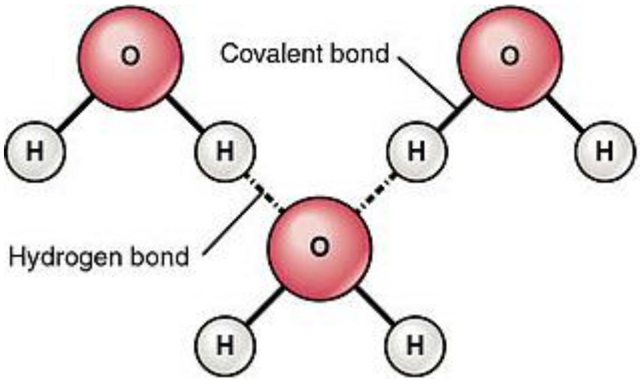
UNIT 2

PARTICLES, BONDING AND STRUCTURE

PART 2 – INTERATOMIC AND INTERMOLECULAR BONDING



Contents

Key words: ionic bond, Lewis-dot structure, covalent bond, dative covalent bond, metallic bond, electronegativity, polar covalent bond, temporary dipole, induced dipole, permanent dipole, Van der Waal's force, polar molecule, non-polar molecule, hydrogen bond

Units which must be completed before this unit can be attempted:
Unit 1 – Atomic Structure and the Periodic Table

1) Ionic Bonding

An ionic bond is an attraction between oppositely charged ions.

Most simple ions are formed when electrons are transferred from one atom to another. In general, atoms in Groups I, II and III lose electrons, and atoms in Group V, VI and VII gain electrons.

Atoms in Groups I, II and III of the Periodic Table tend to form positively charged ions (cations) by losing all of the electrons in their outer shell:

Na would lose one electron to form Na^+
Mg would lose two electrons to form Mg^{2+}
Al would lose three electrons to form Al^{3+}

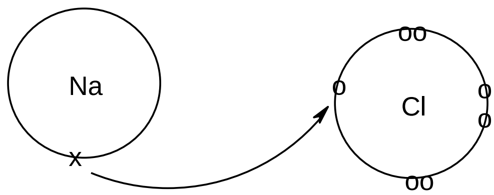
Simple positive ions have the same name as the atom they were formed from, so Na^+ is a sodium ion and Mg^{2+} is a magnesium ion.

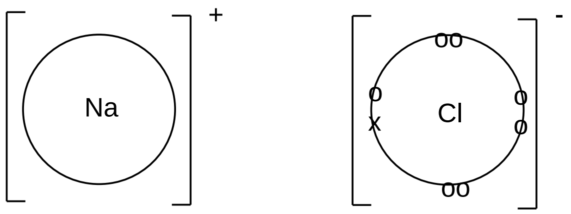
Atoms in Groups V, VI and VII of the Periodic Table tend to form negatively charged ions (anions) by gaining electrons until their outer shell is full:

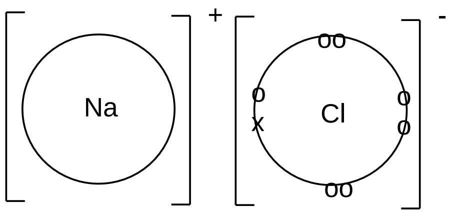
Cl would gain one electron to form Cl^-
O would gain two electrons to form O^{2-}
N would gain three electrons to form N^{3-}

Simple negative ions are named by combining the first syllable of the atom they were formed from and then adding the ending "ide", so Cl^- is a chloride ion and O^{2-} is an oxide ion.

Eg In sodium chloride, each sodium atom transfers an electron to a chlorine atom. The result is a sodium ion and a chloride anion. These two ions attract each other to form a stable compound.





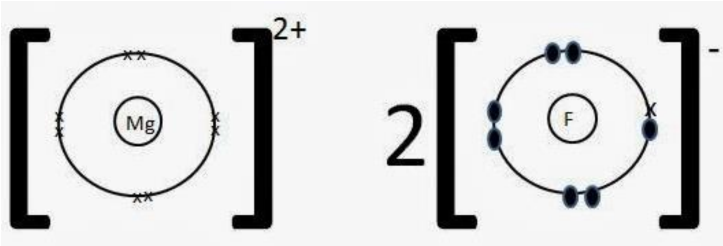


sodium chloride (NaCl)

The representation of ionic compounds as above, showing the outer electrons and charges on the ions, is an example of a **Lewis dot structure** (or dot-cross diagram).

