Chem Factsheet

September 2000 **Number 05**

Bonding

To succeed with this topic you need to
- be able to recall the basics of Atomic Structure (Factsheet 1)
- understand the concepts of
  - Ionization Energy
  - Electron Affinity
  - Electronegativity
- recall the idea of electron shells and orbitals

After working through this Factsheet you will
- know the different kinds of intramolecular bonding
- know the different kinds of intermolecular bonding
- be able to represent the different bonding types diagrammatically and give a written explanation for each type

***Exam Hint**: - Exam questions on bonding will require you to know the specific examples covered here and to be able to apply the same thinking to similar atoms forming other compounds. Questions involving bonding will usually lead to other questions about structure and physical/chemical properties of the compound. (See Factsheet 6 - Structure of Elements & Compounds).*

Types of bonding

There are two main types of bonding:
1. **Intramolecular** - this is the bonding that takes place when atoms join to other atoms. The bonding **within** ('intra') a molecule or crystal.
2. **Intermolecular** - the bonding **between**(inter) molecules.

Bonding is important because it determines the structure and properties of compounds.

Remember:
Atoms ⇒ Bonding ⇒ Structure ⇒ Physical/Chemical Properties

Intramolecular bonding

Why do atoms bond together?
All atoms "want" to achieve the stability of a complete outer orbital of electrons i.e. the electronic configuration of the Noble Gases. They do this by losing or gaining outer electrons to form ions, or by sharing outer electrons with other atoms.

*Remember : All types of bonding involve just the **outer electrons** of the atoms concerned*

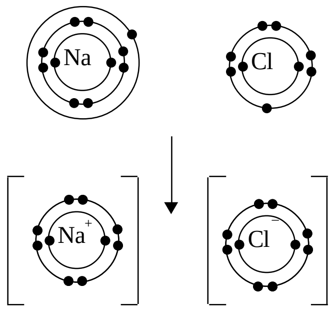
Atoms to atoms – the main bonding types
1. Ionic bonding - takes place between an atom that wants to lose one or more electrons and an atom that wants to gain one or more electrons.

- The atoms that lose electrons are classified as being **metallic.** They form **positive** ions (called **cations**) because they are losing electrons, which are negatively charged.

- The atoms that gain electrons are classified as being **non-metallic**. They form **negative** ions (called **anions**) because they are gaining negatively charged electrons.

The classic example is NaCl (Fig 1)

Fig 1. NaCl



Na (2.8.1)	Cl (2.8.7)	⟶	Na^+ (2.8)	Cl^- (2.8.8)
$1s^22s^22p^63s^1$	$1s^22s^22p^63s^23p^2$		$1s^22s^22p^6$	$1s^22s^22p^63s^23p^6$
			(electronic configuration of neon)	(electronic configuration of argon)

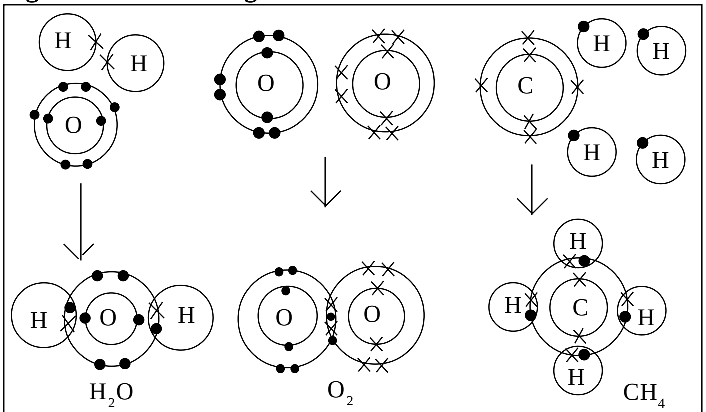
The more electrons that are transferred between the atoms, the larger the changes on the cations and anions. Example

Mg	+	O	⟶	Mg^{2+}	+	O^{2-}
$1s^22s^22p^6$		$1s^22s^22p^43s^2$		$1s^22s^22p^6$		$1s^22s^22p^6$

***Remember** - Ionic bonding is when there is complete transfer of an electron (or electrons) from one atom to another, and the subsequent formation of oppositely charged ions. These ions are held together by non-directional forces of electrostatic attraction.*

