Chapter 8: Chemical bonding

Atoms use their electrons to form **chemical bonds.** Chemical bonds are strong attractive forces holding atoms or ions together.

In order to gain stability, **atoms tend to follow a rule called the Octet rule.**

The Octet rule states that atoms tend to undergo chemical changes in order to reach an electron arrangement with 8 electrons in their outer energy level (or valence shell).

Limitations: It is important to be aware that the octet rule is a general guideline but there are exceptions. Elements near helium (e.g. hydrogen, lithium) want to have 2 electrons in their outer energy level not 8, and many transition metals do not follow the octet rule since they have variable valency.

Atoms achieve this – having 8 electrons in their outermost energy level – by either gaining, losing, or sharing electrons. **Valency is a measure of how many bonds an atom will form to satisfy the octet rule.**

The valency of an element is the number of bonds an atom of that element forms when it reacts (i.e. it is the combining power of that element).

Group number	1	2	13	14	15	16	17	18
Valency	1	2	3	4	3	2	1	0

For valency purposes, **consider hydrogen to be in group 1**, with a valency of 1. Also note that the transition metals – the block of elements between groups 2 and 13 – are not included here.

Using valency to write chemical formulas

Predict the chemical formula of a compound made from carbon and hydrogen.

Step 1: Write down the valency of each element
Carbon = group 4 = valency of 4 = will form 4 bonds
hydrogen = group 1 = valency of 1 = will form 1 bond

Step 2: Work out the ratio needed
Since each hydrogen will form only 1 bond, carbon needs 4 hydrogen atoms to satisfy its need for 4 bonds.

Step 3: Write the formula
Predicted formula = **CH_4**

Predict the chemical formula of a compound made from calcium and chlorine.

Step 1: Write down the valency of each element

Calcium = group 2 = valency of 2 = will form 2 bonds
Chlorine = group 17 = valency of 1 = will form 1 bond

Step 2: Work out the ratio needed
Since each chlorine will form only 1 bond, calcium needs 2 chlorine atoms to satisfy its need for 2 bonds.

Step 3: Write the formula
Predicted formula = **$CaCl_2$**

Ionic bonding

Ionic bonding is the force of attraction between oppositely charged ions.

- Ionic bonding generally occurs between a **metal and non-metal**.
- The **metal** donates an electron to become a **cation**, while the **non-metal** gains an electron to become an **anion**.
- The **force of attraction** between the cation and anion is an **ionic bond.**
- An **ionic compound** is formed – a compound composed of ions held together by ionic bonds.

Ionic bonding: Sodium (Na) and Chlorine (Cl)

Sodium is in group 1 → has a valency of 1.
Chlorine is in group 17 → has a valency of 1

Sodium will donate its electron to chlorine; Na becomes Na^+ and **Cl becomes Cl^-**.
Opposites attract – the Na^+ ion is attracted to the Cl^- ion. **The force of attraction between these oppositely charged ions is called an ionic bond.**

The compound formed is **NaCl, sodium chloride**. Sodium chloride is also known as table salt. However, it is important to note that for ionic compounds, the formula given, e.g. NaCl, represents the **simplest whole number ratio** of the ions present. In reality, an ionic compound is made of hundreds of thousands of ions.

NaCl exists as a **crystal lattice** – a rigid 3-D structure of ions that appears as a crystal, e.g. crystals of table salt.

It is important to note that:

- **only electrons in the outer energy levels of the atom are involved in bonding.**
- **Ionic compounds are neutral overall. The positive charges of the cations must balance the negative charges of the anions.**

To name an ionic compound the **cation is named first**, **then the anion**. If an ionic compound contains two elements the ending of the second element changes to 'ide', e.g. sodium and chlorine becomes sodium chloride.

Ionic bonding: Magnesium (Mg) and Fluorine (F)

Magnesium, in group 2, has a valency of 2 (electronic arrangement: 2,8,2).
Fluorine is in group 17 and has a valency of 1 (electronic arrangement: 2,8,7).
Therefore, one Mg will need two F atoms.