In magnesium chloride, the Mg loses two electrons. It give one electron each to two different chlorine atoms to form $MgCl_2$:

Lewis dot structure for magnesium chloride (MgF_2):



Test Your Progress: Topic 2 Part 2 Exercise 1

Deduce the formula, and draw the Lewis dot structure, of the following compounds:

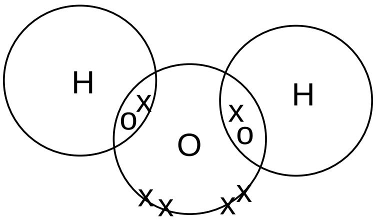
1. sodium oxide
2. calcium sulphide
3. aluminium bromide
4. potassium nitride
5. aluminium oxide

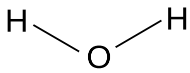
2) Covalent bonding

A covalent bond is a pair of electrons shared between two atoms.

In a normal covalent bond, each atom provides one of the electrons in the bond. A covalent bond is represented by a short straight line between the two atoms.

Eg water



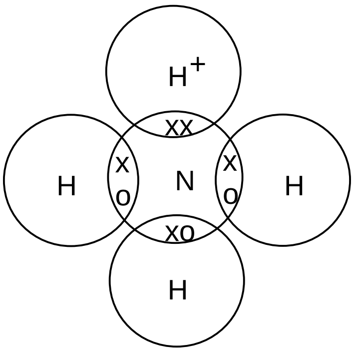


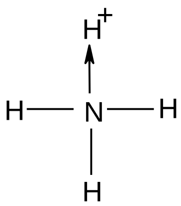
In a dative covalent bond, one atom provides both electrons to the bond.

A dative covalent bond is a pair of electrons shared between two atoms, one of which provides both electrons to the bond.

A dative covalent bond is represented by a short arrow from the electron providing both electrons to the electron providing neither.

Eg ammonium ion





Covalent bonding happens because the electrons are more stable when attracted to two nuclei than when attracted to only one.

A small group of two or more atoms held together by covalent bonds is called a **molecule**. Covalent bonding usually results in the formation of molecules.

Test Your Progress: Topic 2 Part 2 Exercise 2

Draw the Lewis dot structure of the following molecules:

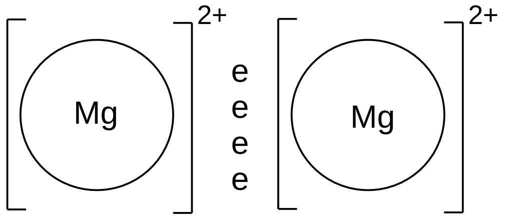
1. H_2	2. HCl	3. H_2O	4. CH_4	5. NH_3
6. O_2	7. N_2	8. CO_2		
Extension:	9. O_3	10. CO		

3) Metallic bonding

A metallic bond is an attraction between cations and a sea of electrons.

Metallic bonds are formed when atoms lose electrons and the resulting electrons are attracted to all the resulting cations.

Eg Magnesium atoms lose two electrons each, and the resulting electrons are attracted to all the cations.



Sodium atoms lose one electron each and aluminium atoms lose three electrons each.

Metallic bonding happens because the electrons are attracted to more than one nucleus and hence more stable. The electrons are said to be delocalized – they are not attached to any particular atom but are free to move between the atoms.

4) Electronegativity

(i) Introduction to electronegativity

The type of bond formed between two atoms depends on the relative ability of the two atoms to attract the electrons in the bond, or the **electronegativity** of the atom.

Electronegativity is the relative ability of an atom to attract electrons in a bond.

The electronegativity of an atom depends on its ability to attract electrons (measured by electron affinity) and its ability to hold onto electrons (measured by ionisation energy).

If the ionisation energy and electron affinity are high, the atom attracts bonding electrons strongly and is said to have a high electronegativity. These atoms are said to be electronegative.

If the ionisation energy and electron affinity are low, the atom does not attract bonding electrons strongly and is said to have a low electronegativity. These atoms are said to be electropositive.

Electronegativity increases across a period as the nuclear charge on the atoms increases but the shielding stays the same, so the electrons are more strongly attracted to the atom. **Electronegativity decreases down a group** as the number of shells increases, so shielding increases and the electrons are less strongly attracted to the atom.