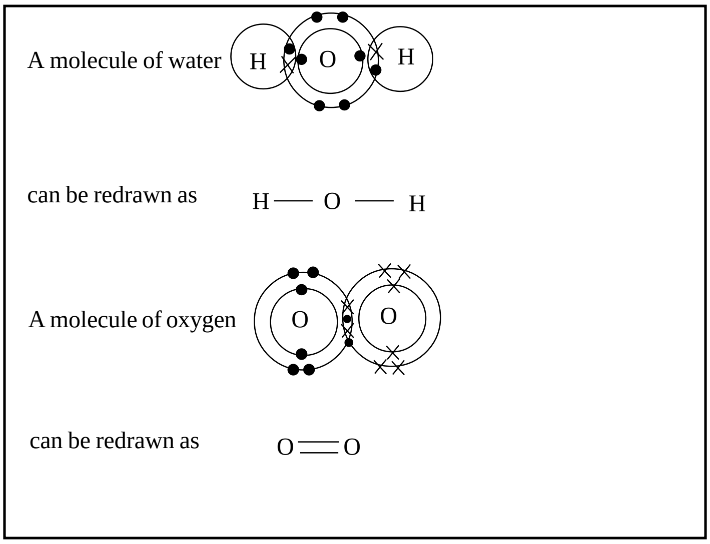
2. Covalent bonding - takes place between non-metallic atoms, both of which are electron deficient in their outer orbitals. The only way they can achieve the electronic configurations of noble gas is by the **sharing** of electrons. The bond pair of electrons is formed when each atom donates 1 electron. This type of bonding is always shown using dot/cross diagrams. The following represent some examples of covalent molecules (Fig 2).

Fig 2. Covalent bonding



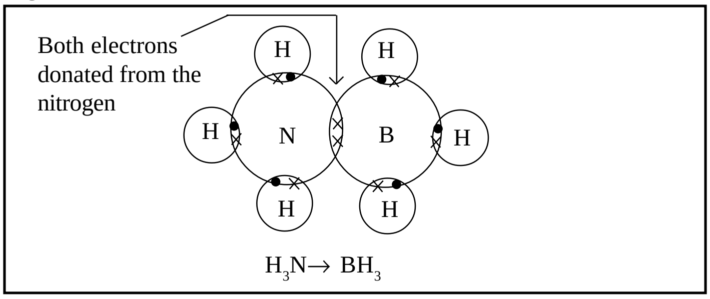
Stick diagrams are another way of showing the bond pairs and their positions.

Fig 3. Stick diagrams



3. Dative covalent bonding/ coordinate bonding - This is a special case of covalent bond where 1 atom donates **both** electrons that form the shared bond pair (see fig 4)

Fig 4. Dative covalent bond

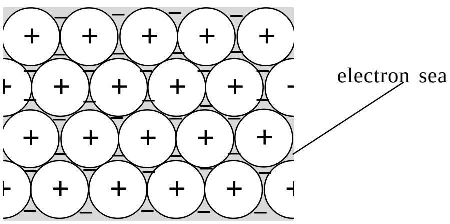


Notice that instead of a stick (—) an arrow (→) is used to signify the dative covalent bond.

***Remember:** Once the bond is formed, it does not make any difference whether it is dative covalent or normal covalent - it behaves in exactly the same way.*

4. Metallic bonding - The bonding in metals is caused by metal atoms losing their outer electron(s) to gain the stability of a noble gas electronic configuration. The metal atoms therefore become positive ions (cations) and the electrons move around this structure of cations, holding it together through electrostatic attraction (Fig 5).

Fig 5. Metallic bonding



this is called the 'sea of electrons' model. The electrons are said to be <u>delocalised</u> (meaning they are not fixed in one place but are free to move around).

What decides the type of bonding between two atoms?

The examples given so far are the classic examples, showing **ideal** ionic, covalent and metallic bonding.

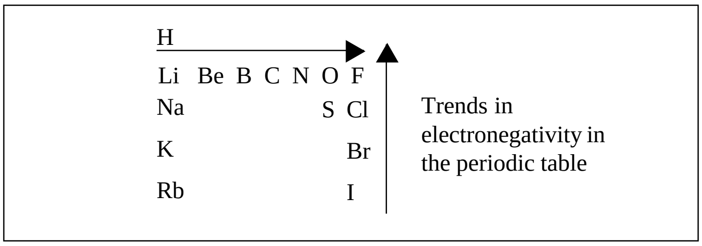
However, this does not explain everything! For example, we would expect, from what we have seen so far, that aluminium chloride ($AlCl_3$) would be ionic (as it involves a metal and a non-metal). However, is actually covalent!

At AS-level we need to use the concept of **electronegativity** to explain why different atoms bond in the way that they do.

Definition : The electronegativity of an atom is the ability of its nucleus to attract electrons in a bond pair.