The forces of attraction between the **Mg^{2+} and F^- ions** are **ionic bonds**. The compound formed has a formula of **MgF_2** and is named **magnesium fluoride.**

Ionic bonding: Aluminium (Al) and Oxygen (O).

Aluminium, in group 13, has a **valency of 3** (electronic arrangement: 2,8,3). Al wants to become Al^{3+}.

Oxygen in is group 16 and has a **valency of 2** (electronic arrangement: 2,6). O wants to become O^{2-}.

Since the ratio is not easy to figure out (i.e. it isn't 1:1 or 1:2), we look for the lowest common multiple. Here, it is 6. Two aluminium atoms are needed to lose 6 electrons, while three oxygen atoms are needed to gain those 6 electrons.

The formula of the compound is **Al_2O_3**, and it is named **aluminium oxide.**

Polyatomic ions

ammonium	NH_4^+	hypochlorite	ClO^-
hydroxide	OH^-	nitrate	NO_3^-
hydrogencarbonate	HCO_3^-	carbonate	CO_3^{2-}
sulfate	SO_4^{2-}	sulfite	SO_3^{2-}
permanganate	MnO_4^-	phosphate	PO_4^{3-}

Write the chemical formula of calcium carbonate

Calcium in group 2 has a valency of 2 (wants to lose 2 electrons and form the ion Ca^{2+}). The carbonate ion is CO_3^{2-}. One Ca^{2+} will need one CO_3^{2-} ion to balance its charge.

Formula = **$CaCO_3$**

Write the chemical formula of magnesium hydrogencarbonate

Magnesium in group 2 has a valency of 2 (wants to lose 2 electrons and form the ion Mg^{2+}).
The hydrogencarbonate ion is HCO_3^-.
One Mg^{2+} will need two HCO_3^- to balance its charge.

Formula = **$Mg(HCO_3)_2$**

Note the brackets around the HCO_3 and the '2' after the bracket to indicate that there are two hydrogencarbonate polyatomic ions present. Brackets and subscripts are used to indicate multiples of polyatomic ions.

Investigate, using primary data, the presence of ions in solutions and identify an anion in an unknown salt

Anion	Salt	Reagents added	Positive result	Chemical equation
Chloride **Cl^-**	$NaCl$	$AgNO_3$	White precipitate *(that dissolves in NH_3 solution)*	$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$ $Ag^+ + Cl^- \rightarrow AgCl\downarrow$
Nitrate **NO_3^-**	KNO_3	$FeSO_4$ Conc.H_2SO_4	**Brown ring** forms at junction of the two liquids	$NO + [Fe(H_2O)6]^{2+} \rightarrow$ $\mathbf{[Fe(H_2O)_5NO]^{2+}} + H_2O$
Phosphate **PO_4^{3-}**	Na_2HPO_4	Ammonium molybdate Conc. nitric acid	Yellow precipitate	$PO_4^{3-} + 3NH_4^+ + 12MoO_4^{2-} + 24H^+ \rightarrow$ $(NH_4)_3PO_4.12MoO_3 + 12H_2O$
Sulfate **SO_4^{2-}**	Na_2SO_4	Add $BaCl_2$ then HCl	White precipitate that does not dissolve in HCl	$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$ $BaSO_4 + HCl \rightarrow$ no reaction
Sulfite **SO_3^{2-}**	Na_2SO_3	Add $BaCl_2$ then HCl	White precipitate that dissolves in HCl	$Ba^{2+} + SO_3^{2-} \rightarrow BaSO_3\downarrow$ $SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$
Carbonate **CO_3^{2-}**	$CaCO_3$	Add HCl Add $MgSO_4$	CO_2 produced White precipitate	$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$ $Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3\downarrow$
Hydrogen-Carbonate **HCO_3^-**	$Ca(HCO_3)_2$	Add HCl Add $MgSO_4$	CO_2 produced No precipitate forms	$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ $Mg^{2+} + 2HCO_3^- \rightarrow Mg(HCO_3)_2$

Covalent bonding

- **Covalent bonding involves the sharing of electrons to form covalent bonds.**
- It can occur between atoms of the same element or between atoms of different elements.
- Covalent bonding generally occurs **between non-metals.**
- Atoms share electrons, are bound together by a covalent bond, and form molecules.

