BONDING

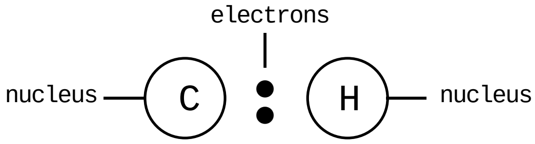
All bonds between atoms are the result of the pairing of unpaired electrons. The negative electrons on one atom attract the positive nucleus of the other. This attractive force (electronegativity) increases across a period (L -> R) and decreases slightly down a group (T -> B).

The Hydrides

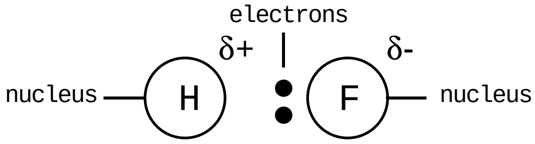
Li^+H^-	BeH_2	B_2H_6	CH_4	NH_3	OH_2	FH
Na^+H^-	$Mg^{2+}(H^-)_2$	$(AlH_3)_n$	SiH_4	PH_3	SH_2	ClH

Hydrogen's electronegativity is abnormally high because it is such a small atom. The bonding electrons are thus very close to the nucleus and therefore more strongly attracted. Hydrogen's electronegativity is about the same as Carbon's.

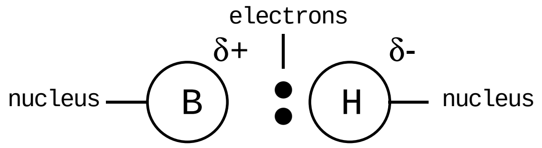
When Hydrogen is bonded to an atom of about the **same** electronegativity, e.g. Carbon or Silicon, the electron pair is equally shared between the two atoms and there is no charge at either end of the bond. We call this type of bond a **non-polar covalent bond**.



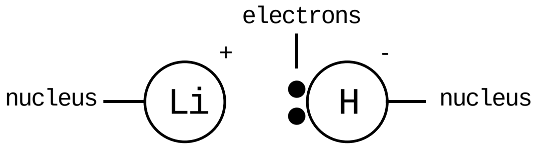
When Hydrogen is bonded to an atom of **higher** electronegativity, e.g. Fluorine, Hydrogen has the lower attraction for electrons and the electron pair is therefore distorted away from Hydrogen, making this end of the bond slightly positive δ+, and towards Fluorine making this end of the bond slightly negative δ-. We call this type of bond a **polar covalent bond**.



When Hydrogen is bonded to an atom of **lower** electronegativity, e.g. Boron, Hydrogen now has the greater attraction for electrons and the electron pair is therefore distorted towards Hydrogen, making this end of the bond slightly negative δ-, and away from Boron making this end of the bond slightly positive δ+. A polar covalent bond containing negative Hydrogen is the result.



Notice that if Hydrogen is bonded to an atom of **very much lower** electronegativity, e.g. Lithium, the electron pair is pulled completely off Lithium on to Hydrogen resulting in an electrovalent bond:



There is therefore an increasing distortion of electrons towards Hydrogen as we go left, away from CH_4 to Li^+H^-.

There is a corresponding increasing distortion of electron away from Hydrogen as we go right, away from CH_4 to FH.

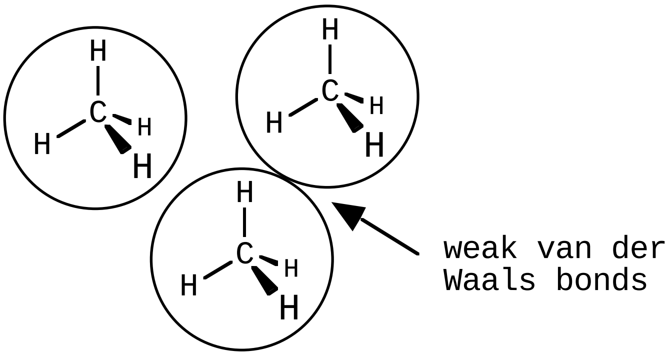
Li^+H^-	BeH_2	B_2H_6	CH_4	NH_3	OH_2	FH
Na^+H^-	$Mg^{2+}(H^-)_2$	$(AlH_3)_n$	SiH_4	PH_3	SH_2	ClH
	negative H		neutral H		positive H	