Electronegativities are relative; electronegativity has no units and is measured on a scale from 0.7 to 4.0. The electronegativities of some elements in the periodic table are shown below:

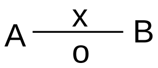
									H 2.1								He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr

Note that the noble gases cannot be ascribed an electronegativity since they do not form bonds.

(ii) Using electronegativities

Electronegativity is a very useful concept for predicting whether the bonding between two atoms will be ionic, covalent or metallic.

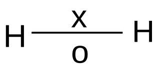
Consider a covalent bond between two atoms A and B.



Example 1 – both atoms have the same, high electronegativity

If both atoms have a similar electronegativity, both atoms attract the electrons with similar power and the electrons will remain midway between the two. The bond will thus be covalent - the electrons are shared between the two atoms.

Eg H (2.1) and H (2.1)

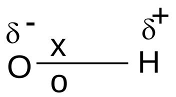


a pure covalent bond

Example 2 – both atoms have slightly different electronegativities

If one atom is significantly more electronegative than the other, it attracts the electrons more strongly than the other and the electrons are on average closer to one atom than the other. The electrons are still shared, but one atom has a slight deficit of electrons and thus a slight positive charge and the other a slight surplus of electrons and thus a slight negative charge. Such a bond is said to be a **polar covalent bond**. The positive charge on one end of the bond and the negative charge on the other end of the bond is called a **dipole**.

Eg H (2.1) and O (3.0)



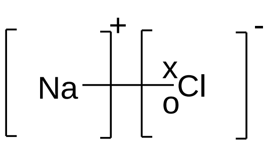
a polar covalent bond

A partial positive charge or negative charge on an atom is represented by a δ^+ or a δ^- symbol respectively.

Example 3 – both atoms have very different electronegativities

If the difference between the two atoms is large, then the sharing of electrons is so uneven that the more electronegative atom has virtually sole possession of the electrons. The electrons are, in effect, not shared at all but an electron has essentially between transferred from one atom to the other. The more electropositive atom is positively charged and the more electronegative atom is negatively charged. The bonding is thus ionic.

Eg Na (0.9) and Cl (3.0)

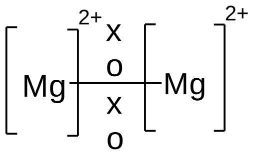


an ionic bond

Example 3 – both atoms have low electronegativities

If both atoms are electropositive, neither has a great ability to attract electrons and the electrons do not remain localised in the bond at all. They are free to move, both atoms gain a positive charge and the bonding is metallic.

Eg Mg (1.2) and Mg (1.2)



a metallic bond

Given suitable electronegativity data, it is thus possible to predict whether a bond between two atoms will be ionic, polar covalent, covalent or metallic by using the following simple rules:

If both atoms have electronegativities less than 2.0 then the bond is metallic.
If both atoms have the same electronegativity higher than 2.0 then the bond is pure covalent.
If the atoms have different electronegativities, at least one of the atoms has an electronegativity greater than 1.9 and the electronegativity difference is less than 1.8, then the bond is polar covalent.
If the atoms have an electronegativity difference greater than 1.8 then the bond is ionic.

These rules are not perfect and there are notable exceptions; for example the bond between Si (1.8) and Si (1.8) is covalent but the bond between Cu (1.9) and Cu (1.9) is metallic. The bond between Na (0.9) and H (2.1) is ionic but the bond between Si (1.8) and F (4.0) is polar covalent. However as basic giudelines they are very useful provided that their limitations are appreciated.

Note that:

- bonds between identical atoms cannot be ionic as there is no difference in electronegativity; they will therefore be either covalent or metallic
- bonds between non-identical atoms are all essentially intermediate in character (ionic-covalent or covalent-metallic)
- if both atoms have high electronegativity, the bond is mostly covalent; if both have low electronegativity, the bond is mostly metallic; if one atom has high electronegativity and the other has low electronegativity, the bond is mostly ionic

Test Your Progress: Topic 2 Part 2 Exercise 3

Use the electronegativity values in the table above to deduce whether the bonds between the following pairs of atoms are likely to be ionic, covalent, polar covalent or metallic:

1. Be and F	2. Be and Cl	3. Al and Al	4. Al and Cl	5. Mg and Cl
6. H and Cl	7. Mg and O	8. C and C	9. H and N	10. C and H

5) Molecular shapes

When an atom forms more than one covalent bond, the two covalent bonds arrange themselves at a very specific angle. The angles between the covalent bonds in a molecule result in the molecule having a characteristic shape.