The incomplete picture of the periodic table shows the trends in electronegativity in periods and groups - it increases across each period and up each group, so fluorine is the most electronegative element, with electronegativity 4.0 (fig 6). Textbooks and databooks give tables of electronegativity values.

Fig 6. Electronegativity trends

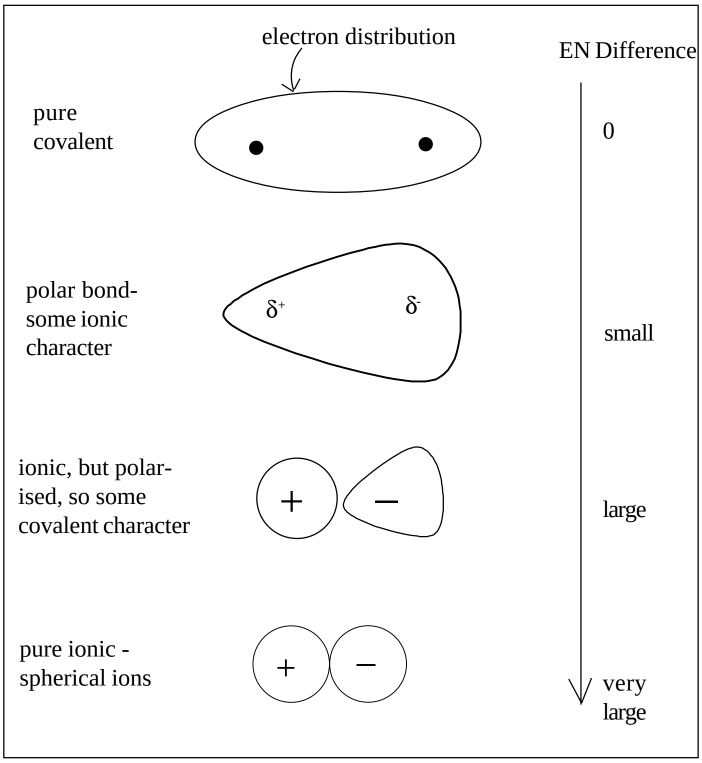


To explain types of bonding think 'differences in EN values' !!

- If the EN difference is **0** (the same atoms, e.g. Cl – Cl) there will be a **pure covalent bond**.
- If the EN difference is **very large** there will be a complete transfer of electrons causing an **ionic bond**.

The diagram shows the effect of EN differences on bond – types (Fig 7).

Fig 7. EN difference and bonding



The diagram shows the change from pure covalent through **intermediate bond-types** to pure ionic. It is vital that you understand that whilst you have seen a few examples of pure covalent and pure ionic (to illustrate these bond types) in reality most bonds lie somewhere in between the two.

We can now explain why $AlCl_3$ is covalent - the EN difference between Al and Cl is not large enough to cause the transfer of electrons from Al to Cl, therefore bonding is covalent not ionic. However, it will be a polar covalent bond, since there is an EN difference.

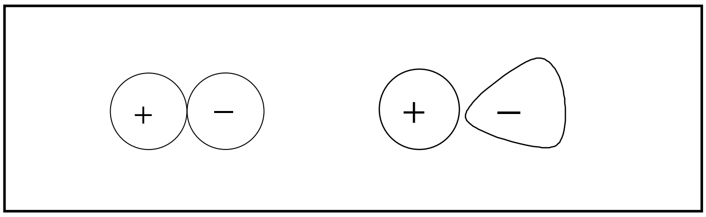
Intermediate bonds

We need to look in more detail at the 2 intermediate bond types shown in Fig 7.

1. Polarization of anions

Pure ionic compounds have ions which are perfectly spherical. However, if there is a large difference in **charge density** between the cation and the anion, then the anion (because it has the extra electron cloud) becomes distorted by the pull of the cation. (Fig 8).

Fig 8. Electron cloud distortion



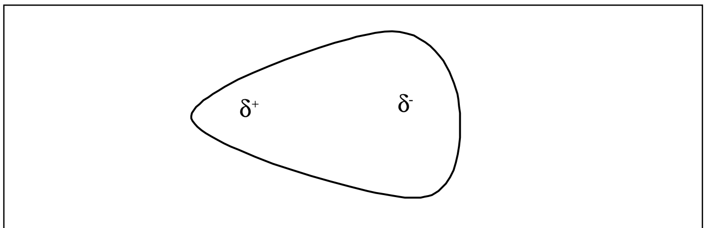
This is called **polarization** of the anion and **Fajan's Rules** explain the effect of ion size and ion charge in this situation:

Fajan's Rules: An ionic compound will have appreciable covalent character if:
- ***either the anion or the cation is highly charged*** *(as this would make the cation highly polarising and the anion highly polarisable)*
- ***the cation is small*** *(so it will have a high charge density)*
- ***the anion is large*** *(so the electrons are far from the nucleus and hence less under its control)*

2. Polar covalent molecules

In a molecule differences in electronegativity between the bonded atoms leads to the bond pair of electrons being pulled towards the more electronegative atom (Fig 9).