Physical properties of the hydrides

Physical properties depend on bonding:

- Non-polar covalent hydrides e.g. CH_4

  van der Waals bonds between the molecules are very weak since there are no charged atoms to attract:

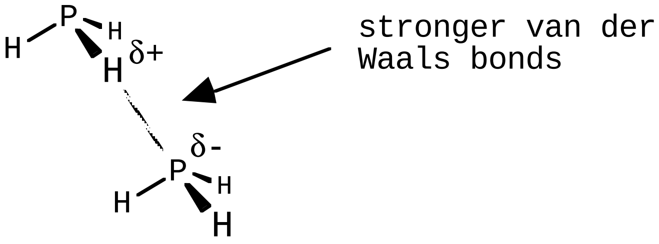


  Melting points and boiling points are therefore very low
  e.g. CH_4 MP = - 182 ^{0}C ; BP = - 161 ^{0}C

  These hydrides are non-conductors of electricity since they do not contain ions or delocalised electrons.

- Polar covalent hydrides e.g. PH_3

  van der Waals bonds between the molecules are slightly stronger since there are charged atoms which can attract:

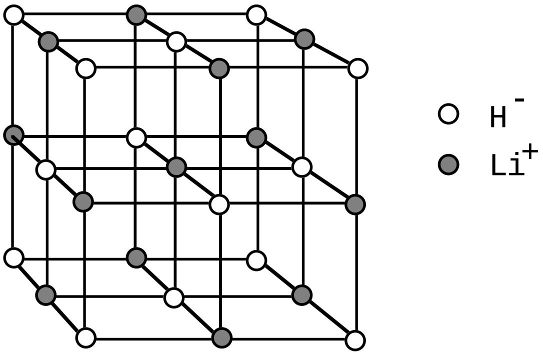


  Melting points and boiling points are correspondingly higher:
  e.g. PH_3 MP = - 132 ^{0}C ; BP = - 87 ^{0}C

  These hydrides are also non-conductors of electricity since they do not contain ions or delocalised electrons.

- Electrovalent hydrides e.g. Li^+H^-

There are no molecules - just giant lattices held together by the attraction between oppositely charged ions. Melting points and boiling points are therefore very high.



e.g. Li^+H^- MP = + 688 ⁰C (decomposes at higher temperatures)

These hydrides are non-conductors of electricity in the solid state but do conduct when molten when the ions are free to move.

Electrolysis of molten Lithium hydride produces Hydrogen at the positive electrode:

$$2\ H^- \rightarrow H_2 + 2e$$

The Hydride Ion

The H^- ion is both **base** and **reducing agent** (reducing in the sense of 'adding Hydrogen')

As a **base** it will react vigorously with the H^+ ions in Water:

$$Li^+H^- + H_2O \rightarrow Li^+OH^- + H_2$$

As a **reducing agent** it will convert carbonyl compounds into alcohols in two stages e.g.

$$Li^+H^- + H_2C{=}O \rightarrow CH_3O^-Li^+$$

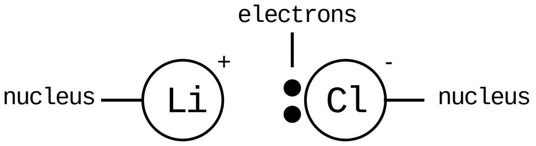
$$CH_3O^-Li^+ + H_2O \rightarrow CH_3OH + Li^+OH^-$$

The Chlorides

Li^+Cl^-	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	FCl
Na^+Cl^-	$Mg^{2+}(Cl^-)_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	

Since Chlorine is so electronegative, polarisation of bonds is towards Chlorine resulting in negative Cl atoms.

