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INTRODUCTION

This standard is all about Structure and Bonding...

Everything on this planet is made up of atoms. The same atoms and molecules make up the food we eat to the microbes covering our bodies, all of which is dictated by the same laws of chemistry. To understand how these molecules interact with each other and their surroundings requires an understanding of bonding and structure.

Join us as we expand upon the ideas and concepts covered in Level 2: Structure and Bonding.

What will you learn in this cram guide?

Kicking off this cram guide takes us right down to the atomic level. We start by looking at electron configuration, introducing the idea of electron orbitals, rather than just the electron shell. Last year was about the make-up of the atom, and this year we look at another aspect: its size. We’ll have a look at the atomic radius and what determines how big it is.

Coming back for round two will be Lewis structures and molecular shapes, except will add a few more complexities and a handful of extra molecular shapes.

The last part of this standard is thermochemistry, which looks at the energy changes and entropy changes that occur in chemical reactions.

So, take a deep breath and dive in!

A word on exam strategy.

This standard can be quite daunting at first as there is A LOT of content to cover! The good thing is that each part of this topic builds on the last, giving you one big picture in the end.

Here at StudyTime, we’re pretty much GCs (good citizens), so to help you out, we’ve made this guide in plain English as much as we can. We’ve also included a glossary for some of the key terms that you’ll need to master for your exam.

However, the language we use isn’t always something you can directly write in your exam. When this is the case, we offer a more scientific definition or explanation (in a handy blue box) underneath. These boxes are trickier to understand on your first read through, but contain language you are allowed to write in your exam. Look out for them to make sure you stay on target!
Remember, the structure of an atom involves a nucleus made up of positively-charged protons and neutral neutrons.

Orbiting the nucleus are negatively-charged electrons, which exist in electron shells around the nucleus.

In Level 1 Science and Level 2 Chemistry you will have figured out the electron configuration using the 2,8,8,2 method.

If you have a geez at the Periodic Table you’ll notice that there’s just 2 elements in the first row, 8 in the second row, 8 in the third row, and then 18 for the rest of the rows. Conveniently, this matches the number of electrons in each electron shell of these elements. (It’s almost as if somebody deliberately designed of the Periodic Table – shout-out to our main man, Dmitri Mendeleev). This explains why the basic electron configuration is 2,8,8,2 for the first 20 elements.

But, we’re going to expand on these past concepts:

⇒ First, we’ll look at the idea of electron orbitals, which will be slightly different to how we’ve talked about “electron shells” in the past.
⇒ Next, we’ll figure out how to write out the electron configuration of atoms and ions using our new method.
For those who are too lazy to write out a full electron configuration, or for those who like to waste no time, we’ll cover “shortened electron configurations”.
Finally, we’ll finish off with the exceptions to the electron configuration rules.

Electron Orbitals

It wouldn’t be Level 3 if there wasn’t a new challenge to conquer. Rather than being limited to the familiar first 20 elements, the you can expand your horizons by looking as far as Krypton, with 36 electrons.

Unfortunately, though, you need to toss aside the 2,8,8,2 electron configuration, walk away, and never look back

Although there are still electron shells (or electron levels, we can use either term) that surround the atom, the electrons in each level don’t just zip around, doing whatever they please.

Rather, try to think about them having their own place within each shell, called “orbitals”

These orbitals represent the space around the atom where the electron is most likely to be found. Each electron has a flatmate, so in each orbital home there’s 2 electrons just chilling.

There are 3 types of orbitals:

- s-orbitals
- p-orbitals
- d-orbitals

Each orbital contains a maximum of 2 electrons and each electron shell will have a number of these orbitals. A few good rules to stick to be aware of:

- The 1st electron shell just has s-orbitals, the 2nd electron shell has s- and p-orbitals and the 3rd has s-, p- AND d-orbitals.

  • In Level 3 we only look at elements up to krypton (atomic number = 36) which means you only have to worry about the s- and p-orbitals in the 4th electron shell.

- There is always 1 s-orbital in each shell.
When there are p-orbitals in a shell there is always a maximum of 3 p-orbitals that can be filled.

When there are d-orbitals in a shell there is always a maximum of 5 d-orbitals that can be filled.

1\textsuperscript{st} electron shell:

In the first electron shell, there is just a single s-orbital (1s orbital – 1 for 1\textsuperscript{st} shell) that can be filled. With 2 electrons in each orbital the maximum number of electrons in the 1\textsuperscript{st} electron shell is 2.

This is just like what we had with the 2,8,8 electron configuration – 2 electrons in the 1\textsuperscript{st} shell.

2\textsuperscript{nd} electron shell:

In the second electron shell, there is a single s-orbital (called the 2s orbital) and 3 p-orbitals (each called the 2p orbitals) which can be filled. With 2 electrons in the s-orbital and 2 in each of the 3 p-orbitals there is a maximum of 8 electrons in the 2\textsuperscript{nd} electron shell.

3\textsuperscript{rd} electron shell:

In the third electron shell, there is a single s-orbital (called the 3s orbital), 3 p-orbitals (each called 3p orbitals) and 5 d-orbitals (the 3d orbitals) which can be filled. With 2 electrons in each one there is actually a maximum of 18 electrons that can be in the 3\textsuperscript{rd} electron shell.

This is quite different to the 2,8,8,2 electron configuration we used in previous years.

Elements which have partially filled d-orbitals are known as the transition metals and include metals such as titanium, chromium and iron.

4\textsuperscript{th} electron shell:

Only the first 36 elements are assessed in Level 3 Thermochemistry which means we’re only worried about the single s-orbital (4s orbital) and 3 p-orbitals (4p orbitals) in the fourth electron shell.

(For interest only) The Periodic Table is split up into different blocks:

These blocks represent the types of electron orbitals and can tell us where the valence electrons in each element lie.
The s-block elements, which are in Groups 1 and 2, have their valence electrons in s-orbitals.
The p-block elements, which are in Groups 13 to 18, have the p-orbitals partially or fully occupied.
The d-block elements, which are in Groups 3 to 12, have the d-orbitals partially or fully occupied.

Their place in the block tells us how many electrons they have.

For example, vanadium (V) is the 3rd d-block element in the 4th period which tells us it has 3 d-orbital electrons.

STOP AND CHECK:

Turn your book over and see if you can remember:

- How electron orbitals are different to the idea of electron shells you covered in Level 2 Chemistry.
- The 3 types of electron orbitals.
- Which electron orbitals are found in each electron shell.
- How many electrons will be found in a single orbital.

Try to explain it in your own words.

Writing out the Electron Configuration

The electrons can’t just move in to wherever they like. Just like most things in chemistry, everything wants to be as low in energy as possible, so we need to fill up our shells from the bottom.
Electrons are placed in the lowest energy orbital possible

This means that when determining the electron configuration of an atom there is a particular way that they are filled up.

The 1\textsuperscript{st} electron shell orbital (the single 1s orbital) has the lowest energy which means the first two electrons are placed here. The next lowest energy are the orbitals in 2\textsuperscript{nd} electron shell, which have lower energy than the 3\textsuperscript{rd} electron shell orbitals followed by the 4\textsuperscript{th} electron shell orbitals.

What this means is that we need to fill up the 1\textsuperscript{st} electron shell before moving onto the 2\textsuperscript{nd} electron shell before moving onto the 3\textsuperscript{rd} electron shell.

The s-orbital always have lower energy than the p-orbitals in the same electron shell with d-orbitals having the highest energy.

What this means is that we need to fill up the s-orbital first before filling the p-orbitals, adding any remaining electrons to the d-orbitals last.

As always however, there is one exception to this rule. As it turns out the 4s orbital is actually lower in energy than the 3d orbital. That means as we are filling up our orbitals, when we are all finished with our 3p orbitals we have to make a slight detour to the 4s orbital before getting back to filling the 3d orbitals.

The order of the orbitals based on energy determines the electron configuration

Basically, we end up following the order: 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6}3s\textsuperscript{2}3p\textsuperscript{6}4s\textsuperscript{2}3d\textsuperscript{10}4p\textsuperscript{6}

- The large numbers in front of the letter tell us which electron shell we’re in: the 1\textsuperscript{st} electron shell, the 2\textsuperscript{nd}, 3\textsuperscript{rd} or 4\textsuperscript{th}, and so on.
- The letters relate to the electron orbitals we just met, like the s-orbital (s), p-orbital (p) and d-orbital (d).
- Those little numbers that look like exponents tell us the maximum number of electrons.

To write out the electron configuration you just need to determine the number of electrons using the Periodic Table and the fill up each orbital, starting with 1s, until you run out of electrons.
The “Diagonal Rule” can be used to determine the order of the electron configuration:

\[
\begin{align*}
1s & \quad 2s \quad 2p \\
3s & \quad 3p \quad 3d \\
4s & \quad 4p
\end{align*}
\]

1s\(^2\) 2s\(^2\) 2p\(^2\) 3s\(^2\) 3p\(^6\) 4s\(^2\) 3d\(^{10}\) 4p\(^6\)

If you write the s-orbitals in the 1\(^{\text{st}}\) column, p-orbitals in the 2\(^{\text{nd}}\) column and the d-orbitals in the 3\(^{\text{rd}}\) column, and write out which orbitals are found in each electron shell, then drawing diagonal lines tells you the order of filling up the electrons. This is a handy tool to help you with remembering to fill the 4s shell first.

What about the electron configuration for ions?

When determining the electron configuration for cations and anions you simply need to add or subtract the right number of electrons.

- For cations, you need to take away 1 electron for every positive charge.
- For anions, you need to add 1 extra electron for every negative charge.

Adding electrons for anions is easy as you fill the electrons in the same way: 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)4s\(^2\)3d\(^{10}\).

However, when removing electrons for cations things are a bit different

You always remove electrons from the shell that is furthest away from the nucleus. So, even though we fill up the 4s orbital first because it is lower in energy before moving onto the 3d orbital, when removing electrons, we take them away from the 4s orbital first as it is further away from the nucleus, and then we remove them from the 3d orbital. For example, the electron configuration for Mn is 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)4s\(^2\)3d\(^{5}\), but if the examiners ask for the manganese ion Mn\(^{2+}\), we have to remember that we take away the electrons from 4s orbital first, leaving 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d\(^5\).

STOP AND CHECK:

Turn your book over and see if you can remember:

- The order of electron orbitals from lowest energy to highest energy.
- How to determine the electron configuration for an atom.
- How to determine the electron configuration for an ion.

Try to explain it in your own words.
Exceptions to the Rule

This wouldn’t be science if there weren’t a few annoying exceptions to the rule!

The electron configurations of chromium (Cr) and copper (Cu) are a bit peculiar

- The electron configuration of chromium, Cr, is $1s^22s^22p^63s^23p^64s^13d^5$, rather than $...4s^23d^4$.
- The electron configuration of copper, Cu, is $1s^22s^22p^63s^23p^64s^13d^{10}$, rather than $...4s^23d^9$.

These exceptions are both due to half-filled orbitals and full orbitals being more stable than partially-filled orbitals

So, rather than filling the 4s orbital and then having a 3d orbital that is just one electron away from being half-filled or totally full, 1 of the electrons from 4s jumps down and chills out in the 3d, making the atom very happy and stable.

Having a half-filled or totally full d-orbital brings these atoms to a lower energy state which is what every atom craves.

We will talk about this a bit more in a later section but the main takeaway is that half filled and completely filled subshells are pretty stable.

STOP AND CHECK:

Turn your book over and see if you can remember:
- Which two atoms are exceptions to the rule when it comes to electron configurations.
- Why these two atoms are exceptions.