When an atom forms a covalent bond with another atom, the electrons in the different bonds and the non-bonding electrons in the outer shells of the atom repel each other. In order to minimise this repulsion, all the outer shell electrons spread out as far apart in space as possible. The resulting molecular shapes, and the angles between the covalent bonds, can be predicted by the VSEPR theory (VSEPR = valence shell electron pair repulsion).

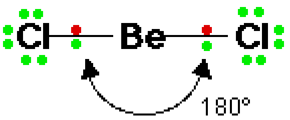
VSEPR theory consists of two basic rules:

i) All bonded electron pairs and all lone pairs arrange themselves as far apart in space as is possible. Double bonds are counted as one pair of electrons for the purposes of determining shapes.
ii) Lone pairs repel more strongly than bonding pairs and result in the angle between the bonds becoming slightly smaller.

These two rules can be used to predict the shape of any covalent molecule or ion, and the angles between the bonds.

a) 2 electron pairs

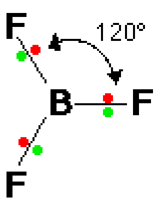
If there are two electron pairs on the central atom, the angle between the bonds is 180°.

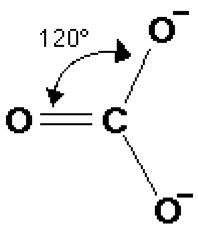


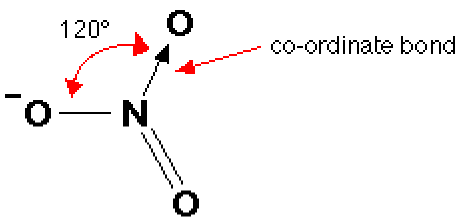
Molecules which adopt this shape are said to be LINEAR.
E.g. $BeCl_2$, CO_2

b) three electron pairs

If there are three electron pairs on the central atom, the angle between the bonds is 120°.



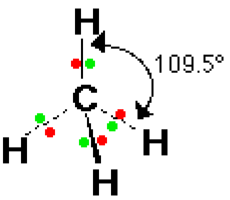


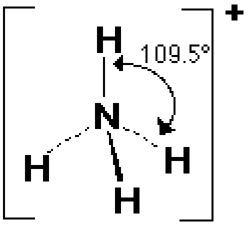


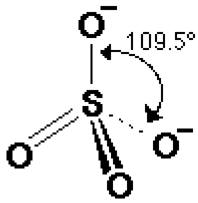
Molecules which adopt this shape are said to be TRIGONAL PLANAR.
E.g. BF_3, $AlCl_3$, CO_3^{2-}, NO_3^-

c) Four electron pairs

If there are four bonded pairs on the central atom, the angle between the bonds is approx 109°.

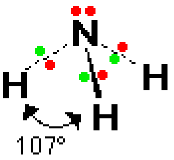






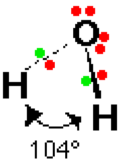
Molecules which adopt this shape are said to be TETRAHEDRAL.
E.g. CH_4, $SiCl_4$, NH_4^+, SO_4^{2-}

If one of the electron pairs is a lone pair, the bond angle is slightly less than 109°, due to the extra lone pair repulsion which pushes the bonds closer together (approx 107°).



Molecules which adopt this shape are said to be PYRAMIDAL.
E.g. NH_3, PCl_3

If two of the electron pairs are lone pairs, the bond angle is also slightly less than 109°, due to the extra lone pair repulsion (approx 104°).

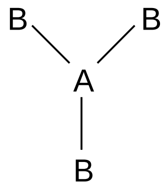
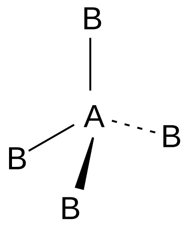
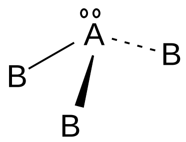
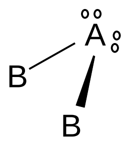


Molecules which adopt this shape are said to be NON-LINEAR.
E.g. H_2O, OF_2

d) Diatomic molecules

Molecules such as H_2 and O_2, which only contain two atoms and one bond, are generally described as **linear**.

e) Summary of molecular shapes

Valence shell electron pairs around central atom	Bonding Pairs around central atom	Lone Pairs around central atom	Shape	Bond Angle (º)
2	2	0	LINEAR 	180
3	3	0	TRIGONAL PLANAR 	120
4	4	0	TETRAHEDRAL 	109.5
4	3	1	PYRAMIDAL 	107
4	2	2	NON-LINEAR 	104.5