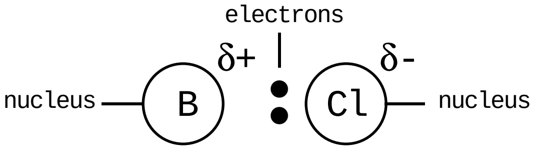
When the other atom is towards the left of the periodic table, and therefore of much lower electronegativity than Chlorine, Chlorine is able to pull the electrons completely off the other atom forming ions e.g. $Li+Cl-$



Note that electrovalent bonding is more likely when large metal atoms bond to small non-metal atoms. When the metal atom is large the outer electrons are far from the nucleus and therefore less strongly held. When the non-metal atom is small the electrons are added closer to the nucleus and therefore more strongly held.

e.g. Li^+Cl^- has more electrovalent character than Li^+I^-
Cs^+Cl^- has more electrovalent character than Li^+Cl^-

When the other atom is towards the right of the periodic table, it has a greater attraction for electrons. Chlorine is only able to partially distort the electrons towards itself forming polar covalent chlorides e.g. BCl_3.



There is thus an increasing distortion of electrons towards Chlorine as we go left away from FCl to Li^+Cl^-.

Li^+Cl^-	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	FCl
Na^+Cl^-	$Mg^{2+}(Cl^-)_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	

Electrovalent Chlorides

These occur when the electronegativity of Chlorine is **very much greater** than the electronegativity of the element it is bonded to. Electrovalent chlorides can be made by direct combination of the elements e.g.

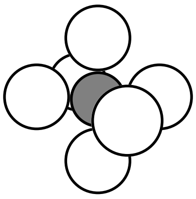
$Na + Cl_2 \rightarrow Na^+Cl^-$

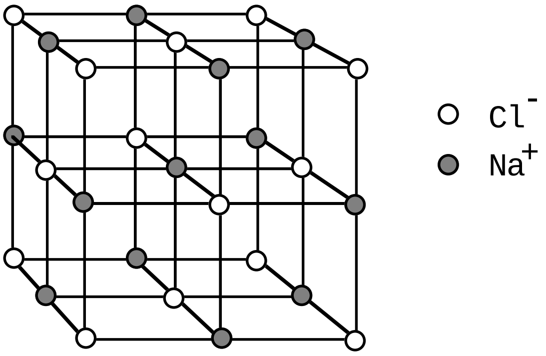
They do not react with Water --- they simply dissolve.

Electrovalent chlorides have high melting points and boiling points and conduct electricity when molten or in solution.

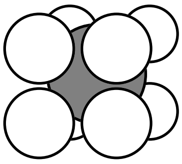
Group 1 metal chlorides can have two structures dependant on the size of the metal ion.

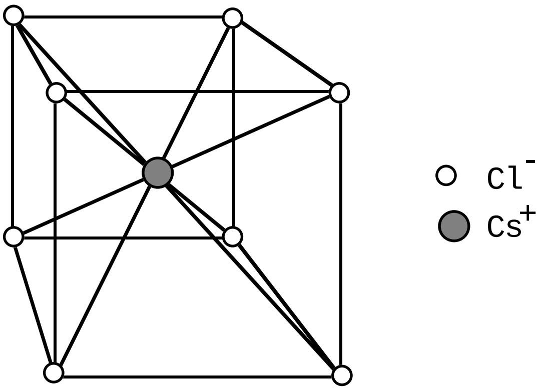
Small metal ions like Li^+ and Na^+ can only pack 6 Cl^- around themselves resulting in the 'Sodium chloride' structure:





Large metal ions like Cs^+ and NH_4^+ can pack 8 Cl^- around themselves resulting in the 'Caesium chloride' structure:

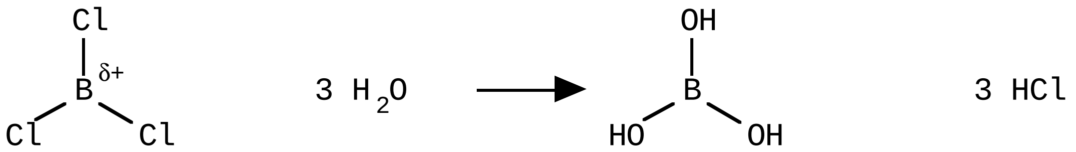




Polar Covalent Chlorides

These occur when the EAP of Chlorine is **slightly greater** than the EAP of the element it is bonded to.