Quick Questions

Write out the electron configuration for the following elements:
- Calcium (Ca)
- Iron (Fe)
- Oxygen (O)
- Iron(III) ion (Fe$^{3+}$)
- Sulphide (S$^2-$).
ATOMIC RADIUS

The atomic radius is a good way of thinking about the size of atoms

The atomic radius is defined as “the distance between the nucleus and the outermost, or valence, electron/s”.

So, if you were somehow able to pull the electron a little further away, the atomic radius would increase and you would make the atom bigger.

Thankfully, this section isn’t about memorising the size of every single atom.

But you do have to understand the trends in atomic radii so that you can get given two atoms and be able to say, “that one is going to be bigger than the other one”.

There are 4 factors that influence the radius of an atom. These factors include:

1. The number of electron shells and levels
2. The number of protons (nuclear charge)
3. The number of electrons in the valence shell
4. Shielding

Trend in Atomic Radius across a Period

Remember, the periods are the rows going left and right in the Periodic Table. The first trend in atomic radius is that the atomic radius decreases going across a period, from left to right.
For example, comparing carbon and oxygen – which are both in the 2\textsuperscript{nd} period of the Periodic Table – shows that oxygen has a smaller atomic radius than carbon as it is further to the right.

The dominant factor influencing the change in atomic radius across the periodic table is the number of protons (nuclear charge).

1. Number of protons (nuclear charge)

**The number of protons increases going across a period**

The reason that electrons don’t go whizzing away through time and space is because the attraction between the negatively-charged electrons and positively-charged protons inside the nucleus.

**Remember, opposites attract!**

Squeeze some more protons into the nucleus and the attraction between protons and electrons increases, which means it is going to get stronger.

The stronger this ‘electrostatic attraction’ is, the closer the electrons are pulled in towards the nucleus. We’re not talking about the electrons clinging around the protons, they’ll just move ever so slightly towards the nucleus.

The weaker the electrostatic attraction is, the further away the electrons will be.

As we go from left to right across the periodic table, the number of protons in the nucleus increases and so the attraction between the nucleus and electrons increases, pulling the valence electrons in slightly and reducing the size of the atomic radius.
You may be thinking that the number of electrons also increases going across the period...

...and you’d be right!

Although the valence electrons are held in the valence shell by the attraction between them and the protons, the valence electrons will distance themselves from each other as much as they can due to the repulsion of like-charges.

So, the more electrons there are, the higher the repulsion will be. This would tend to increase the distance from the nucleus to the valence shells. HOWEVER, the increase in nuclear charge and therefore the increase in attraction outweighs the additional electron-electron repulsion in the valence shell when going across the period.

STOP AND CHECK:

Turn your book over and see if you can remember:

- Whether the atomic radius increases or decreases going across a period.
- What happens to the nuclear charge going across the period.
- Why the increase in electron-electron repulsion in the valence shell going across the period is not a determining factor.

Try to explain it in your own words.

Trend in Atomic Radius within a Periodic Table Group

Remember, the groups are the columns going up and down in the Periodic Table. The second trend in atomic radius is that the atomic radius increases going down a group.
For example, comparing lithium and sodium – both in Group 1 – shows that sodium has a larger atomic radius than lithium as it is further down:

![Atomic radius comparison diagram]

The dominant factors influencing the change in atomic radius going down the group in the Periodic Table are:

1. **Number of electron shells**
2. **Shielding**

**The number of electron shells increases going down a group**

These electron shells are a bit like the floors of a building as they’re basically stacked on top of one another. So, you can imagine if you have more electron shells the ‘building’ is taller, and so the atom has a larger atomic radius.

The more electron shells there are, the further the valence shell and valence electrons will be from the nucleus.
It’s important to realise that we’re just talking about overall shells, such as the 1st, 2nd and 3rd electron shells. We’re not worried about the individual orbitals, such as the 2s and 2p orbitals, as these don’t have much effect on the atomic radius since they are so close together.

As you go down a group the number of electron shells increases which puts the valence electrons at a further distance from the nucleus, and so the atomic radius increases.

**There is increased amount of shielding as you go down the group**

The valence electrons are held in position by their attraction to the nucleus. This is because the positively-charged protons in the nucleus and the negatively-charged electrons attract.

But, it’s not just the valence electrons that are attracted to the nucleus, we’ve also got the inner electrons in the lower electron shells. What happens is that these inner electrons will interfere and weaken the attraction between the nucleus and the valence electrons.

With more electrons shells as you go down a group, there is more shielding by the inner electron shells. This reduces the attraction between the nucleus and the valence electrons, letting the valence electrons drift a little further away and increasing the atomic radius.

In other words, shielding is when the inner electrons block the outer electrons from being attracted to the nucleus a little bit. Because there is decreased electrostatic attraction, the outermost electrons will be a bit further away and so the atomic radii increases going down a group.

**STOP AND CHECK:**

Turn your book over and see if you can remember:

- Whether the atomic radius increases or decreases going down a group.
- What happens to the number of electron shells when going down a group.
- Why shielding increases going down a group.

Try to explain it in your own words.

**Quick Questions**

Compare and contrast the atomic radii of the two atoms in each pair:

- Lithium (Li) and fluorine (F)
- Oxygen (O) and sulphur (S)
IONIC RADIUS

As well as comparing the atomic radii between two different atoms, you will also need to compare an atom with its corresponding ion. In this section, we’ll cover two things:

- Compare the radius of the cation with the atom it was formed from, and explain the reason for any differences.
- Compare the radius of the anion with the atom it was formed from, and explain the reason for any differences.

Radius of Cations

The radius of a cation is smaller than the radius of the corresponding atom.

Metal atoms only have a couple of valence electrons and so it’s easier just to chuck ‘em away and have the next inner electron shell be its full valence shell. By reducing the negative charges around the positively-charged nucleus, metal atoms will form cations.

Metal cations have one less electron shell/level than the metal atom and so they will have a smaller radius.

The number of protons – the nuclear charge – remains the same when an atom forms a cation since we are only changing the number of electrons. This means that we have the same number of protons pulling on fewer electrons. In other words, the same amount of electrostatic attraction is being experienced by fewer electrons and so the ‘pull’ on each individual electron is higher. Therefore, the electrons are pulled closer to the nucleus so the radius of the metal ion is smaller than the neutral atom.

STOP AND CHECK:

Turn your book over and see if you can remember:

- Whether cations have a smaller or bigger radius than the atom they were formed from.
Why cations have a different radius compared to the atom they were formed from.

Try to explain it in your own words.

**Radius of Anions**

The radius of an anion is larger than the radius of the corresponding atom.

Non-metal atoms are just a few electrons away from having a full valence shell and so they may as well scavenge for those extra few. By increasing the negative charges around the positively-charged nucleus, non-metal atoms will form anions.

**The only difference between the non-metal atom and its anion is that the anion has more electrons in the valence shell**

This increases the electron-electron repulsion and these electrons move apart from one another. This is because the more electrons there are the higher the repulsion will be, increasing the distance from the nucleus to the valence shell (and therefore increasing the radius).

The nuclear charge and the number of electron shells both remain the same. What this means is that the same amount of electrostatic attraction is having to be shared among more valence electrons. Therefore, they can’t pull as strongly on these outermost electrons.

So, anions will have a larger radius than the corresponding atom.

**STOP AND CHECK:**

Turn your book over and see if you can remember:

- Whether anions have a smaller or bigger radius than the atom they were formed from.
Which of the four factors that determine atomic radius change when an atom forms its anion. Try to explain it in your own words.

Quick Questions

- Compare and contrast the radii of the following atom-ion pairs:
- Fluorine (F) and fluoride (F\(^{-}\))
- Calcium (Ca) and the calcium ion (Ca\(^{2+}\))

ELECTRONEGATIVITY AND IONISATION ENERGY

Great! So, we’ve covered everything you will possibly want to know about atomic and ionic radii. But, why do we make you learn them? It’s really useful knowing the trends in atomic radius because you can link it to these two important properties:

1. Electronegativity
2. Ionisation energy

So, by the end of this section you should be able to explain why electronegativity increases going across the period and decreases down a group, and which kinds of atoms have higher ionisation energies.

Ionisation Energy

Ionisation energy tells us how hard it is to remove an electron from an atom

NZQA is crazy about definitions, so ionisation energy is, “the amount of energy required to remove one mole of electrons from one mole of atoms in their gaseous state”. It’s very important to use this specific wording in the exam.

Ionisation energy can be shown by the equation: \(X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}\) where ‘X’ represents any atom and ‘e\(^{-}\)’ is an electron.

Let’s break down this definition a bit more

It seems a bit weird to explicitly state that it must be in the gaseous state. This is important
because if we have a liquid or solid, energy will first go into breaking intermolecular forces and converting to gas BEFORE removing electrons from the atoms. So, you’d be measuring more than just the ionisation energy.

You can imagine if an electron is really close to the atom, there is no way the atom is going to say goodbye unless you try very hard which means putting in a lot of energy.

Looking back at what we have talked about already, we can look for factors that would mean an electron is held more tightly by the nucleus.

For example if the nuclear charge is higher then it will be harder to remove an electron because it will be more attracted to the nucleus. We already saw that as we move across the periodic table that our nuclear charge increases and so we can conclude...

**As we go across the periodic table ionisation energy increases**

If we look at the effect of adding extra electron shells, as we have already talked about, adding extra shells means more shielding from the inner electrons and electrons being further away from the nucleus.

Both of these effects have the same result, there will be less attraction between the nucleus and the outermost electrons. If there is less attraction, then those electrons won’t be held so tightly and it will be easier to pull them away.

**As we go down a group, ionisation energy decreases**

But why stop at just taking one electron off, what about taking a second one? If taking the first electron was called the first ionisation energy, then it makes sense that taking the second electron would be called second ionisation energy.

The first ionisation energy is: \( X_{(g)} \rightarrow X^{+}_{(g)} + e^- \)

The second ionisation energy is: \( X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^- \)

**The second ionisation energy is higher than the first for all atoms**

When an electron has already been removed, the cation holds onto the valence electrons more tightly than the corresponding atom. Removing an electron reduces the electron-electron repulsion in the valence shell and brings them closer to the nucleus, increasing the electrostatic attraction between the nucleus and valence electron.

By removing the first electron we have made a positive ion, trying to take the second electron would make the ion even more positive. Removing the second electron, which is now bound more tightly, will take even more energy than removing the first.
**Electronegativity**

Electronegativity is the tendency of an atom to attract bonding electrons in a covalent bond

Simply put, it’s how desirable electrons are to these atoms.

If we stop and look for a second, ionisation energy was all about how hard it was to take electrons away from atoms, and electronegativity is all about how much atoms want to hold on to their electrons.

Since these two things are essentially opposites we could imagine that they will be influenced by similar things.

If we increase the nuclear charge by going across a period then the electrons will be held more tightly by the nucleus. This means they will want to keep holding on to them.

As a result, electronegativity increases across the periodic table

As we go down a group, not only are the electrons further out and so less attracted to the nucleus, there is also extra shielding from the inner electrons and so they are held even less tightly. This means they won’t be holding on to their electrons so tightly.

So, electronegativity decreases down a group in the periodic table

**STOP AND CHECK:**

Turn your book over and see if you can remember:

- The definition of electronegativity.
- The trend for electronegativity across the periodic table.
- The trend for electronegativity down a group of the periodic table.
- Explanations for both of these trends.

Try to explain it in your own words.
Quick Questions

Explain the following observations:

- Fluorine is more electronegative than carbon.
- Cesium is considered one of the least electronegative elements on the Periodic Table.
- Oxygen has a higher ionisation energy than sulphur.
- The ionisation energy of sodium is a lot smaller than the ionisation energy of the sodium ion.
- Nitrogen has a higher ionisation energy than oxygen. (Hint: drawing out the electron configuration of these atoms would help)

Lewis Structures

Revision from Level 2 Chemistry

Lewis structures, or Lewis diagrams, show the position of atoms within a molecule and the covalent bonds that connect them.