Fig 9. Polarised covalent bond



The atoms gain a small charge because of this electron shift (δ = "delta", is used to show a small amount). The existence of this δ+ and δ- within a bond is called a **dipole**.
- If these δ+ and δ- charges are spread symmetrically in a molecule there is no **overall** polarity (Fig 10).
- Unsymmetrical molecules containing polar bonds will be **polar molecules** and are described as having a **permanent dipole**. (Fig 11)

Fig 10. Molecules with polarised covalent bonding, but no dipole

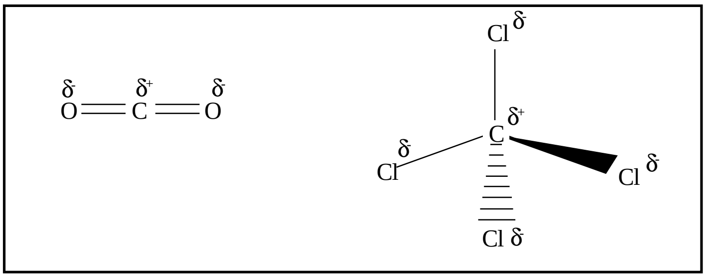
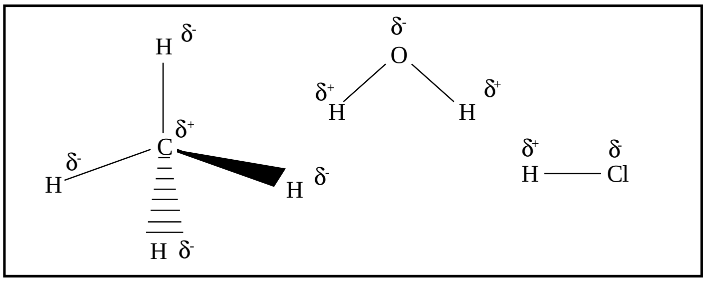


Fig 11. Molecules with permanent dipoles



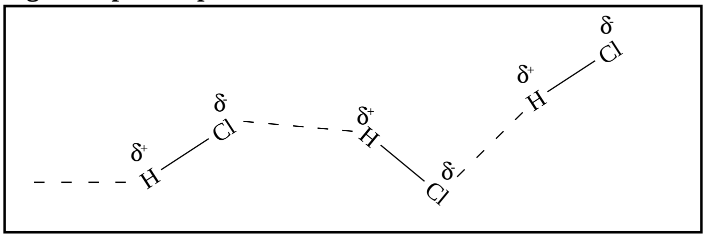
The existence of permanent dipoles of molecules means that the positive and negative ends of these molecules will be attracted to these on other molecules, leading to **inter-molecular forces.**

Inter-molecular forces

There are 3 types of intermolecular forces (bonds between molecules).

1. Permanent dipole – Permanent dipole attraction - the negative part of one molecule is attracted to the positive part of another, hence there is a bond between the molecules.

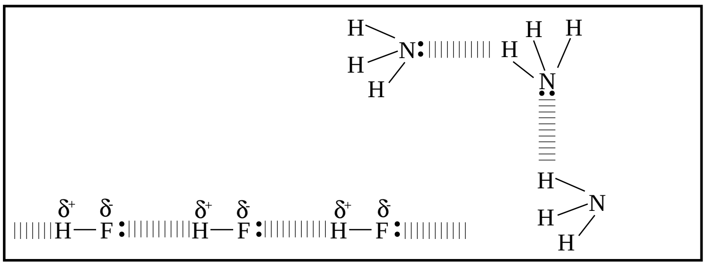
Fig 12. Dipole - dipole attraction



2. Hydrogen Bonding - This is a special case of permanent dipole – permanent dipole bonding.
- The "δ+" is always on a **hydrogen** atom.
- The "δ –" is on one of the three most electronegative atoms - **nitrogen,oxygen or fluorine**