Covalent bonds are bonds in a molecule and so are called intramolecular bonds (intra = inside).

A covalent bond is formed when electrons are shared between two atoms.

A single covalent bond is formed when one pair of electrons is shared.
A double bond = 2 pairs of electrons are shared
A triple bond = **3** pairs of electrons are shared.

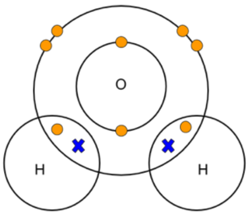
A hydrogen molecule, H_2

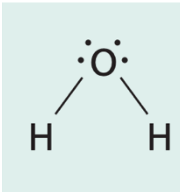
A hydrogen atom has 1 electron and a valency of 1. When 2 hydrogen atoms bond to form a hydrogen molecule, each hydrogen atom shares its single electron with the other. This results in a **covalent bond**, where both electrons are shared between the two atoms. By sharing electrons, both hydrogen atoms achieve a stable electronic configuration. The covalent bond is represented by a dash, e.g. H-H.

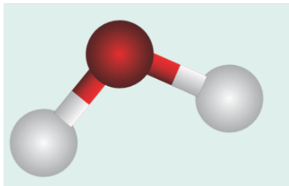
Water, H_2O

We can use valency to work out that a water molecule has a chemical formula of H_2O.

Hydrogen and oxygen are both non-metals and bond covalently to form water, H_2O. Oxygen shares one of its electrons with each of the two hydrogen atoms. In return, each hydrogen atom shares its single electron with oxygen. This way, oxygen achieves a full outer energy level (8 electrons), and each hydrogen atom achieves a stable configuration, with 2 electrons in its outer shell.







Electronegativity

- Electronegativity is a measure of the ability of an atom in a molecule to attract a shared electron pair to itself.
- Each element on the periodic table is assigned an **electronegativity value**.
- These values range on a scale from 0 to 4, and indicate how well an atom can 'pull' electrons towards itself.

Electronegativity is the relative attraction that an atom in a molecule has for a shared pair of electrons in a covalent bond.

The general rule is that if the difference in electronegativity values between two atoms is greater than 1.7 they form an ionic bond; if it's less than 1.7 they form a covalent bond.

However, there are actually two different types of covalent bonds that can be formed - pure and polar.

Polar vs. pure covalent bonds

Pure covalent bonds = electrons shared equally (electronegativity difference approx. 0 – 0.4)
Polar covalent bonds = electrons shared unequally (EN difference approx. 0.4 – 1.7)

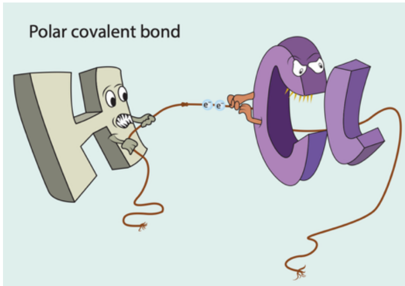
In polar covalent bonds, one atom is better able to 'pull' the shared pair of electrons towards itself, resulting in a greater electron density around this atom. The other atom is less able to 'pull' the shared pair of electrons towards itself, resulting in lower electron density around this atom.

Hydrogen chloride, HCl (polar covalent bond between H and Cl)

H = 2.20, Cl = 3.16, electronegativity difference = 0.96

The shared pair of electrons is more attracted to Cl, **making Cl slightly negative and hydrogen slightly positive.** We show slightly **positive charges and negative as δ^+ and δ^- and call them delta positive and delta negative.** The bond between the atoms is a **polar covalent bond**.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

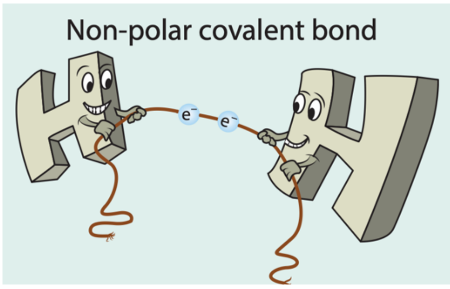


Hydrogen, H_2 (non-polar covalent bond between H and H)