We represent the electrons using either dots (like above) or crosses.

Covalent bonds can be shown as two electrons between atoms (like on the left) or the two electrons can be replaced with a line (like on the right).

The following steps should help you to draw any Lewis diagram:

1. For each atom in the molecule determine the number of valence electrons. Add these all up to find the total number of valence electrons in the molecule.
2. Figure out which of the atoms in the molecule is the “central atom”. This is the atom that has the most bonds required. How do we know which one this is? It is the atom that is furthest from having a full valence shell - i.e. a valence electron number furthest away from 8.
3. We have to connect all the other atoms to the central atom, so the best thing to do first is to place a covalent bond, which is represented by two valence electrons, between the central atom and each of the outer atoms.
4. Most atoms obey the Octet Rule where they must have 8 valence electrons in order to be stable. In Level 2, the exceptions to this rule are hydrogen, which only needs 2, beryllium which only needs 4, and boron, which only needs 6. So, what you want to do is add electrons around the central atom and outer atoms so that they all have full valence electrons.

5. Now, you need to check how many electrons you have allocated. You have to use all of the total number of electrons you calculated in Step 1.

6. If you have used more electrons than you started with there’s a bit of a problem. In this case, you need to form double bonds between the central atom and some of the outer atoms.

   a. If you have used 2 more electrons that what you started with you need to make an additional bond.

   b. If you have used 4 more electrons that what you started with you need to make two additional bonds etc.

But, running through an example is much more useful

Consider the molecule carbon dioxide, \( \text{CO}_2 \)

- Carbon, C, is in Group 14 of the Periodic Table and so has 4 valence electrons.
- Each oxygen, O, has 6 valence electrons.

The total number of valence electrons in the molecule is: \( 4 + 6 + 6 = 16 \).

Our central atom is going to be carbon as it is the furthest from having a full valence shell. We place carbon in the centre and place the oxygen atoms around it. Our next step is to place a single covalent bond between carbon and each of the oxygen atoms:

\[
\text{O} \quad \text{C} \quad \text{O}
\]

Great! Now it’s time to make sure each atom has a full valence shell. All of our atoms need 8 electrons in total. Carbon currently has 4 around it so we place an extra 4, while oxygens only have 2 so need 6 more.

\[
\text{X X X X X X X X}
\]

So far we have used 20 valence electrons (2 covalent bonds + 8 non-bonding pairs) which means we have used more electrons than we started with (we only started with 16). If we have used 4 extra electrons we need 2 more covalent bonds. Therefore, let’s try make a double bond between the carbon and each of the oxygen atoms:
O  x  x  C  x  x  O

Just like before we can make sure each atom has a full valence shell:

Checking again, we have used 16 valence electrons (4 covalent bonds + 4 non-bonding pairs) which means we have used all the electrons up. Looks like we’re done - that’s the Lewis structure for carbon dioxide.

Making it a Little Bit Harder: Expanding the Octet

This year we expand upon the Lewis Structures you drew last year.

One of the main changes is the idea that the Octet can be expanded

This means we can start to use atoms which can form more than 4 bonds and have more than 8 valence electrons. They have more than 8 electrons as a result of bonding.

Since none of the atoms in the second period of the Periodic Table have easy access to d-orbitals, the maximum number of electrons is 8: 2s²2p⁶. This means none of these atoms disobey the Octet Rule.

Jump to the third period, and atoms like silicon, phosphorous, sulphur and chlorine, are able to expand their octet by utilising their nearby d-orbitals.

Let’s have a look at an example:

Consider the molecule iodine pentafluoride, IF₅

Iodine, I, and fluorine, F, are in Group 17 of the Periodic Table and so have 7 valence electrons each.

The total number of valence electrons in the molecule is: 7 + (5 x 7) = 42.

Our central atom is going to be iodine. Although iodine and fluorine are equally as far away from having a full valence shell, we place iodine in the centre as it is the least electronegative. It is also common sense to have the single iodine in the centre with all the fluorine atoms surrounding it, rather than placing a fluorine in the centre.
Our next step is to place a single covalent bond between iodine and each of the fluorine atoms:

![Lewis structure](image)

Great! Now it’s time to make sure each atom has a full valence shell. The fluorine atoms need 8 electrons so we place 6 more electrons around them. We’ll leave iodine for now, as it is a bit more complex.

![Lewis structure](image)

So far, we have used 40 valence electrons (5 covalent bonds + 15 non-bonding pairs) which means we have 2 electrons left to allocate. These last 2 electrons are placed as a non-bonding, or lone, pair of electrons around the iodine:

![Lewis structure](image)

This Lewis structure shows us that iodine has 12 electrons around it. Therefore, it has an expanded octet – bigger than the normal 8 we’ve been used to.
STOP AND CHECK:

Turn your book over and see if you can remember:

- A few examples of atoms that can never disobey the Octet Rule, and why they aren’t able to.
- A few examples of atoms that can disobey the Octet Rule, and why they are able to.

Try to explain it in your own words.

Mixing Things Up: Lewis Structures of Polyatomic Ions

Polyatomic ions are molecules, made up of 2 or more atoms, that have an overall charge

These include molecules such as the hydronium ion (H₃O⁺), hydroxide ion (OH⁻) and ammonium ion (NH₄⁺).

When drawing the Lewis Structures for polyatomic ions only a few adjustments need to be made:

- Since they have a positive or negative charge overall, they either have less or more electrons. So, for each positive charge you need to remove 1 electron from the total number of valence electrons in the molecule (calculated from the valence electrons of each atom involved), and for each negative charge you need to add 1.
- You stick the Lewis Structure inside square brackets and write the overall charge outside it.

Let’s have a look at an example:

Consider the molecule hydronium ion, H₃O⁺

Oxygen, O, is in Group 16 of the Periodic Table and so has 6 valence electrons. Each hydrogen, H, has just 1 valence electron.

The total number of valence electrons in the molecule is: 6 + 1 + 1 + 1 = 9.

But! The hydronium ion has a positive charge of 1. This means that 1 electron has been removed. We remove this electron from the total number of valence electrons leaving us with 9 – 1 = 8 electrons.

Our central atom is going to be oxygen as it is the furthest from having a full valence shell. We place oxygen in the centre and place the hydrogen atoms around it.
Our next step is to place a single covalent bond between oxygen and each of the hydrogen atoms:

\[
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\]

Great! Now it's time to make sure each atom has a full valence shell. The hydrogen atoms only need 2 electrons so they're already sorted. Oxygen, however, needs 8. It only has 6 around it at the moment so we just place two more electrons above it.

\[
\begin{array}{c}
\text{H} \\
\text{X} \\
\text{X} \\
\text{O} \\
\text{H}
\end{array}
\]

So far, we have used 8 valence electrons (3 covalent bonds + 1 non-bonding pair) which means we have used them all up.

Since this is a Lewis Structure for a polyatomic ion, we need to place the structure in square brackets and show the charge of +1:

\[
\left[\begin{array}{c}
\text{H} \\
\text{X} \\
\text{X} \\
\text{O} \\
\text{H}
\end{array}\right]^+
\]

Consider another example, the nitrate ion (NO\textsubscript{3}^-):

- Oxygen, O, is in Group 16 of the Periodic Table and so each one has 6 valence electrons.
- Nitrogen, N, is in Group 15 of the Periodic Table and so has 5 valence electrons.

The total number of valence electrons in the molecule is: \((6 \times 3) + 5 = 23\).

But! The nitrate ion has a negative charge of 1. This means that 1 electron has been added. We add this electron to the total number of valence electrons giving us \(23 + 1 = 24\) electrons.

Our central atom is going to be nitrogen as it is the furthest from having a full valence shell. We place nitrogen in the centre and place the oxygen atoms around it. Our next step is to place a single covalent bond between nitrogen and each of the oxygen atoms:
Great! Now it’s time to make sure each atom has a full valence shell. The oxygen atoms need 8 electrons so each one needs an additional 6. Nitrogen also needs 8 and currently has 6 around it. Therefore, we place two more electrons above it.

So far, we have used 26 valence electrons (3 covalent bonds + 1 non-bonding pair around nitrogen + 18 electrons around the oxygen atoms) which means we have used more electrons than we started with (we only started with 24). If we have used 2 extra electrons we need 1 more covalent bond. Therefore, let’s try make a double bond between one of the oxygen atoms and the nitrogen:

Just like before we can make sure each atom has a full valence shell:

Checking again, we have used 24 valence electrons (4 covalent bonds + 16 electrons around the oxygen atoms) which means we have used all the electrons up.

So, two oxygen atoms have a single bond to nitrogen while one forms a double covalent bond.

STOP AND CHECK:

Turn your book over and see if you can remember:

- The difference between drawing a Lewis Structure for a charged and an uncharged molecule.

Try to explain it in your own words.
Quick Questions

Have a go at drawing Lewis Structures for the following:

- \( \text{NH}_4^+ \)
- \( \text{SO}_4^{2-} \)
- \( \text{PCl}_5 \)
- \( \text{ClF}_3 \)
- \( \text{CH}_4 \)

MOLECULAR SHAPES AND POLARITY

Time for a blast from the past: molecular shapes and polarity was one of the important topics covered last year in Level 2 Chemistry Structure and Bonding. If you’re a champion and remember every little detail, this section will be a breeze! If you’ve completely had a mind blank and can’t remember much, don’t worry we won’t judge, and this section will include some revision for your pleasure.

Back in Level 2, molecules came in just 5 shapes and sizes:

- Linear, bent/v-shaped, trigonal planar, trigonal pyramidal, and tetrahedral.

Back in those days you only needed to count to 4, as the molecules covered had a maximum of 4 atoms surrounding a central atom.

Now that this is Year 13 it’s time for a challenge: counting to 6

In Level 3 we are dealing with atoms which have expanded octets and can have more than 8 valence electrons. This allows some molecules to have 6 outer atoms around the central one.

This means we have some exciting new characters to add to our collection of molecular shapes: trigonal bipyramidal, see-saw, T-shaped, octahedral, square pyramidal, and square planar.
We’re going to cover:

- VSEPR Theory – what is stands for and what it means for our molecules.
- How we get each of the molecular shapes.

**VSEPR Theory**

Valence Shell Electron Pair Repulsion (VSEPR) theory can be used to predict the shapes of molecules

It sounds quite daunting, but stick with us.

Remember that, as like-charges repel, electrons want to move away from one another. As they do this, they end up in a number of different shapes - depending on how many are there to repel each other.

![Electron Pair Diagram]

In Level 3, the different shapes of molecules can be predicted by VSEPR theory, you will be determining the shapes of molecules that contain up to 7 atoms.

VSEPR theory is all about electrons. In fact, when it comes to molecular shapes they’re the only ones who matter.

The first thing to remember is that electrons like to work in pairs.

**These pairs come in two flavours:**

1. Bonding pairs (shared between two atoms and make up the covalent bonds)
2. Non-bonding (lone) pairs.

To determine the shape of a molecule you need to do some counting.
You must count the number of bonding pairs of electrons (remember, these are the covalent bonds, where double and triple covalent bonds are counted as just 1), and the number of non-bonding (lone) pairs of electrons around the central atom.

But what about everything else? At this point, you can forget about the outer atoms the central atom is bound to.

STOP AND CHECK:

Turn your book over and see if you can remember:

- How we can use VSEPR Theory to figure out molecular shapes.
- The two types of electron pairs around an atom in a molecule.

Try to explain it in your own words.

The Molecular Shapes

Before we start this section it’s important to cover how we are going to draw them

Because these molecules shapes are three-dimensional, we have a bit of a problem when we try to draw them out on our two-dimensional paper.