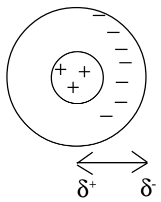
The high EN difference results in the N, O or F atom having a much greater "share" of the electrons than the H atom. As hydrogen only has electrons in the lowest energy level, this results in its nucleus being unshielded. The O, N or F atom has lone pair(s), which are attracted strongly to the hydrogen nucleus. (See Factsheet 4 Shapes of molecules for more on lone pairs)

Fig 13. Hydrogen bonds



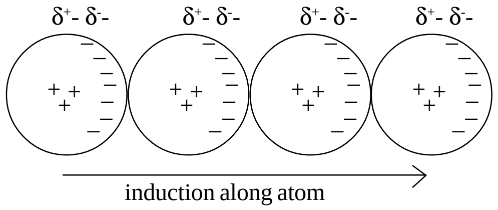
3.Temporary Dipoles/ Van der Waals (VdW) Forces - If you consider an atom to be a central positive nucleus surrounded by electrons which are constantly in motion , there will at any one time be at least one atom whose electrons are on one side or the other. This causes a **temporary dipole** within the atom itself.

Fig 14. Temporary dipoles



This atom will affect the other atoms around it producing induced dipoles (Fig 15).

Fig 15. Induced dipoles



Therefore there will be attraction between atoms or molecules that have no permanent dipole. This weak force explains many structural and physical properties e.g. – the properties of graphite, different boiling points of the elements etc.

*** All molecules have VdW Forces in them ***

> ***Remember -*** in terms of strength of intermolecular forces:
>
> H-Bonds → Permanent dipole → Temporary dipole

The strength of the Van der Waals forces increases with the number of electrons in the atom or molecule, since the temporary dipoles can be of a larger size if there are more electrons. For noble gases such as helium or neon, which exist as single atoms and have relatively few electrons, the forces are weak - this explains the very low boiling point of these gases.

The strength also depends on the shape of the molecule - long molecules can have induced temporary dipoles all along them. In general, larger molecules will have larger Van der Waals forces.

Practice Questions

1. Silicon tetrachloride, $SiCl_4$, is a colourless liquid. The individual bonds are polar, but the molecule is not. Explain these facts.

2. Explain what is meant by the following
   (a) Ionic bond (b) Covalent bond (c) Dative covalent bond

3. Indicate whether each of the following molecules has an overall polarity.
   (a) Carbon dioxide (b) Ethanoic acid (c) Ethane
   (d) Propanone (e) Trichloromethane (f) Tetrachloromethane
   (g) Ethanol

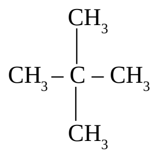
4. Explain why aluminium iodide is covalent but aluminium fluoride is ionic.

5. (a) Which chloride of the Group 2 elements would you expect to have the greatest degree of covalency?
   (b) Explain the reasons for your choice of chloride in part (a).

6. What type of bonding is present in each of the following?
   (a) Bromine
   (b) Caesium fluoride
   (c) Ammonia

7. HCl is very soluble in water, but HF is not. Explain the difference in properties.

8. Explain why $CH_3(CH_2)_3 CH_3$ has a higher boiling point than its isomer



9. Hydrogen sulphide, H_2S, is a gas while the lighter molecule, water, H_2O, is a liquid. Explain this difference in physical properties.

Answers

1. Si and Cl have different ENs so bonds are polar
   Si Cl_4 is tetrahedral - it is symmetrical so no overall polarity

2. (a) The complete transfer of electrons from one atom to another
   (b) A shared pair of electrons where each atom donates one electron
   (c) A shared pair of electrons where one atom donates both electrons

3. (a) N (b) Y (c) N (d) Y (e) Y (f) N (g) Y

4. The difference in ENs between Al and I is small
   so leading to electron sharing i.e. covalent bonding
   The difference in ENs between Al and F is large
   so leading to a complete transfer of electrons/ionic bonding

5. (a) $BeCl_2$
   (b) Be is a small atom
   Be is more polarising
   EN differences between Be and Cl is small

6. (a) pure covalent
   (b) pure ionic
   (c) covalent with partial ionic/ polar character

7. HF has strong H-bonding so hard to break when put into water
   HCl is polar - bond breaks with water molecules

8. The linear molecule has larger Van der Waals forces
   because of the induction effect along the chain
   The molecule which has smaller chain lengths has less VdW forces

9. H_2O has H-bonding which leads to strong intermolecular forces which require energy to break
   H_2S has no H-bonding so less energy is needed to vaporise it.

Acknowledgements:
This Factsheet was researched and written by Sam Goodman & Kieron Heath
Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF
ChemistryFactsheets *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber.*
No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher. ***ISSN 1351-5136***