They react with Water. The OH^- ions in the Water attack the $\delta+$ centres leaving excess H^+ ions. Thus acidic solutions are formed e.g.



Polar covalent chlorides have low melting points and boiling points and do not conduct electricity.

The Oxides

$(Li^+)_2O^{2-}$	BeO	B_2O_3	CO_2	N_2O_5		F_2O
$(Na^+)_2O^{2-}$	$Mg^{2+}O^{2-}$	Al_2O_3	SiO_2	P_2O_5	SO_2	Cl_2O

basic oxides amphoteric oxides acidic oxides

Basic oxides

These occur when the electronegativity of Oxygen is **very much greater** than the electronegativity of the element it is bonded to. These are electrovalent oxides. They tend to be oxides of metals.

The strong attractive forces between the ions result in high boiling points and melting points (all are solids at room temperature). All conduct electricity when molten.

They react with Water. The H^+ from Water attacks the O^{2-} ion forming OH^- so alkaline solutions are formed e.g.

$(Na^+)_2O^{2-}$ H_2O -> **2** Na^+OH^-

Acidic oxides

These occur when the electronegativity of Oxygen is **slightly greater** than the electronegativity of the element its bonded to. These are covalent oxides. They tend to be oxides of non-metals.

The majority are liquids or gases at room temperature reflecting the weak attractive forces between the molecules. Melting points and boiling points are low. None conducts electricity in any state.

They react with Water. OH^- from Water attacks the δ+ centre leaving excess H^+ so acidic solutions are formed e.g.

$$SO_2 \quad + \quad H_2O \quad \rightarrow \quad (H^+)_2SO_3^{2-}$$

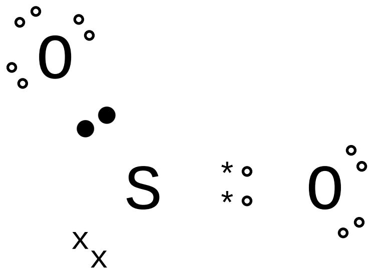
The bonding in Sulphur dioxide is worthy of note:

Sulphur has SIX electrons in the outer energy level.
It uses these electrons to form bonds with Oxygen as follows:

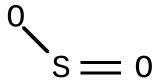
TWO (**) are paired with electrons from O and used to form an S=O bond

TWO (●●) are donated as a pair and used to form an S-O bond.
The two electrons in this bond therefore both come from S - it is known as a **dative covalent bond**.

TWO (x x) are not used in bonding - they are called a **non-bonded pair**.

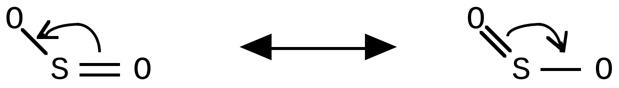


N.B. Oxygen electrons are denoted thus: o
The structure is more usually represented as:

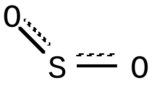


It is puzzling that both SO bonds are the same length - the double bond should be shorter!

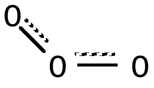
Resonance is believed to occur: a pair of electrons moves backwards and forwards from the double bond into the single bond:



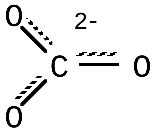
This creates two equivalent bonds of the same length better represented by:



This type of resonance also occurs in Ozone and the carbonate ion:



Ozone O_3



carbonate ion CO_3^{2-}

Amphoteric oxides

These behave as basic oxides if [H^+] is high e.g.