Luckily, there are some special conventions which come to the rescue and show how to draw molecular shapes on paper:

- A solid line (like on a lewis diagram) represents a bond running along the paper.
- A dashed line represents a bond going into the paper.
- A ‘wedge’ shape represents a bond coming out of the paper - and towards the viewer.

These may seem a little odd to begin with, but the more you draw them, the more you will get used to them!

Ultimately, the shape of the molecule comes down to the repulsion of negative charges around the central atom.
This repulsion comes from bonding pairs of electrons in the covalent bonds between atoms and the non-bonding (lone) pairs of electrons around the central atom. As “like charges repel”, these negative charges try to get as far away from each other possible.

The bonding and non-bonding pairs of electrons around the central atom are referred to as “areas/regions of electron density”. Basically, this just tells us there are separate areas where electrons lie, and the arrangement of these areas gives rise to the molecular shapes. They are also called “areas/regions of negative charge” since electrons are negatively-charged.

Depending on the combination of bonding and non-bonding pairs of electrons, we get left with different arrangements

In this guide, we will first run through the molecular shapes covered in Level 2 Structure and Bonding, which are the molecules containing 2, 3 and 4 areas of electron density.

There are 6 new molecular shapes in Level 3 Thermochemistry - so not too many - and these all have either 5 or 6 areas of electron density around the central atom.

2 Areas of Electron Density:

The simplest molecular shape contains just 2 areas of electron density. Imagine a central atom with two outer atoms joining onto it. The regions of electron density repel and try to get as far away from each other as possible. This ends up producing something that looks like a line.

This is the linear molecular shape - which, as the name suggests, just places the central atom and two other atoms in a line. Because we know from maths that angles on a straight line add to 180°, we know the angles between each bond will all be 180°.

When a molecule is composed of two atoms - such as HCl and O₂ - the molecular shape is also considered linear. However, there may be more than 2 areas of electron density as each atom will need to have a full valence shell.

3 Areas of Electron Density:

The simplest molecule with 3 areas of electron density contains 3 bonding pairs
of electrons and no non-bonding pairs. If you have 3 negatively-charged covalent bonds they will all repel one another. You can imagine that if they all exist in the same plane - i.e. ‘flat on the page’ - they will be evenly distributed around the central atom in a circle.

This results in the trigonal planar shape with bond angles of 120°

Let’s swap out one of the bonding pairs of electrons with a lone pair around the central atom. First, imagine having these two bonding pairs arranged in a linear shape, as far away from one another as possible. If we bring in a lone pair of electrons, this new group repels and pushes the two bonded pairs of electrons down and closer together, resulting in what is called a ‘bent’ or ‘v-shaped’ molecule.

Because they sit closer to the central atom than the bonded atoms, the lone pair actually exerts slightly more repulsion on the two bonded pairs we had earlier. This means that the bond angles in the ‘bent’ shape are just less than 120° even though they contain 3 areas of electron density like trigonal planar molecules.

4 Areas of Electron Density:

The simplest molecule with 4 areas of electron density contains 4 bonding pairs of electrons and no non-bonding pairs. It would be understandable to think that these 4 bondings pairs would arrange themselves in the same plane, 90° apart from one another. However, they can get further away from each other by arranging themselves in a 3-dimensional structure:
This is the **tetrahedral** shape where the bonding pairs of electrons are at angles of 109.5° from each other. Two of the bonds will be in the same plane, will one bond goes ‘out of the page’ and one bond goes ‘into the page’, shown by the wedge and dashed line, respectively.

If we swap out one of the bonding pairs of electrons with a lone pair - i.e. 3 bonding pairs and 1 non-bonding pair of electrons - we produce a shape that looks a lot like tetrahedral except the bond going straight up is replaced with a lone pair. This is called the **trigonal pyramidal** shape.

![Trigonal Pyramidal](image)

This is called trigonal pyramidal because the 3 bonding pairs of electrons look like the 3 edges of a triangular based pyramid.

Remember, because they sit closer to the central atom than the bonded atoms, the lone pair actually exerts slightly more repulsion on the three bonded pairs we had earlier. This means that the bond angles in the trigonal pyramidal shape are just less than 109.5° even though they contain 4 areas of electron density like tetrahedral molecules.

The last shape with 4 areas of electron density is ‘**bent**’ or ‘v-shaped’. No, that isn’t a typo - the bent shape can either have 2 bonding and 1 non-bonding pair of electrons, or 2 bonding and 2 non-bonding pairs of electrons. Both have the same shape, but if we add an additional lone pair there is extra repulsion which pushes the bonding pairs even closer together. It also has a smaller bonding angle than tetrahedral for the same reasons as with trigonal pyramidal shapes.

![Bent](image)

5 Areas of Electron Density:

Now, it’s time to introduce the new molecular shapes.

The first one is the simplest shape with 5 areas of electron density: 5 bonding pairs of
electrons and no non-bonding pairs. This shape is **trigonal bipyramidal**. It is a bit of an odd shape because it looks like it contains trigonal planar and linear in the same shape:

3 of the bonding pairs of electrons are in the same plane, with a bonding angle of 120°.

The other 2 bonding pairs of electrons are in different planes, with the angle between them 90°.

Keep four of the bonding pairs of electrons but chuck on a lone pair of electrons and you end up with the **see-saw** shape:

You can see that this shape looks very similar to trigonal bipyramidal, except one of the bonds in the plane of the page (from the triangle) is replaced with that lone pair of electrons.

We get similar bonding angles as we did with trigonal bipyramidal.

You may be wondering why we take one of the atoms from the triangle instead of one of the ones from above or below. The answer is because of repulsion! The lone pair is further away from the other groups by being here than anywhere else.

We can replace a second bonding pair of electrons with another lone pair of electrons around the central atom. Let’s start with the trigonal bipyramidal shape. What happens is that the 3 bonding pairs of electrons are arranged in the same plane approximately 90° from one another, while the lone pairs will be into and out of the page:
The resulting shape is called **T-shaped**:

![T-shaped diagram](image)

Since we have a minimum of 2 bonding pairs of electrons around the central atom, we can replace yet another bonding pair with a lone pair of electrons. With 2 bonding pairs and 3 non-bonding pairs of electrons we end up with the **linear** shape again.

Trigonal bipyramidal was said to be a combination of trigonal planar and linear in the same shape. If we have 3 non-bonding pairs of electrons they get arranged in the trigonal planar shape, leaving the 2 bonding pairs to be in the linear arrangement.

![Trigonal bipyramidal diagram](image)

**6 Areas of Electron Density:**

Our last 3 shapes have a total of 6 regions of electron density, or negative charge.

As always, let’s begin with the shape that has all regions of electron density as bonding pairs of electrons. This first shape is the octahedral molecule. It doesn’t seem to make a lot of sense at first calling it **octahedral** when “oct-” means 8, but it refers to the 3-dimensional shape the molecule forms: an octahedron which has 8 faces.

Arranging the 6 bonds equally around the central atom due to electron-electron repulsion gives bonding angles of 90°.

![Octahedral diagram](image)
Replacing one of the bonding pairs of electrons with a lone pair gives us a similar shape to octahedral. This is the **square pyramidal** or **square based pyramid** shape:

![Square Pyramidal Shape](image)

Our final molecular shape is composed of 4 bonding pairs of electrons and 2 non-bonding pairs of electrons. This is the **square planar** shape. When you think “square” think 4 bonding pairs of electrons, and when you think “planar” think that these 4 bonds are in the same plane. The bonding angle will therefore be 90°.

The square planar is based off the octahedral shape. In order to minimise repulsion, the non-bonding pairs of electrons go on opposite sides of the central atom:

![Square Planar Shape](image)

The following table gives the list of molecular shapes that you need to know for Level 3 Chemistry:

<table>
<thead>
<tr>
<th>Areas of Electron Density</th>
<th>Bonding Pairs</th>
<th>Non-bonding Pairs</th>
<th>Molecular Shape Name</th>
<th>Bonding Angle</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>Linear</td>
<td>180°</td>
<td>O = C = O</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0</td>
<td>Trigonal Planar</td>
<td>120°</td>
<td>S = O</td>
</tr>
<tr>
<td>Z</td>
<td>X</td>
<td>Y</td>
<td>Molecular Structure</td>
<td>Bond Angles</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---------------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>Bent/V-shaped</td>
<td>&lt; 120°</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0</td>
<td>Tetrahedral</td>
<td>109.5°</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1</td>
<td>Trigonal Pyramidal</td>
<td>&lt; 109.5°</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>Bent/V-shaped</td>
<td>&lt;&lt; 120°</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0</td>
<td>Trigonal Bipyramidal</td>
<td>90°, 120° and 180°</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>1</td>
<td>See-saw</td>
<td>180°, 120° and 90°</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>2</td>
<td>T-shaped</td>
<td>90° and 180°</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>3</td>
<td>Linear</td>
<td>180°</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0</td>
<td>Octahedral</td>
<td>90° and 180°</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>1</td>
<td>Square Pyramidal</td>
<td>90° and 180°</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>2</td>
<td>Square Planar</td>
<td>90°</td>
<td></td>
</tr>
</tbody>
</table>
Polarity

Chemical bonds and molecules can be polar or non-polar

Here, polarity just means the “separation of charge”. Polarity can apply to both molecules and individual bonds - and it’s important to know the difference between them.

- Polar molecules will have a positively-charged region and a negatively-charged region, while non-polar molecules will have no real charge difference across the molecule.

- In a polar covalent bond, one of the atoms ends up with a partial positive charge while the other a partial negative charge. In a non-polar covalent bond, there is no difference in charge.

Let’s have a look at how non-polar covalent bonds form:

Take two identical non-metal atoms - say two hydrogen atoms. They both have 1 valence electron but need 2 in total to be stable. Sharing them sounds like a great idea.

Even though they want to share, both hydrogen atoms secretly want the electrons to themselves. This attraction to bonding electrons is the electronegativity which we talked about earlier on! Remember, if you go down a group in the Periodic Table the electronegativity decreases, but if you go across a period (from left to right), the electronegativity increases.
This means that the least electronegative atoms are caesium and francium, whereas the most electronegative atoms are nitrogen, oxygen and fluorine. (We ignore the Noble Gases since they are unreactive).

So, there is a bit of tug of war going on. But, because both atoms are the same, they pull on these bonding electrons with the same amount of strength. This means that bonding electrons will happily zip around the nucleus of both hydrogen atoms, spending the same amount of time around each one.

This means there is no real difference in charge between these two atoms, so their covalent bond is non-polar.

A non-polar bond is easy to picture, because it will always be symmetrical!

So, how about a polar bond?

Take two different non-metal atoms - say a hydrogen atom a chlorine atom.

Chlorine has 7 valence electrons but needs 8, while hydrogen has 1 but needs 2. So, they both decide to share 1 electron.

Since chlorine is more electronegative than hydrogen, chlorine has a larger tendency to attract the bonding electrons. This means that bonding electrons are attracted more to the chlorine than they are to the hydrogen.
Although the 2 bonding electrons are shared, chlorine pulls more tightly on them. We end up with the bonding electrons spending more time around chlorine nucleus than with hydrogen.

\[
\delta^+ \quad H \quad Cl \quad \delta^-
\]

**Partial charges**

Since chlorine isn’t being fair and is being greedy instead (and because electrons are negatively charged), it ends up being slightly more negative than hydrogen.

When this happens, we say that chlorine has a partial negative charge, which is represented by the “delta negative” symbol (\(\delta^\text{-}\)).

As this happens, it makes sense that hydrogen ends up with a partial positive charge, which is represented by the “delta positive” symbol (\(\delta^+\)).