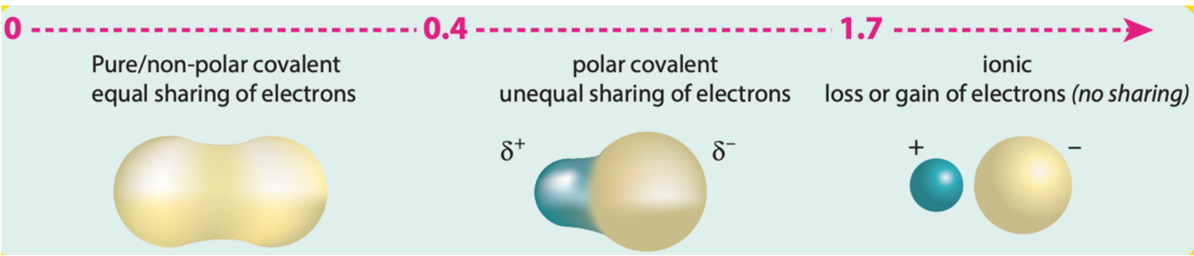
H = 2.20, H = 2.20, electronegativity difference = 0

When we look at a molecule of hydrogen, H_2, both atoms are equally electronegative. The **electrons are shared equally**. Neither atom needs a δ^+ or δ^-. This is a **pure covalent bond** (also called a non-polar covalent bond, as there are no opposite 'poles' of charge within the molecule).

$$H - H$$



<u>Using electronegativity values</u>



Chemical bonding is a continuum – from the complete transfer of electrons in an ionic bond to the completely equal sharing of electrons in a pure covalent bond.

For example, a difference of 1.6 indicates a much more polar bond than a difference of 0.5.

Electronegativity values can be used to predict where a bond lies along the continuum.

Electronegativity values **increase across a period** of the periodic table and **decrease down a group**. Due to these trends, **elements far apart on the periodic table are more likely to form ionic compounds than those close together.**

Properties of chemical compounds

Electrical conductivity

Ionic compounds will conduct electricity when those ions are free to move, i.e., when the substance is **molten (melted) or dissolved in aqueous solution**. However ionic compounds **do not conduct electricity when in solid form.**

Covalent compounds do not conduct electricity since they are made of neutral molecules.

Melting and boiling points

Ionic compounds typically have high melting points due to the strong ionic bonds between their ions. Generally exist as **hard solids** at room temperature.

Covalent compounds have **relatively low melting and boiling points**. Generally exist as **liquids and gases** at room temperature.

Solubility in water

The solubility of a compound refers to the ability of a substance to be dissolved. For covalent compounds, the general rule is that **like dissolves like**, i**.e. polar solvents dissolve polar solutes, and pure (non-polar) solvents dissolve pure (non-polar) solutes** (see Chapter 9 notes).

Ionic compounds can dissolve in water because the ionic bonds in their compounds are overcome by the strong attraction between the ions and the polar water molecules. Ions are dragged away from the crystal lattice (see Chapter 9 notes).

Modelling chemical bonding

Lewis diagrams

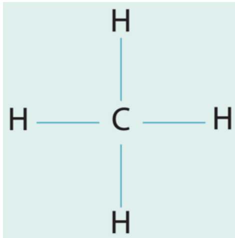
In Lewis structures, shared pairs of electrons are drawn as lines and lone pairs of electrons (electrons that are not shared, but belong to only one atom) are drawn as dots.

Drawing Lewis diagrams for covalent compounds

1. Determine the total number of valence electrons in the molecule.
2. Draw a ‘skeleton’ that connects the central atom (the atom with the most available bonds, i.e. highest valency) to all other atoms using single bonds.
3. Count electrons involved in those bonds, subtract them from the total and place the remainder to fill the outer energy levels of as many atoms as possible (begin with the most electronegative atom).
4. If all of the atoms do not have a full outer energy level, use multiple bonds to ensure they do.

