higher BP).

9.6 Intermolecular forces and physical properties: solubility

In Chapter 8 we learnt that the golden rule for solubility is 'like dissolves like'. Now that we've studied intermolecular forces, we can explain why this is the case.

Polar solute in a polar solvent

Imagine using water (polar) as a solvent to dissolve ammonia (also polar). The partial positive and negative charges on the water will be attracted to the partial positive and negative charges of the ammonia. In fact, the attractions between the water (H_2O) and ammonia (NH_3) are hydrogen bonds. The water can surround the ammonia molecules and drag them apart – i.e. dissolve them.

PROOFS



Ionic solute in a polar solvent

lonic compounds like sodium chloride dissolve in polar solvents, e.g., salt in water, because the ionic bonding in NaCl is overcome by the **strong attraction between the ions and the polar water molecules – i.e. ion-dipole forces.**

The partially negative charges of the polar molecules attract positive ions (e.g. the $O^{\delta-}$ in H_2O attracts Na⁺ in NaCl), while the partially positive charges of the polar molecules attract negative ions (e.g. the $H^{\delta+}$ in H_2O attracts Cl⁻ in NaCl).

It's these ion-dipole forces that allows the NaCl to dissolve – i.e. that allow ions to be dragged away from the crystal lattice and dispersed throughout the soution.



Non-polar solute in polar solvents

Non-polar substances have no charged ions or permanently partially charged molecules. Therefore, a polar solvent will not dissolve a non-polar solute – e.g. iodine crystals will not dissolve in water. This is because the water molecules will be more attracted to each other (they'll form hydrogen bonds with each other) than to the iodine. **The intermolecular forces between water molecules are stronger than those between water and iodine.**

Non-polar solute in non-polar solvent

A non-polar solvent will dissolve a non-polar solute because, in the absence of stronger polar attractions, the non-polar solvent and solute will be attracted to each other by London dispersion forces. Therefore, iodine crystals will dissolve in cyclohexane.



9.7 Effect of molecular shape on physical properties

The shape of its molecules determines some physical properties of the compound. For example, a molecule with intramolecular polar covalent bonds may be symmetrical – i.e. be a non-polar molecule. As a result it will have only London dispersion forces and have relatively low melting points and boiling points, as well as being insoluble in water.



) Test yourself!

- 1. Would you expect (a) methane (CH_4) , (b) HCl to dissolve in water? Justify your answer.
- 2. Name a suitable solvent to dissolve hydrogen fluoride, HF.

For more questions on the molecular shapes and intermolecular forces, please see Chapter 9 in the workbook.



LEAVING CERTIFICATE CHEMISTRY

Features of the Student Textbook

Cracking Chemistry is a carefully constructed textbook that, in appropriate detail, prompts students to question, connect and integrate the various aspects of the new course. It will empower students to develop a scientific habit of mind and a secure understanding of the core concepts and fundamental principles of chemistry. Students will be able to apply these confidently to analyse and solve problems.

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- Higher Level only content is clearly marked throughout, making it easy to distinguish between Ordinary Level & Higher Level content.
- **Calculations:** All calculations are broken down into step-by-step instructions to aid student learning.
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 - research investigations.

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- Class notes/student notes for each chapter – condensed down to the essentials.
- Stimulus material, activities and ideas for class.

These resources will be regularly updated with extra materials (worksheets, tests, revision material, and more).

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