**This kind of covalent bond is polar**

That’s because there is a separation of electrical charge. Since it is polar it creates what is called a “dipole”.

The letters ‘di-’ mean ‘two’ and ‘pole’ means one end - so a dipole is a way of describing the separation of electrical charge that we just talked about.
When it comes to molecules, things aren’t so clear cut

There could be many positive and negative charges present, but they may be arranged in such a way that everything gets cancelled out. When this happens we end up with a non-polar molecule.

\[
\text{Cl}_4 \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\delta^- \quad \delta^+ \quad \delta^- \quad \delta^-
\]

\(\text{CCl}_4\) is a non-polar molecule even though there are partially-negative chlorine atoms and a partially-positive carbon atom. Since the chlorine atoms are arranged symmetrically around the carbon there is no overall separation of charge.

Polar molecules tend to have charged regions sticking out from the rest of the molecule; so, if this region is more positively-charged, the rest of the molecule is negatively-charged by comparison.

\[
\text{O} \quad \text{H} \quad \text{H} \\
\delta^- \quad \delta^+ \quad \delta^+
\]

Water is a good example of a polar molecule. There are partially-positive hydrogen atoms and a partially-negative oxygen atom due to electronegativity differences. Since there is an asymmetrical shape the molecule has a region of partial positive charge and a region of partial negative charge on the other end. Therefore, we have a polar molecule.

Let’s start things off simply by assuming there is only one type of atom around the central atom in the molecule

Here, the polarity of the molecule depends upon the symmetry of the molecule’s shape. With the new, slightly-more-complicated shapes it can be get pretty gnarly trying to work out whether its symmetrical or not. So just have a geez at the table below:
Symmetrical Molecule Shapes | Asymmetrical Molecule Shapes

<table>
<thead>
<tr>
<th>Linear</th>
<th>Bent/V-shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal planar</td>
<td>Trigonal pyramidal</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>See-saw</td>
</tr>
<tr>
<td>Trigonal bipyramidal</td>
<td>T-shaped</td>
</tr>
<tr>
<td>Square planar</td>
<td>Square pyramidal</td>
</tr>
<tr>
<td>Octahedral</td>
<td></td>
</tr>
</tbody>
</table>

⇒ The general rule of thumb is that all the symmetrical shapes have no non-bonding pairs of electrons around the central atom! This should make things a bit easier to remember. The exception is square planar which does have non-bonding pairs.

Even when the bonds around the central atom are polar, if the molecule has a symmetrical shape the polar bonds cancel out, leaving the molecule non-polar overall. It’s all down to symmetry!

On the other hand, when the molecule is asymmetrical, this cancelling of polar bonds doesn’t occur. This leaves the molecule polar instead.
But what about when there is more than one type of atom around the central atom?

In this case the molecule will ALWAYS be polar, regardless of the molecule’s shape and symmetry. This is because the different atoms, with different electronegativity values, produce different strength dipoles. These different dipoles will not be cancelled out even when the molecular shape is symmetrical.

STOP AND CHECK:

Turn your book over and see if you can remember:

- What helps us to determine polarity.
- The importance of symmetry when it comes to polarity.
- Why molecules with more than one type of atom around the central atom are always polar no matter what.

Try to explain it in your own words.

Quick Questions

Which of the following molecules are polar and which are non-polar:

- SF₆
- CH₃Cl
- XeF₄
- IF₅

Make sure you explaining why by talking about the molecular shape of each.
INTERMOLECULAR FORCES

Level 2 Chemistry was the good life. Back then you could just get away with the vague statement that all molecules are held together by weak intermolecular forces. While this is 100% correct, this simplicity isn’t going to fly around here!

There are in fact three different types of intermolecular forces:

1. Instantaneous dipole forces (dispersion forces or van der Waals forces, at level 3 these are all interchangeable so no worries there)
2. Permanent dipole forces (or dipole-dipole interactions)
3. Hydrogen bonding

Your mission is to be able to look at a molecule and be able to list the different types of intermolecular forces that can occur between that individual molecule and neighbouring ones, and explain why.

Instantaneous Dipole Forces

Instantaneous dipole forces (or dispersion forces, if you can’t be bothered saying an extra word) are the least exciting as they occur between each and every molecule, no matter how big or how small.

Picture a molecule: there are atoms covalently bonded to one another to form one unit

Each atom has electrons around it, so you can almost imagine the whole molecule is littered with electrons.

The electrons like to be active and they’re constantly moving around.

This means that at any point in time, these electrons won’t be evenly distributed throughout the whole molecule

This leads to a partial negative electric charge, where there are more electrons and a partial positive electric charge on the opposite side, where there are less electrons.

Now that the once-non-polar molecule has charged ends, it thinks it’s better than all of its neighbours. It now believes that being charged is the only way to live. It goes around and forces (or induces) neighbouring molecules to also have charged ends, and it does this through electron-electron repulsion.
Now that all these molecules have positively-charged and negatively-charged regions, they can interact with each other through the attraction between opposite charges.

This is exactly how instantaneous dipole forces form and how they hold molecules together. And since all molecules contain electrons, all molecules can form dispersion forces.

When the molecules increase in size the dispersion forces get a whole lot stronger.

That’s because when there are more electrons, the positive and negative charges can be stronger, and the uneven electron distribution leading to charged ends happens more often. So, the larger the molecule, the greater the dispersive forces.

But overall, these dispersion forces are actually pretty weak.

Since the electrons are always zipping around, the charge at a given point around the molecule is constantly changing which means these dispersion forces are constantly being formed and broken, being formed and broken, and so on.

STOP AND CHECK:

Turn your book over and see if you can remember:

-floating The types of molecules that are held together by instantaneous dipole forces.
Why instantaneous dipole forces get stronger as the molecular size increases.
How non-polar molecules, or uncharged molecules, can be attracted to one another.

Try to explain it in your own words.

### Permanent Dipole Forces

Non-polar molecules only get a taste of the charged life. It’s only when there is that instantaneous uneven distribution of electrons that positive and negative charges form. However...

**Polar molecules always have charged ends**

What this means is there is a permanent positively-charged region and a permanent negatively-charged region, no matter what the electrons get up to.

**Permanent dipole forces occur between polar molecules**

In permanent dipole forces, the positively-charged regions are attracted to the negatively-charged regions of a neighbouring molecule, and vice versa. That’s because “unlike charges attract”.

Since permanent dipole forces are always there between polar molecules, they’re a lot stronger than the instantaneous dipole forces. This explains why polar molecules can hold off melting until higher temperatures.

⇒ It is very important to remember that these polar molecules also have instantaneous dipole forces, as well as permanent dipole forces. It’s just that the instantaneous dipole forces are much weaker than the permanent dipole forces.
STOP AND CHECK:

Turn your book over and see if you can remember:

- Whether non-polar or polar molecules are held together by permanent dipole forces.
- The difference between permanent dipole forces and instantaneous dipole forces.

Try to explain it in your own words.

Hydrogen Bonding

Hydrogen bonds are for the crème de la crème of the molecular world.

**Only molecules with certain types of atoms will make the cut**

The molecule needs to contain a hydrogen atom attached to either a fluorine, oxygen or nitrogen atom.

That’s because these special group of atoms are really, really electronegative.

Electronegative atoms don’t like to share bonding electrons with other atoms (who are less electronegative) when a covalent bond is formed. But when fluorine, oxygen or nitrogen covalently bond with hydrogen, they take it to a whole new level.

**The electronegative atom hogs the electrons so that the hydrogen is pretty much just a proton**

Hydrogen bonding occurs when this proton bonds to negatively-charged regions of neighbouring molecules due to the attractiveness of “unlike charges”.

Hydrogen bonds are the strongest of all the intermolecular forces, giving the molecules that partake in hydrogen bonding high melting and boiling points.
STOP AND CHECK:

Turn your book over and see if you can remember:
- What atoms a molecule needs to be able to use hydrogen bonding.
- How hydrogen bonds differ from permanent dipole forces.

Try to explain it in your own words.

Melting and Boiling Points

All substances can exist as gases, liquids and solids at different temperatures and pressures

For example, water molecules exist as a solid (ice) at temperatures below 0°C. As we turn up the dial and get things heated up, the ice melts and forms liquid water. If we want to take things to the next level, we can boil the water up to 100°C and produce a gaseous form of water (steam).

When the temperature increases the amount of heat energy increases

This is used to break any bonds holding the solid or liquid together.

As a general rule, the stronger the force of attraction the more heat energy is required to break it.

The melting point is the temperature at which solid melts into a liquid, while the boiling point tells us what temperature is needed to boil that liquid into a gas.

When thinking about the strength of the force of attraction we need to think about the strength of the intermolecular forces that are holding the molecule together.
Remember, we have our 3 types of intermolecular forces:

1. Instantaneous dipole forces
2. Permanent dipole forces
3. Hydrogen bonding

**These intermolecular forces differ in strength.**

Instantaneous dipole forces are the weakest intermolecular force. Permanent dipole forces are much stronger but not as strong as hydrogen bonds which are the strongest intermolecular forces. This means that polar molecules will generally have higher melting/boiling points than non-polar molecules, since polar molecules are held together by both instantaneous dipole forces and the much stronger permanent dipole forces.

**It is also important to consider the size of the molecule.**

Although non-polar molecules are all held together by instantaneous dipole forces they don’t all have the same melting and boiling points. That’s because the strength of the instantaneous dipole forces differ. Remember, the bigger the molecule is, the more electrons it will have and the stronger the forces will be.

**So, how should you approach questions about comparing melting/boiling points?**

The first step is to determine which molecules are polar and which are non-polar. Generally they will have a similar molecular mass so it will be safe to say that the polar molecules will have higher melting and boiling points than the non-polar ones.

If you are comparing two non-polar molecules you simply need to compare their molecular masses. The one that has the higher molecular mass will have the higher melting/boiling point.

Always look out for molecular that will be involved in hydrogen bonding. Remember, these molecules will have fluorine, oxygen or nitrogen covalently bonded to a hydrogen atom. Hydrogen-bonding molecules will usually have the highest melting and boiling points because hydrogen bonding is the strongest intermolecular force.

**STOP AND CHECK:**

Turn your book over and see if you can remember:

- How solids are converted to liquids and how liquids are converted to gases.
What the melting and boiling points tell us about the molecule.

The relationship between melting/boiling point and the intermolecular forces.

Which intermolecular forces are the weakest and which are the strongest.

Try to explain it in your own words.

Quick Questions

Order the following molecules from highest to lowest melting/boiling point justifying your choices:

- Nitrogen ($N_2$)
- Nitric oxide (NO)
- Ammonia ($NH_3$)

Thermochemistry

There are so many chemical reactions that can occur, with almost endless different products formed from heaps of different reactants. But they all have two things in common:

1. They all involve bonds breaking and/or bonds forming.
2. They all involve a change in energy.

From just these two points this topic blows up and covers:

- Enthalpy, including a revisit of endothermic and exothermic reactions.
- Heat and Specific Heat
- Entropy – what is it, and what are positive and negative entropy changes.
- Spontaneous and non-spontaneous reactions.
- Hess’s Law.

Enthalpy

Enthalpy is back for more. First introduced last year in Level 2 Structure and Bonding, enthalpy changes describe the heat transfer that occurs in a chemical reaction.

All molecules possess a specific amount of energy

This specific amount of energy is referred to by a special term called ‘enthalpy’, which is stored within the chemical bonds inside the molecule.
Energy is required to break these bonds and energy is released when these bonds are formed.

Therefore, in a chemical reaction, the energy of the reactants will be different to the energy of the products, as bonds are broken and formed to make different molecules - each with different amounts of energy.