Al_2O_3 **6** H^+ -> **2** Al^{3+} **3** H_2O

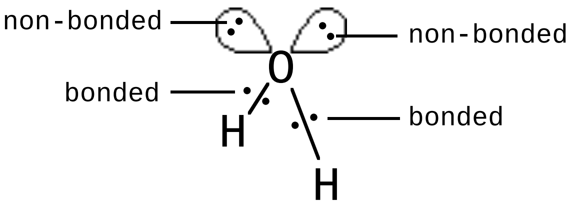
and as acidic oxides if [OH^-] is high e.g.

Al_2O_3 OH^- -> $Al(OH)_4^-$

N.B. [X] means 'the concentration of X'.

THE SHAPES OF MOLECULES

The shape of a molecule is determined by the repulsive forces which act between the pairs of electrons. There are two types of electron pairs : bonded and non-bonded e.g.



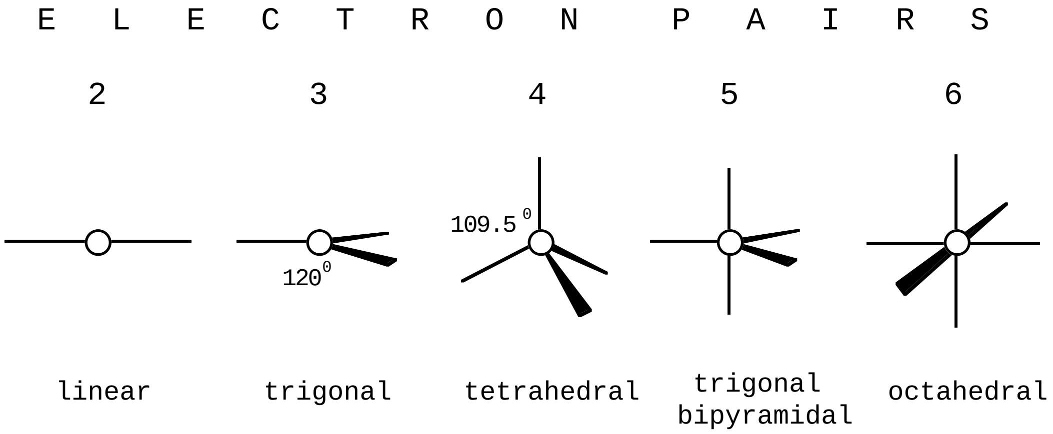
Non-bonded electron pairs are attracted by only one nucleus. They therefore protrude more from the atom and exert a greater repulsive force than bonded electrons. In general two non-bonded pairs repel each other most, a bonded/non-bonded pair repels less and two bonded pairs repel least of all. The molecule will assume a shape which minimises these repulsions.

Rules for determining molecular shape:

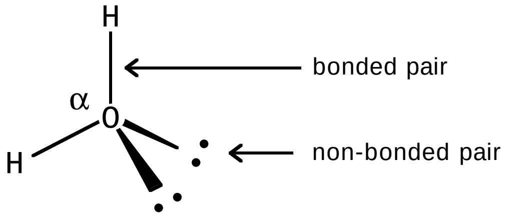
First we must calculate the number of electron pairs in the valence state. In the Water molecule there are 4 electron pairs : 2 bonded and 2 non-bonded.

	H_2O example
1. Deduce the number of electrons contributed by the central atom. This is the number in the outer quantum level.	6
2. Each atom bonded to the central atom contributes 1 electron.	2
3. Add 1 electron for each negative charge on the molecule.	0
4. Subtract 1 electron for each positive charge on the molecule.	0
5. Divide the total by 2 to get the number of pairs of electrons.	8/2=4

6. The electron pairs minimise repulsion by adopting the shapes shown below :



H_2O, with 4 electron pairs, therefore adopts a tetrahedral shape :



Repulsions between non-bonded and bonded pairs squeezes the two H atoms closer together reducing the bond angle α from 109.5^{0} to 104^{0}

Further examples

1. $BeCl_2$

No. of electron pairs in valence state :