Draw a Lewis diagram of CH_4

1. A carbon atom has 4 valence electrons; each hydrogen has 1. Total = 8 electrons.



2. Draw a ‘skeleton’ with carbon in the centre (since carbon has a higher valency than hydrogen), attached to all 4 hydrogen atoms by single bonds.

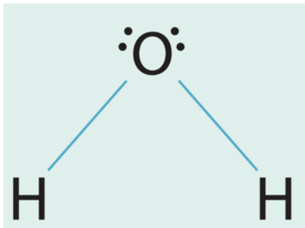
3. Count electrons involved in those bonds = 8 (each bond represents a pair of electrons). There are no electrons left over.

4. Each atom has a full outer energy level – no need to do anything else.

Draw a Lewis diagram of H_2O

1. An oxygen atom has 6 valence electrons; each hydrogen has 1. Total = 8 electrons.

2. Draw a ‘skeleton’ with oxygen in the centre, attached to the two hydrogen atoms by single bonds.



3. Count electrons involved in those bonds = 4 (each bond represents a pair of electrons). There are 4 electrons left over. Place these around oxygen (the most electronegative atom).

4. Each atom has a full outer energy level – no need to do anything else.

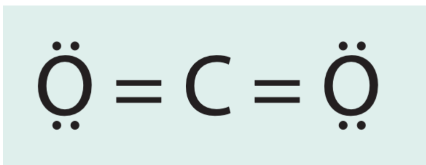
Draw a Lewis diagram of CO_2

1. A carbon atom has 4 valence electrons; each oxygen has 6. Total = 16 valence electrons.

2. Draw a ‘skeleton’ with carbon in the centre, attached to both oxygen atoms by a single bond.

3. Count electrons involved in those bonds = 4. There are 12 remaining electrons. Let’s place these 12 electrons to fill the outer shells of as many atoms as possible (beginning with the more electronegative atom – oxygen).

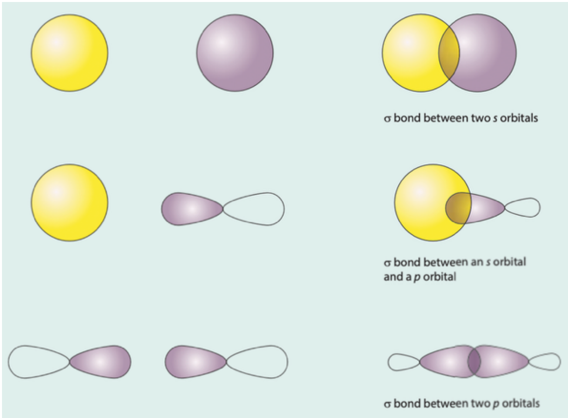
4. Not all of the atoms have full outer energy levels– carbon does not. Therefore, we must use multiple bonds to ensure it does. Remove 2 electrons from each oxygen atom and draw double bonds to the carbon. Now each atom achieves a full outer shell, and the correct number of electrons has been used.



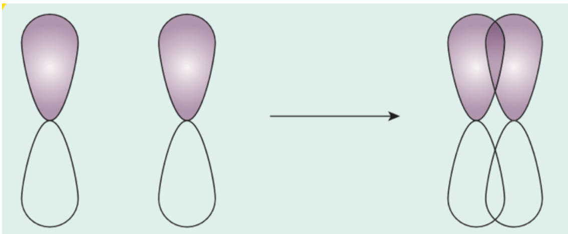
Orbital overlap

Another model used to describe chemical bonding in molecules is **valence bond theory.** The valence bond theory states that chemical bonds are formed from the **overlapping of atomic orbitals of different atoms.**

Sigma bonds are formed when atomic orbitals overlap head-on.



Pi bonds are formed when atomic orbitals overlap sideways.

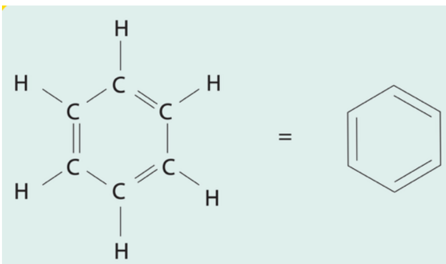


Sideways overlap is less efficient than head-on overlap so **pi bonds are weaker** than sigma.