**This change in energy is referred to as the enthalpy change of reaction**

One way to calculate the enthalpy change of a reaction is to take the energy required to break all bonds and subtract the energy released when all bonds are formed. The enthalpy change of a reaction has the symbol, \( \Delta \text{H} \). Let’s break this symbol down:

- The triangle, “delta”, means “change in”. Remember, we’re not just looking at the enthalpy of a reaction, it is the enthalpy change of a reaction.
- The small “r” just stands for “reaction”.
- Finally, “H” is the symbol for enthalpy.

**Remember, energy is conserved and cannot be created or destroyed**

If energy is required by the chemical reaction, it needs to come from somewhere else, and if energy is released by the reaction it needs to go somewhere.

The actual chemical reaction, containing all the reactants and products, is called the “system”. The “surroundings” is everything that’s not the system; the rest of the universe!
Energy can come from the surroundings or energy can be released into the surroundings.

There are two types of enthalpy change:

1. An exothermic reaction involves the release of heat from the system to the surroundings. The reactants have more energy than the products, and so this is a process with a negative enthalpy change (-\(\Delta H\)).

2. An endothermic reaction involves the input of heat/energy from the surroundings into the system. The products have more energy than the reactants, and so this is a process with a positive enthalpy change (+\(\Delta H\)).

Using the same core principles we can look at specific types of enthalpy changes.

All enthalpy changes are measured under standard conditions

If a reaction occurs under standard conditions, it just means we make sure the temperature is 25°C and the pressure is 1 atmosphere (101 kPa). We need to make sure all measurements are under the same conditions to make accurate comparisons, and any differences aren’t due to different environmental conditions.

If a reaction is under standard conditions we chuck on a degree sign after the enthalpy change symbol.

⇒ For example, the enthalpy change of reaction under standard conditions is \(\Delta_r H^\circ\), but \(\Delta_r H\) indicates the reaction is not under standard conditions.
The enthalpy of formation, combustion, vaporisation, fusion and sublimation - which you will soon come across - are all under standard conditions so will all need that degree sign in their symbols.

**Enthalpy of Formation**

The enthalpy of formation ($\Delta_f H^\circ$) is the energy required to produce 1 mole of product from its constituent atoms in their standard states at standard conditions.

These definitions are EXACTLY what you need to write in the exam, so make sure you’re familiar with them! Each component of the definition is super duper important so can’t be left out.

Hang on! We’ve heard of “standard conditions”, but what are “standard states”?

This is the state of matter (e.g. solid, liquid or gas) that the substance exists in during standard conditions. To put it more simply, it is the state of matter it exists in at room temperature.

E.g. the standard state iron is solid, the standard state of water is liquid, and the standard state of oxygen is gas.

When it comes to the standard states of the elements there are a few rules that will help you out:

- Only two elements are liquids at standard conditions: bromine and mercury.
- All of the Noble Gases (the elements in Group 18) as well as fluorine, chlorine, hydrogen, oxygen and nitrogen are gases at room temperature.
- The standard states of all other elements is solid.

But some elements do not exist as individual atoms in their standard state. All of the gases, other than the Noble Gases, exist as, what we call, diatomic molecules. These are molecules composed of two atoms, which in this case are identical.

So, oxygen exists as $O_2$ - two oxygen atoms bonded together - same with nitrogen ($N_2$), hydrogen ($H_2$), fluorine ($F_2$), chlorine ($Cl_2$) and bromine ($Br_2$).

**Back to enthalpy of formation**

The definition we gave you before is something that you need to be able to spit out as this is what the markers are looking for.
Let’s break it down though. We have a molecule or substance of interest. This molecule is made up of different types of atoms. The formation reaction takes these individual atoms in their standard state and reacts them together to produce our molecule or substance of interest.

⇒ Enthalpy of formation is basically the enthalpy change when one mole of stuff is formed.

The enthalpy of formation of elements is by definition 0. This is because elements are already in their standard states and they are made from a combination of different elements.

Let’s have a look at the enthalpy of formation of water:

Water has the symbol, H\(_2\)O, which tells us that it is made up of hydrogen and oxygen atoms.

⇒ Hydrogen exists as a diatomic gas: H\(_2\)(g)
⇒ Oxygen exists as a diatomic gas: O\(_2\)(g)

Remember, formation involves producing a single mole of product. Therefore, we are producing 1 mole of H\(_2\)O\(_l\)). In order to balance the equation we are going to need to use half mole ratios in the reactants.

Formation of water: H\(_2\)(g) + ½O\(_2\)(g) → H\(_2\)O\(_l\)

⇒ We don’t usually use half mole ratios, but for formation reactions it’s definitely okay to make sure the product is only 1 mole!

Let’s have a look at the enthalpy of formation of ethanol:

Ethanol (CH\(_3\)CH\(_2\)OH) is made up of carbon, hydrogen and oxygen atoms.

⇒ Carbon exists as a solid in its standard state: C\(_s\)
⇒ Hydrogen and oxygen both exist as diatomic gases: H\(_2\)(g) and O\(_2\)(g).
⇒ Ethanol is a liquid at room temperature.

Remember, formation involves producing a single mole of product, so just 1 mole of ethanol. In order to balance the equation we will need 2 moles of C\(_s\), 3 moles of H\(_2\)(g) and just half a mole of O\(_2\)(g) since ethanol only has 1 oxygen atom per molecule.

Formation of ethanol: 2C\(_s\) + 3H\(_2\)(g) + ½O\(_2\)(g) → CH\(_3\)CH\(_2\)OH\(_l\)
Enthalpy of Combustion

The enthalpy of combustion ($\Delta_c H^\circ$) is the energy required to react 1 mole of product with oxygen under standard conditions.

It is sometimes called “the enthalpy change when 1 mole of stuff is burnt”. But keep this is as your own personal definition as you will need to write the proper one above in the exam.

Unlike the enthalpy of formation, which involved making 1 mole of product, here we are combusting 1 mole of reactant.

So, what happens in a combustion reaction?

The enthalpy of combustion refers to the complete combustion of a molecule or compound. In complete combustion we simply react something with oxygen. Generally in complete combustion, carbon dioxide ($CO_2$) and water ($H_2O$) are produced - both $CO_2$ and $H_2O$ will be in their gaseous state.

A good example is the combustion of methane: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

When it comes to balancing combustion equations, the first thing you want to do is produce a $CO_2$ molecule for every carbon in the combusting reactant.

⇒ So, if there are 3 carbon atoms in the reactant, 3 moles of $CO_2$ will be made.

Most of the combustion reactions involve burning hydrocarbons. Therefore, the reactants will also contain hydrogen. For every 2 hydrogen atoms in the reactant, 1 mole of $H_2O$ needs to be made.

Then you can finish off by balancing oxygen.

What if the reactant doesn’t have any carbon atoms?

Although carbon dioxide and water are typically made, a combustion reaction is defined as reacting something with oxygen ($O_2$) - $CO_2$ and $H_2O$ don’t always have to be made.

For example, the combustion of sulfur looks like: $S(s) + O_2(g) \rightarrow SO_2(g)$

⇒ Note: remember, sulfur is a solid at standard conditions.

Notice, since we don’t have any carbons no carbon dioxide is produced. Instead, we
add the oxygen to sulfur to produce SO$_2$.

Water is only produced when hydrogen atoms are present in the compound being combusted.

**Enthalpy Changes associated with Phase Changes:**

There are 3 specific enthalpy changes associated with phase changes that you need to know:

- Enthalpy of vaporisation ($\Delta_{\text{vap}}H^\circ$)
- Enthalpy of fusion ($\Delta_{\text{fus}}H^\circ$)
- Enthalpy of sublimation ($\Delta_{\text{sub}}H^\circ$)

**Vaporisation is the conversion of a liquid to a gas**

Vapor really has a more specific definition, but you can simply think of it as a gas. Therefore, the enthalpy of vaporisation is the amount of energy required to convert a liquid into a gas. It occurs at standard conditions, so to be more precise, the enthalpy of vaporisation is the amount of energy required to convert 1 mole of a liquid into 1 mole of gas at the boiling point.

For example, the vaporisation of water looks like: $\text{H}_2\text{O}_\text{(l)} \rightarrow \text{H}_2\text{O}_\text{(g)}$

Notice, 1 mole of water on both sides of the reaction - the only thing that changes is the state of matter. This will be the same for any vaporisation reaction.

**Enthalpy of vaporisation is always positive**

In order to convert a liquid to a gas bonds must be broken. In order to break these bonds, energy must be used.

If we are taking energy from the surroundings and putting them into the system (the reaction), then this is an endothermic reaction with a positive enthalpy change: the products are of higher energy than the reactants.

The stronger the bonds are, the more energy needs to be put into the system and the bigger the enthalpy of vaporisation will be.

- E.g. helium has a very low enthalpy of vaporisation (0.0845 kJmol$^{-1}$) since it is only held together by instantaneous dipole forces, while water has a fairly high enthalpy of vaporisation (40.8 kJmol$^{-1}$) since it is held together by the much stronger permanent dipole forces and hydrogen bonding, as well as instantaneous dipole forces.
Fusion is the conversion of a solid to liquid

Therefore, the enthalpy of fusion is the amount of energy required to convert 1 mole of a solid to 1 mole of the same compound in its liquid state at the melting point.

For example, the fusion of water looks like: $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$

**Enthalpy of fusion is always positive**

- There are a few weird exceptions but at Level 3 all enthalpy of fusions will be positive.

Just like with vaporisation, fusion involves breaking intermolecular forces to convert a solid into a gas. Therefore, energy needs to be put into the system from the surroundings and so we’ve got a positive enthalpy change.

Sublimation is the conversion of a solid to a gas

Therefore, the enthalpy of sublimation is the amount of energy required to convert 1 mole of a solid to 1 mole of the same compound in its gaseous state at the sublimation point.

In order to convert a solid to a gas, all the intermolecular forces must be broken and so energy is required. This is similar to the vaporisation and fusion reactions which were also positive enthalpy changes.

The enthalpy of sublimation will also be larger than the enthalpy of fusion and the enthalpy of vaporisation for the same substance. This makes sense as we are basically doing both steps at once so quite a bit of energy will be required.

For example, the sublimation of water looks like: $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g)$

**STOP AND CHECK:**

Turn your book over and see if you can remember:

- What is meant by the “system” and the “surroundings”.
- The energy diagram for both an endothermic and exothermic reaction.
- The energy transfer that takes place in both an endothermic and exothermic reaction.
- What is meant by the terms “standard conditions” and “standard states”.
- The definitions of the following:
  - Enthalpy of formation.
• Enthalpy of combustion.
• Enthalpy of vaporisation.
• Enthalpy of fusion.
• Enthalpy of sublimation.

Try to explain it in your own words.

Also, have a go at writing out the reactions which represent:

- The enthalpy of formation of ethanoic acid (CH$_3$COOH)
- The enthalpy of formation of ammonia (NH$_3$)
- The enthalpy of combustion of ethanol (CH$_3$CH$_2$OH)
- The enthalpy of combustion of carbon (C)
- The enthalpy of sublimation of carbon dioxide (CO$_2$)

Enthalpy Calculations Revision

The enthalpy change of reaction, which is measured in kilojoules per mole, or kJmol$^{-1}$, is useful as it allows us to calculate the amount of heat released by a particular amount of substance. This involves multiplying the $\Delta_r H$ by the number of moles used in the reaction.

Before we can do that, we need to know the $\Delta_r H$ and the number of moles being reacted.

**The formula for calculating the number of moles from the mass of a substance is: $n = \frac{m}{M}$**

In this formula, ‘$n$’ is the number of moles of a substance, ‘$m$’ is the mass of a substance (measured in grams, g), and $M$ is the molar mass of a substance (measured in grams per mole, gmol$^{-1}$).