Test Your Progress: Topic 2 Part 2 Exercise 4

Draw Lewis-dot structures for the following molecules, and then draw and name their shapes:

1. $BeCl_2$
2. BF_3
3. CH_4
4. PCl_3
5. H_2S
6. H_2
7. $SiCl_4$
8. NH_3
9. O_2
10. CO_2

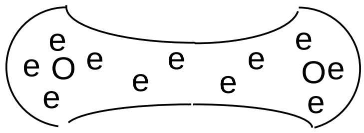
6) Intermolecular Forces

When atoms form covalent bonds with other atoms to form molecules, these molecules act as discrete particles and there are no strong bonds (covalent, ionic or metallic) holding the different molecules together.

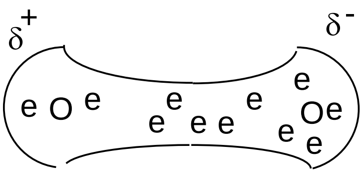
There are, however, weaker forces of attraction between these molecules, and it is these which must be overcome when the substance melts or boils. These forces are known as **intermolecular forces**. There are two main types of intermolecular force:

(a) Van der Waal's forces

Consider a molecule of oxygen, O_2.

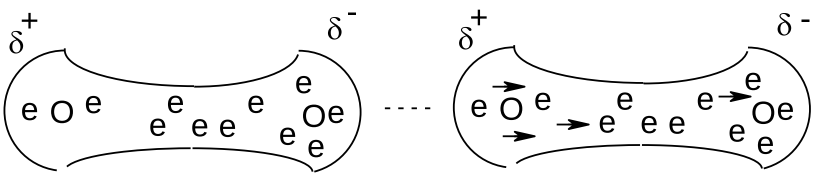


The electrons in this molecule are not static; they are in a state of constant motion. It is therefore likely that at any given time the distribution of electrons will not be exactly symmetrical - there is likely to be a slight surplus of electrons on one of the atoms.



This is known as a **temporary dipole**. It lasts for a very short time as the electrons are constantly moving. Temporary dipoles are constantly appearing and disappearing.

Consider now an adjacent molecule. The electrons on this molecule are repelled by the negative part of the dipole and attracted to the positive part, and move accordingly.

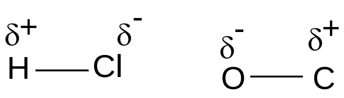


This is known as an **induced dipole**.

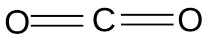
There is a resulting attraction between the two molecules, and this known as a **Van der Waal's force**.

Temporary and induced dipoles exist in all molecules, but in some molecules there is also a **permanent dipole**.

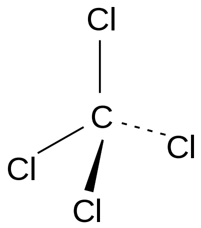
In most covalent bonds there is a difference in electronegativity between the atoms. This causes the covalent bond to be polar and results in a dipole.



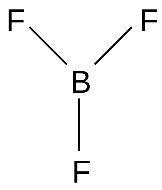
In many cases, however, the presence of polar bonds (dipoles) does not result in a permanent dipole on the molecule, as there are other polar bonds (dipoles) in the same molecule which have the effect of cancelling each other out. This effect can be seen in a number of linear, planar and tetrahedral substances:



CO_2



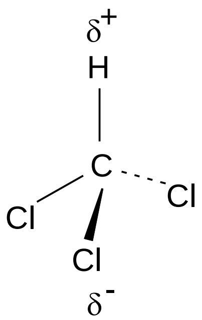
CCl_4



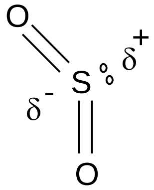
BF_3

In all the above cases, there are dipoles resulting from polar bonds but the vector sum of these dipoles is zero; i.e. the dipoles cancel each other out. The molecule thus has no overall permanent dipole and is said to be **non-polar**. The Van der Waal's forces in these molecules will result from temporary dipoles and induced dipoles only.

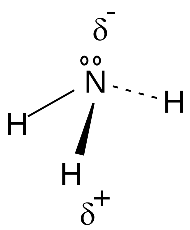
Some molecules, however, contain covalent bonds with dipoles which do not cancel each other out:



$CHCl_3$



SO_2



NH_3

In all the above cases, there are dipoles resulting from polar bonds whose vector sum is not zero; i.e. the dipoles do not cancel each other out. The molecule thus has a **permanent dipole** and is said to be **polar**.