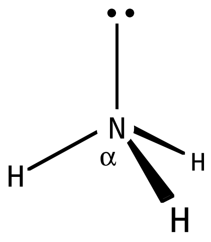
Central atom Be -> 2
Bonded atoms 2Cl -> 2
Total 4
=> No.of pairs 2
=> Shape : linear

Cl——Be——Cl

2. NH_3

No. of electron pairs in valence state :

Central atom N -> 5
Bonded atoms 3H -> 3
Total 8
=> No.of pairs 4
=> Shape : tetrahedral

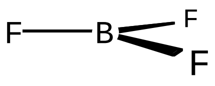


Repulsions between non-bonded and bonded pairs squeezes the three H atoms closer together reducing the bond angle α from 109.5° to 106°

3. BF_3

No. of electron pairs in valence state :

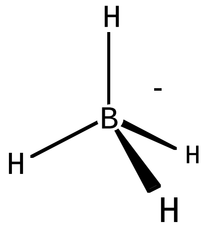
Central atom B -> 3
Bonded atoms 3F -> 3
Total 6
=> No.of pairs 3
=> Shape : trigonal



4. BH_4^-

No. of electron pairs in valence state :

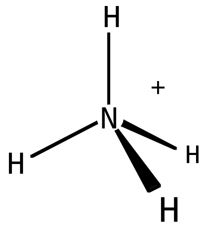
Central atom B -> 3
Bonded atoms 4H -> 4
Negative charge -> 1
Total 8
=> No.of pairs 4
=> Shape : tetrahedral



5. NH_4^+

No. of electron pairs in valence state :

Central atom N -> 5
Bonded atoms 4H -> 4
Positive charge -> -1
Total 8
=> No.of pairs 4
=> Shape : tetrahedral

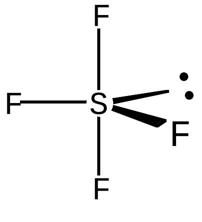


6. SF_4

No. of electron pairs in valence state :

Central atom S -> 6
Bonded atoms 4F -> 4
Total 10
=> No.of pairs 5
=> Shape : trigonal bipyramidal

Two structures are possible :



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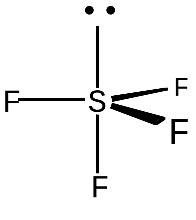


II

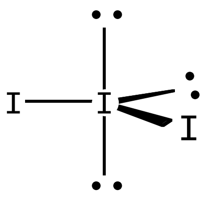
Structure I is preferred. Bonded/non-bonded pair repulsions are more severe at 90^0 than at 120^0. In structure II there are 3 90^0 interactions ; in structure I there are only 2.

7. I_3^-

No. of electron pairs in valence state :

Central atom I -> 7
Bonded atoms 2I -> 2
Negative charge -> 1
Total 10
=> No.of pairs 5
=> Shape : trigonal bipyramidal

Two structures are possible :



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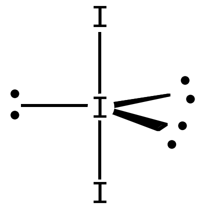


II

Structure II is preferred.

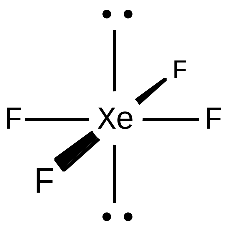
Non-bonded/non-bonded pair repulsions are also more severe at 90^0 than at 120^0. In structure I there are 2 90^0 interactions ; in structure II there are none !

8. XeF_4

No. of electron pairs in valence state :

Central atom Xe -> 8
Bonded atoms 4F -> 4
Total 12
=> No.of pairs 6
=> Shape : octahedral

Two structures are possible :



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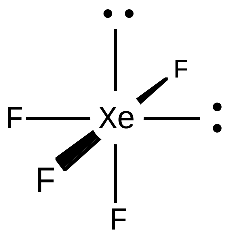

II

Structure I is preferred

In structure II there is 1 90^0 non-bonded/non-bonded pair interaction. In structure I the non-bonded pairs are kept as far apart as possible - at 180^0 !