Let’s look into these a bit more:

**The ‘mole’ is a unit for the amount of substance**

It’s basically a number, a huuuuge number in fact.

One mole of water molecules is equal to $6.022 \times 10^{23}$ molecules, one mole of hydrogen atoms is equal to $6.022 \times 10^{23}$ atoms, and one mole of oxide (O$^{2-}$) ions is equal to $6.022 \times 10^{23}$ ions.

It seems like a bit of a random number, but it’s based around the number of atoms in 12g of carbon-12.
We use moles in our calculations as they are a handy way of expressing very large numbers in numbers we find a lot more friendly. For now, just think of a mole as a specific quantity, like a ‘dozen’.

The molar mass measures the size of each mole we are dealing with.

The molar mass can be calculated by adding the atomic weights of all the atoms in the molecule

Just like humans have a weight associated to them, so too do atoms.

The atomic weight of an atom can be found on the Periodic Table. If you have a look at one of the elements in the Periodic Table you will see 3 main things:

1. The symbol for the element.
2. Two numbers:
   a. The smallest one, which is always a whole number, is the atomic number which tells us the number of protons (and also the number of electrons) in each atom of the same element
   b. The larger number is the atomic weight, which is not usually a whole number. It is also the molar mass, measured in grams per mole.

So, once you have the atomic weight of each atom in the molecule, simply add them all up to get the molar mass of the molecule overall.

≡⇒ For example, to find the molar mass of CO₂ we find the atomic weight of carbon (C) and each oxygen (O), and then add them all up.
   • C = 12 g/mol
   • O = 16 g/mol
   • The molar mass of CO₂ = 12 + (2 x 16) = 44 g/mol

Now that we’ve worked out what we mean by ‘moles’ and ‘molar mass’, let’s jump straight into working out the enthalpy of a reaction with an example:

We’ve got a reaction: H₂(g) + ½O₂(g) → H₂O(g) with an enthalpy change of reaction (Δ_rH) of -242 kJmol⁻¹.

Imagine we want to calculate how much energy is released when 20 grams of hydrogen gas is combusted.

First of all, we need to calculate the number of moles we are dealing with. If we look at the information, we’ve currently got a value for the mass. We also know that the
number of moles can be calculated using \( n = \frac{m}{M} \).
This just means that, in order to calculate the number of moles, we need the molar mass. If we look at the Periodic Table and find hydrogen:

<table>
<thead>
<tr>
<th>Element name</th>
<th>Atomic number</th>
<th>Element symbol</th>
<th>Atomic weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>1</td>
<td>H</td>
<td>1.0079</td>
</tr>
</tbody>
</table>

The molar mass is equal to 1 g/mol (we can round 1.008 down to just 1 in this example). This means that the molar mass of \( \text{H}_2 \) is 2 g/mol. So, plugging those values into our equation for the number of moles gives us \( n = 20\text{g} \div 2\text{g/mol} = 10 \text{ moles} \).

Now that we have our number of moles of hydrogen, we can go about calculating the energy released. Looking at our information, we know that the enthalpy change of reaction is equal to \(-242 \text{ kJ per mole}\). Since there is 242 kJ released per 1 mole of hydrogen released, with 10 moles there will \( 10 \times 242 = 2420 \text{ kJ} \).

\[ \text{STOP AND CHECK:} \]

- The negative sign in front of 242 kJ/mol in the enthalpy change of reaction tells us that this energy is released to the surroundings. Therefore, when talking about the amount of energy released we can drop the negative sign.
- A positive sign in front of the enthalpy change of reaction would tell us that this amount of energy is absorbed.

**Heat and Specific Heat**

The enthalpy changes that we have been yarning about for the last few pages can be determined in the lab by measuring the amount of heat that is transferred.

In combustion reactions, for example, a certain amount of a combustible compound is burned and the resulting energy released is used to heat a known amount of water,
The temperature change can be measured and used to calculate the heat released from the combustion reaction and transferred to the water. This heat can then be used to calculate the enthalpy change by taking into account the number of moles of combustible compound used.

The amount of heat is calculated using \( q = m \times c \times \Delta T \) - let’s break this down

- ‘\( q \)’ represents the amount of heat transferred and is measured in joules (J) or sometimes, kilojoules (kJ) which is just 1000 joules.
- ‘\( m \)’ is the mass of stuff - such as water - that is heated. It is measured in grams (g).
- ‘\( c \)’ represents something called “specific heat capacity” which we will come back to soon. It is measured in joules per gram degree Celsius, \( J/g \cdot °C \) (or sometimes kilojoules per kilogram per degree Celsius).
- ‘\( \Delta T \)’ represents the change in temperature, which is measured in degrees Celsius (°C).

The specific heat capacity is a property of all compounds

The specific heat capacity is defined as, “the amount of heat required to increase the temperature of 1 gram of the compound by 1°C”. Every compound has its own specific heat capacity.

- For example, water has a specific heat capacity of 4.18 \( J/g \cdot °C \) which means that 4.18 joules of energy is required to heat 1 gram of water by 1°C.

Basically, compounds with high heat capacities are harder to heat - they require a lot more energy to heat up - while low heat capacity compounds are easier to heat. Metals tend to have low heat capacities. This helps explain why the pot will heat up a lot quicker than the water inside.

Let’s have a look at an example:

Imagine we burn 4g of propane and use the heat released to heat 1.5 kg of water above the burning propane. By measuring the temperature change of the water we can calculate the amount of heat released by propane combustion since we know water’s specific heat capacity.

Let’s say that burning 4g of propane causes the temperature of the water to increase from 18.1 °C to 50.0 °C.

To calculate the heat transferred we use \( q = mc\Delta T \).

- ‘\( m \)’ is the mass of water. We are told it is 1.5kg which is equal to 1500g - so, \( m = 1500g \).
The ΔT is the change in temperature which is equal to the final temperature minus the initial temperature. Therefore, the change in temperature is 50.0 - 18.1 = 31.9°C.

‘c’ is the specific heat capacity of water which is 4.18 J g⁻¹°C⁻¹ (you will be told this in these types of questions).

Putting it altogether gives us: \( q = 1500 \times 4.18 \times 31.9 = 200,013 = 200,000 \text{ J or 200 kJ}. \)

**Once you know the amount of heat transferred you can calculate enthalpy changes**

The enthalpy change represents the amount of heat transferred per mole. Using a formula, \( \Delta_r H = -q/n \).

The negative sign of ‘q’ is important. This is because a positive amount of heat transferred indicates heat being released to the surroundings which is associated with exothermic reactions that have negative enthalpy changes.

A negative amount of heat transferred indicates heat is being taken from the surroundings which is associated with endothermic reactions that have positive enthalpy changes. Therefore, the negative sign in front of q will cancel the negative value calculated.

In order to calculate the enthalpy change after calculating the value for ‘q’ you simply need to divide by the number of moles of substance reacted.

**Back to our example:**

In our example, 4 g of propane was combusted. Propane has a molar mass of 44 g/mol as it is made up of 3 carbon atoms (3 x 12 g/mol = 36) and 8 hydrogen atoms (8 x 1 g/mol = 8). Remember, the individual atomic weights can be found on the Periodic Table.

To calculate the number of moles, we divide the mass of propane we have by the molar mass. In our example, the number of moles of propane = \( 4/44 = 0.0910 \text{ moles} \). Therefore, the enthalpy change of the combustion of propane is equal to \( -200\text{kJ} \div 0.0910 \text{ mol} = -2197 = -2200 \text{ kJ/mol} \).

You should always check the sign on your enthalpy in these kinds of calculations to make sure it lines up with your observations. For example we know this reaction is exothermic and so the enthalpy sign needs to be negative.

**STOP AND CHECK:**

Turn your book over and see if you can remember:

- How to calculate the amount of heat transferred.
Entropy describes the disorder or randomness of a system, which seems like a weird thing to be worried about.

Think about your room at home for a minute

Unless you make the effort to clean it and put things away, or you’re lucky to have your mum or dad clean it for you, your room gets messier and messier over time. When it’s clean and tidy there isn’t much randomness or disorder – everything has its place, and is kept there nicely.

But as the room gets messier this randomness or disorder increases – it’s like we can’t predict where things are anymore. In other words, the entropy of the room increases.

Having your room get messier over time seems out of your control, and almost seems like the natural course of events – and that’s because it is!

Believe it or not, but everything in the universe tends to increase in entropy overall.

This means that we could say that an increase in entropy is favourable and is associated with a reaction that will be more than happy to go ahead on its own without any extra input.

We call these types of reactions spontaneous

Tidying your room would take effort and energy, and so we could say that a decrease in entropy is not favourable and so is associated with non-spontaneous reactions that require some kind of external input of energy.

Let’s get back into chemistry: imagine your room is the system

Inside your room is all of your stuff which represents the particles of the system, or the atoms and molecules.

When we think of randomness or disorder of particles, we can go back to the states of matter
Solids have a nice structure with predictable shapes, where each atom goes in a certain place. Therefore, solids have low entropy.

Liquids kind of have a defined shape, but is constantly changing or moving. This means that there’s a bit more disorder, and liquids have higher entropy.

Gases, on the other hand, have molecules just doing their own thing; each one zipping around in random directions. As you can imagine they have high entropy.

**Going from solid to liquid, or liquid to gas, is an increase in entropy while going backwards is a decrease in entropy**

Similarly, dissolving a solid in water to produce a solution is an increase in entropy

If a chemical reaction takes a small number of moles of reactants and produces more moles of products, the disorder increases with the larger number of particles, and the entropy increases.
For some reason scientists decided to give entropy the symbol, ‘S’.

STOP AND CHECK:

Turn your book over and see if you can remember:

- What is meant by the term, “entropy”.
- Whether entropy increases or decreases as you go from solid to liquid to gas.
- Why entropy increases when more moles of substance are produced.

Try to explain it in your own words.

Spontaneous and Nonspontaneous Reactions

Whether a reaction occurs spontaneously or non-spontaneously depends on both enthalpy change AND entropy change.

Spontaneous reactions are those that can occur by themselves without any external help like an extra input of energy.

Non-spontaneous reactions are the opposite and can only go ahead if there is some external drive pushing them to go ahead. This requires an input of energy.

Everything wants to be low energy

What this means is that exothermic reactions are favoured. This is because exothermic reactions involve high-energy reactants forming lower-energy products and a release of energy to the surroundings.
Everything also wants to have high entropy

As we have already discussed, the universe always wants to be increasing in entropy, therefore reactions that create a lot of entropy such as combustion reactions (that produce a lot of gas molecules) will be favoured from an entropy standpoint.

A reaction that is exothermic and increases entropy will always be spontaneous

Combustion reactions are a good example of overall spontaneous reactions:

For example, consider the combustion of hexane: $\text{C}_6\text{H}_{14(l)} + 9.5\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 7\text{H}_2\text{O(g)}$

which has an enthalpy change of $-4163 \text{ kJmol}^{-1}$.

So, first of all we have ourselves an exothermic reaction as shown by the negative enthalpy change. Therefore, high-energy reactants are being converted into lower-energy products which is favourable.

Next, have a look at the number of moles of gas. We start with 9.5 moles of gas on the reactants side (9.5 moles of $\text{O}_2$) and end up with 13 moles of gas on the other side (6 moles of $\text{CO}_2$ and 7 moles of $\text{H}_2\text{O}$). Since the number of moles of gas has increased the entropy has increased which is also favourable.

Therefore, the combustion of hexane is always spontaneous.

What about non-spontaneous reactions?

Endothermic reactions and reactions that decrease entropy are not favoured. This is because endothermic reactions involve low-energy reactants forming higher-energy products, and a decrease in entropy is opposite to the universe’s normal tendency to increase entropy.

When we have these two occurring together the reaction will always be non-spontaneous.