The attraction between two molecules with permanent dipoles is another type of Van der Waal's force. Molecules with permanent dipoles attract each other slightly more strongly than similar molecules which only have temporary and induced dipoles.

Van der Waal's forces are present between all molecules, although they can be very weak. They are the reason all compounds can be liquefied and solidified. Van der Waal's forces tend to have strengths between 1 $kJmol^{-1}$ and 50 $kJmol^{-1}$.

The strength of the Van der Waal's forces in between molecules depends on two factors:

- the number of electrons in the molecules

The greater the number of electrons in a molecule, the greater the likelihood of a distortion and thus the greater the frequency and magnitude of the temporary dipoles. Thus the Van der Waal's forces between the molecules are stronger.

- Surface area of the molecules

The larger the surface area of a molecule, the more contact it will have with adjacent molecules. Thus the greater its ability to induce a dipole in an adjacent molecule and the greater the Van der Waal's forces.

- The existence of permanent dipoles on the molecules

If the molecule has a permanent dipole, there is a slightly stronger attraction between the molecules than there would have been if there were only temporary and induced dipoles. Thus the Van der Waal's forces between the molecules are stronger.

(b) Hydrogen Bonding

In most cases, the presence of permanent dipoles only makes a slight difference to the magnitude of the intermolecular forces. There is one exceptional case, however, where the permanent dipole makes a huge difference to the strength of the bonding between the molecules.

Consider a molecule of hydrogen fluoride, HF. This clearly has a permanent dipole as there is a large difference in electronegativity between H (2.1) and F (4.0). The electrons in this bond are on average much closer to the F than the H:

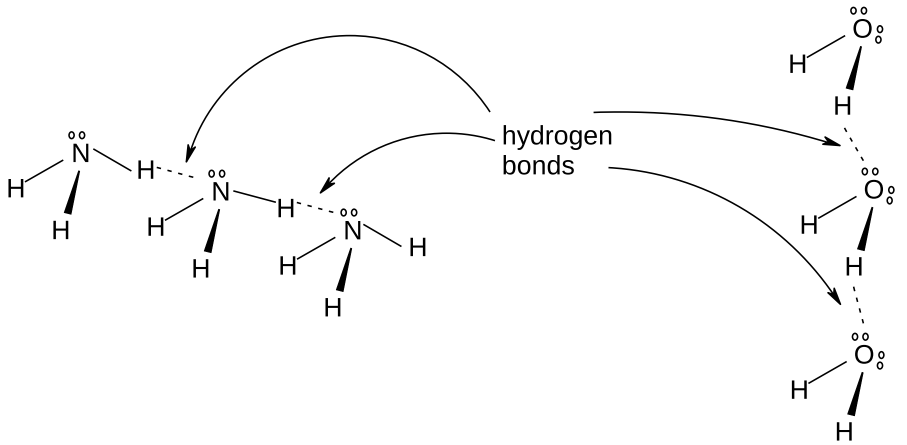
$$\overset{\delta+}{H} — \overset{\delta-}{F}$$

The result of this is that the H atom has on almost no electron density around its nucleus at all and is therefore very small. The H atom is therefore able to approach electronegative atoms on adjacent molecules very closely and form a very strong intermolecular dipole-dipole bond.

H —— F - - - - H —— F - - - - H —— F

This is known a **hydrogen bond**. It is only possible if the hydrogen atom is bonded to a very electronegative element; i.e. N, O or F. **A hydrogen bond is an attraction between an electropositive hydrogen atom (ie covalently bonded to N, O or F) and an electronegative atom on an adjacent molecule.**

Examples of molecules which are held together by hydrogen bonds are HF, H_2O and NH_3,



Molecules which can form hydrogen bonds with each other tend to attract each other more strongly than molecules of similar size which cannot form hydrogen bonds with each other.

Test Your Progress: Topic 2 Part 2 Exercise 5

1. Draw the shapes of the following molecules, state whether they are polar and draw any permanent dipole on the molecule:
   (a) $BeCl_2$ (b) BF_3 (c) CH_4 (d) PCl_3 (e) H_2S
   (f) H_2 (g) HCl (h) NH_3 (i) HF (j) CO_2

2. Deduce which of the molecules in Question 1 can form hydrogen bonds.