All single bonds are sigma bonds (**s**ingle = **s**igma).
A double bond is composed of one sigma bond and one pi bond.
A triple bond is made of one sigma bond and two pi bond.

Benzene

Benzene has a molecular formula of C_6H_6. Based on the formula C_6H_6, scientists believed that the structure of benzene was as shown:



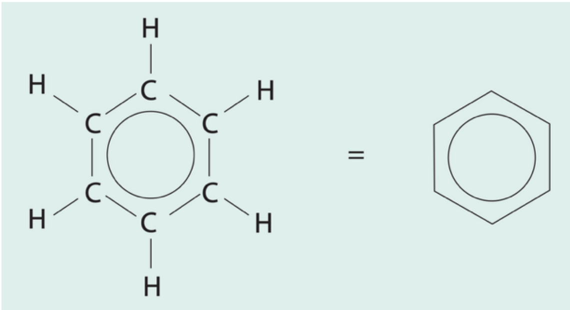
However, there were two puzzling properties of benzene:
1. It was very unreactive
2. When benzene's bond lengths were measured (using x-rays), it was found that all the carbon-carbon bond lengths were identical.

Scientists eventually worked out the accurate structure of benzene and this explained both its bond lengths and unreactivity. There are 12 electrons found in the 6 intermediate bonds (6 electron pairs = 6 bonds), and the remaining 6 electrons are **delocalised.**

Delocalised electrons are electrons that are **shared between more than two atoms** i.e. not associated with a single atom or bond.

These electrons are shared by all of the carbon atoms. This delocalisation of electrons gives **added stability** and accounts for benzene's unreactivity.

We now draw benzene like this – the circle indicates the delocalised electrons.



Sigma, pi bonds in benzene

Each carbon atom in the benzene ring has 4 electrons in its outer shell ($1s^2$ $\mathbf{2s^2}$ $\mathbf{2p^2}$). Each carbon atom uses 3 of these to form sigma bonds (by head-on overlap of atomic orbitals) – 2 with the carbon atoms on either side, and 1 with a hydrogen atom. These bonds are all sigma bonds.

The last electron is in a p orbital and this overlaps with the other carbon p orbitals to form two doughnut-shaped electron clouds. This is called a pi-bonding system, and the 6 electrons in the pi-bonding system are delocalised.

Limitations of predicting bonding between atoms

1. Using electronegativity values is not always reliable (exceptions exist, e.g. using electronegativity values indicates that BF_3 is ionic, but in reality BF_3 exists as molecules).

2. Not all bonds are purely ionic or covalent (bonding is a continuum)

3. Variable valency (transition metals, exhibit variable valency, making it difficult to predict chemical formulae)

Ionic vs. covalent – A summary

	Ionic	Covalent
Formed by	Atoms losing or gaining electrons *(one atom gives electrons to another)*	Two atoms share electrons *(either equally or unequally)*
Between	Metal and non-metal e.*g. NaCl (sodium chloride)*	Non-metal and non-metal *e.g.* CH_4 *(methane)*
Electronegativity difference	Above 1.7	0 – 0.4 (pure/ non-polar covalent) 0.4 – 1.7 (polar covalent)
Bonds	Ionic bonds between cations and anions	Covalent bonds between atoms
Exist as	Ions arranged in a crystal lattice structure *(held together by ionic bonds)*	Molecules *(atoms held together by intramolecular covalent bonds)*
Electrical conductivity	Don't conduct electricity when solid, but do when molten or dissolved in solution *(since the ions are free to move).*	Don't conduct electricity
Melting and boiling points	High melting and boiling points since a lot of energy is needed to break the ionic bonds between ions.	Relatively low melting and boiling points since intermolecular forces are relatively weak.
State of matter at room temperature	Generally hard solids at room temperature	Generally liquid or gases at room temperature.
Solubility in water	Soluble in polar solvents, therefore soluble in water *(Insoluble in non-polar solvents)*	Like dissolves like *(so polar compounds are soluble in water, and non-polar are not)*