It can often be hard to make a call on whether a reaction is spontaneous or not

Often we can have exothermic reactions that reduce entropy or endothermic reactions that increase entropy. If we have a favourable component (exothermic or increase entropy), coupled with an unfavourable component (endothermic or decrease entropy) then we can’t really make a call on whether a reaction will be spontaneous.
What we can say is that sometimes having a favourable component will help drive the reaction forward when there is an unfavourable component. For example, an endothermic reaction, which is unfavourable, can occur when there is a big increase in entropy.

For example, salt dissolving in water is an endothermic process \((\Delta H = +3.9 \text{ KJmol}^{-1})\). But it still occurs spontaneously because there is a huge increase in entropy as we go through a solid to an aqueous solution of ions.

In this case the entropy wins out over the enthalpy, but that may not always be the case. However, even when we can not make the call either way, we should still discuss both factors in our answers.

The table below should help you to identify whether the reaction will spontaneous based on the change in enthalpy and change in entropy:

<table>
<thead>
<tr>
<th>Endothermic (+(\Delta H))</th>
<th>Exothermic (-(\Delta H))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase Entropy (+(\Delta S))</td>
<td>Can’t make a call</td>
</tr>
<tr>
<td>Decrease Entropy (-(\Delta S))</td>
<td>Always non-spontaneous.</td>
</tr>
<tr>
<td></td>
<td>Always spontaneous.</td>
</tr>
</tbody>
</table>

STOP AND CHECK:

Turn your book over and see if you can remember:

💡 What is meant by spontaneous and non-spontaneous reactions.
💡 The features of reactions that are always spontaneous.
💡 The features of reactions that are always non-spontaneous.
💡 Why it can be hard to make a call on whether a reaction is spontaneous.

Try to explain it in your own words.

**Hess’s Law**

Hess’s Law tells us that “the total enthalpy change during a chemical reaction is the same whether the reaction is made in one step or in several steps, made up of multiple component reactions”.

Hess’s Law problems in Level 3 Chemistry generally require you to take several reactions and manipulate them in such a way that you get one reaction, for which you need to calculate the enthalpy of reaction.
The basic steps to figuring out these kinds of problems are:

1. Write out all of the reactions that you will be using in full.
2. Identify the unique molecules in each of the reactions, that is, molecules which only appear once.
3. Make sure that the unique molecules are on the right side of the equation (the same side as in the final equation), with the right number of moles. Usually all other molecules will balance or cancel out in the final equation.
4. Add all of the chemical equations to give a net equation, where all reactants go on a single reactant side and all the products go to a single product side.
5. Any molecule (in the same state) that appears on both sides of the equation can be cancelled out.
6. This should leave the desired equation. To find the enthalpy of reaction you can now simply add all of the modified change in enthalpies for the reactions you used to get the final answer.

Better yet, let’s have a look at an example:

The combustion of ethanol looks like: \( \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \)

Imagine we want to calculate the enthalpy of combustion (\( \Delta_cH^\circ \)) for ethanol, but we only have information on other enthalpy changes:

- The enthalpy of formation (\( \Delta_fH^\circ \)) of ethanol is -277 kJ/mol
- The enthalpy of formation of carbon dioxide is -394 kJ/mol
- The enthalpy of formation of water is -286 kJ/mol

We can calculate the enthalpy of combustion using Hess’s Law

**Step 1**

The first thing we need to do is write out the 3 formation reactions that were given to us.

Formation of ethanol: \( 2\text{C}(s) + 3\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{C}_2\text{H}_5\text{OH}(l) \)

Formation of carbon dioxide: \( \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \)

Formation of water: \( \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \)
Steps 2 and 3

The unique molecules are $\text{C}_2\text{H}_5\text{OH}(l)$, $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ as they only ever appear once in all 3 formation reactions as well as in the combustion of ethanol. In the combustion of ethanol reaction, ethanol is a reactant while carbon dioxide and water are products.

In the formation of carbon dioxide reaction and in the formation of water, carbon dioxide and water are products. This means they are on the right side of the equations. The only problem is that in the combustion of ethanol there are 2 moles of $\text{CO}_2(g)$ and 3 moles of $\text{H}_2\text{O}(l)$, but only 1 of each in their formation reactions. To get the right moles in the final equation, we simply multiply each formation reaction by the right number of moles:

- To get 2 moles of $\text{CO}_2(g)$: $2 \times [\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)] = 2\text{C}(s) + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g)$
- To get 3 moles of $\text{H}_2\text{O}(l)$: $3 \times [\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)] = 3\text{H}_2(g) + 1.5\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l)$

Since we multiplied these reactions by a certain factor we also need to multiply their enthalpy changes:

- The enthalpy change of reaction of $2\text{C}(s) + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) = 2 \times -394 = -788 \text{ kJ/mol}$
- The enthalpy change of reaction of $3\text{H}_2(g) + 1.5\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l) = 3 \times -286 = -858 \text{ kJ/mol}$

In the formation of ethanol reaction, ethanol is a product. However, we need it to be a reactant like it is in the combustion reaction. So, we flip the ethanol formation reaction around to give:

- $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow 2\text{C}(s) + 3\text{H}_2(g) + \frac{1}{2}\text{O}_2(g)$
- When we flip it around, we change the sign of its enthalpy change. This means -277 kJ/mol becomes +277 kJ/mol.

Steps 4 and 5

Our 3 formation reactions to use in Hess’s Law are now:

- $2\text{C}(s) + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g)$ $\Delta H = -788 \text{ kJ/mol}$
- $3\text{H}_2(g) + 1.5\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l)$ $\Delta H = -858 \text{ kJ/mol}$
- $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow 2\text{C}(s) + 3\text{H}_2(g) + \frac{1}{2}\text{O}_2(g)$ $\Delta H = +277 \text{ kJ/mol}$
The next step involves adding them all up by combining their reactants, products and their enthalpies:

\[
2C(s) + 2O_2(g) + 3H_2(g) + 1.5O_2(g) + C_2H_5OH(l) \rightarrow 2CO_2(g) + 3H_2O(l) + 2C(s) + 3H_2(g) + \frac{1}{2}O_2(g)
\]

Any molecules that appear on both sides of the reaction can be cancelled out. There are 2 moles of C\(_{(s)}\) on both sides and 3 moles of H\(_2(g)\) which can be removed completely. O\(_2(g)\) appears on both sides. However, there are 3.5 moles on the reactant side (2 + 1.5 = 3.5) and \(\frac{1}{2}\) moles on the product side. The O\(_2(g)\) on the product side can be removed to leave 3 moles of O\(_2\) on the reactant side (3.5 – \(\frac{1}{2}\) = 3).

Our net equation is:

\[
2C(s) + 3H_2(g) + 3.5O_2(g) + C_2H_5OH(l) \rightarrow 2CO_2(g) + 3H_2O(l) + 2C(s) + 3H_2(g) + \frac{1}{2}O_2(g)
\]

= C\(_2\)H\(_5\)OH(l) + 3O\(_2(g)\) → 2C\(_(s)\) + 3H\(_2\)O(l)

This looks exactly like the enthalpy of combustion of ethanol, so we know we have done it right.

**Step 6**

The last step now involves calculating the enthalpy of combustion of ethanol. Since we know that adding the following reactions was correct:

\[
\Rightarrow 2C(s) + 2O_2(g) \rightarrow 2CO_2(g)
\]

\[
\Rightarrow 3H_2(g) + 1.5O_2(g) \rightarrow 3H_2O(l)
\]

\[
\Rightarrow C_2H_5OH(l) \rightarrow 2C(s) + 3H_2(g) + \frac{1}{2}O_2(g)
\]

We can simply add their enthalpy changes: (-788) + (-858) + (277) = -1369 kJ/mol

In other words, the enthalpy of combustion of ethanol, Δ\(\text{H}^\circ\), is equal to -1369 kJ/mol. This makes sense as combustion reactions are exothermic, with negative enthalpy changes, as they release heat to the surroundings.

**STOP AND CHECK:**

Turn your book over and see if you can remember:

💡 What Hess’s Law is.

💡 How Hess’s Law can be used to calculate the enthalpy change of a reaction.

Try explain it in your own words.
Quick Questions

Question 1:
Using the following pieces of information:

- \( \Delta H^\circ \) for \( \text{NH}_3(g) \) is -46 kJ/mol
- \( \Delta H^\circ \) for \( \text{HCl}(g) \) is -92 kJ/mol
- \( \Delta H^\circ \) for \( \text{NH}_4\text{Cl}(s) \) is -314 kJ/mol

Calculate the enthalpy change of reaction (\( \Delta H^\circ \)) for the following reaction:
\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)
\]

Question 2:
Imagine that 5.12 grams of liquid methanol (\( \text{CH}_3\text{OH} \)) is being used to heat 750g of water. If the temperature of water increases from 15.6 °C to 33.3 °C, show that the enthalpy of combustion of methanol is -347kJ/mol.

- The specific heat capacity of water is 4.18 J/g°C.
- Remember to calculate the molar mass of methanol from the Periodic Table (although, most often it will be given to you).

Question 3:
Without doing any calculations, explain why the enthalpy of formation of sulfur dioxide gas (\( \text{SO}_2(g) \)) is equal to the combustion of solid sulfur (\( \text{S}(s) \)).

\( \text{Hint: write out the reactions which represent the two enthalpy changes.} \)
KEY TERMS

**Activation Energy:**
The energy that is needed to be overcome before a chemical reaction can start, or take place.

**Atomic Radius:**
The distance between the nucleus and the outermost (or valence) electrons.

**Bond Enthalpy:**
The energy required to break a particular chemical bond.

**Covalent Bond:**
The bond between two atoms that forms from a pair of electrons that are shared between two atoms.

**Dipole:**
A term used to describe a separation of positive and negative charges.
*For example, a polar bond is a dipole.*

**Dispersion Forces:**
See “instantaneous dipole forces”.

**Hydrogen Bonding:**
The strongest intermolecular force that occurs between positively-charged hydrogen atoms bonded to high electronegative atoms and negatively-charged regions on neighbouring molecules.

**Electronegativity:**
The tendency of an atom to attract bonding electrons.

**Endothermic Reactions:**
Chemical reactions which involve a transfer, or absorption, of energy from the surroundings into the system.

**Enthalpy:**
The particular energy that a molecule possesses.

**Enthalpy of Combustion:**
The energy required to react 1 mole of a substance with oxygen under standard conditions.
**Enthalpy of Formation:**
The energy required to produce 1 mole of product from its constituent atoms in their standard states at standard conditions.

**Enthalpy of Reaction, Δ\text{rH}:**
The enthalpy change associated with a specific chemical reaction and the mole ratios involved. In other words, it is the difference between the total enthalpy of the products and the total enthalpy of the reactants, under standard conditions, when the amount of reactants and products is equal to the mole ratios.

**Entropy:**
The state of randomness or disorder in the system.

**Exothermic Reactions:**
Chemical reactions which involve a transfer, or release, of energy from the system into the surroundings.

**Instantaneous Dipole Forces:**
Intermolecular forces that occur between all molecules due to the instantaneous dipole created by an uneven electron distribution around the molecule.

**(First) Ionisation Energy:**
The energy required to remove 1 mole of electrons from 1 mole of atoms in their gaseous states.

**Permanent Dipole Forces:**
Intermolecular forces that occur between polar molecules due to the attraction between positively-charged and negatively-charged regions in neighbouring molecules.

**Surroundings:**
In a chemical reaction, the “surroundings” simply refer to everything else that’s not the system. It refers to the rest of the universe, outside the reaction taking place.

**System:**
In a chemical reaction, the “system” refers to all the energy and matter (the particles, or the molecules) involved in a chemical reaction.