

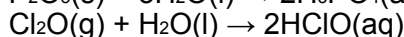
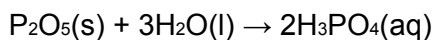


## 3 chemical bonding

## 3.1 Electronegativity

Electronegativity is the ability of an atom to **attract a bonding pair of electrons** in a covalent bond.

The oxygen in non-metal oxides is very electronegative. This causes a permanent dipole across the covalent bond so the atom that oxygen is bonded to becomes partially positive. When the oxide is added to water, lone pairs on oxygen in the water are attracted to the partially positive atom in the oxide causing **hydrolysis**. Below are examples of this reaction:



The magnitude of electro-negativity depends on the following factors.

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**Atomic Size.** The smaller the size of an atom, greater is its tendency to attract towards itself the shared pair of electrons. Thus smaller atoms have greater Electronegativity values than the larger atoms.

**Number of inner shells (shielding effect).** The atom with greater number of inner shells has less value of electro-negativity than the atom with smaller number of inner shells. For example, the electro-negative values of halogens decrease from F to iodine as the number of inner shells increases from F to I.

**Charge on the ion (i.e., Oxidation state).** Electro-negativity is a variable quantity. It varies with the change in the oxidation state of the element. The element in higher oxidation state has more value of electronegativity than in the lower oxidation state. Thus the value of electronegativity of  $\text{Fe}^{3+}$  is higher than that of  $\text{Fe}^{2+}$ .

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Electro-negativity increases from left to right in a period in the periodic table since nuclear charge increases and atomic radius decreases which cause electro-negativity to increase across a period.

With some exceptions (especially within transition metals), electro-negativity decreases in going down a group due to successive appearance of inner shells and increase in atomic radius with increase in atomic number. The addition of extra inner shells in larger atoms screen the shared pair from the nucleus and thus the electron pair is attracted less by the atoms in the combined state. The values are unitless.

4 Electronegativity difference and bond type

If the electronegativity difference (usually called  $\Delta\text{EN}$ ) is less than 0.5, then the bond is nonpolar covalent. If the  $\Delta\text{EN}$  is greater than 2.0, then the bond is ionic. ... If only nonmetals are involved, the bond is considered polar covalent.

Below are ten common elements with electronegativity values.

F 4.0 C 2.5  
O 3.5 S 2.5  
Cl 3.0 H 2.1  
N 3.0 Na 0.9  
Br 2.8 K 0.8

- 3.2 The atom **losing electrons** forms a **positive ion (a cation)** and is usually a **metal**. The atom **gaining electrons** forms a **negative ion (an anion)** and is usually a **non-metallic element**.

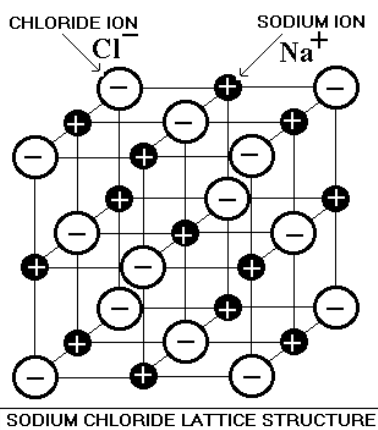
An ionic bond is formed when electrons are transferred from a metal to a non-metal, forming an ionic compound. The compound is held together by the **electrostatic attraction** between **the positively charged metal ions and negatively charged non-metal ions**.

**Ionic compounds are soluble in polar solvents such as water due to opposite charge attraction which separates the two ions in ionic compound.**

- The bonds between the ions is very strong and they club together to form a **giant ionic lattice** with a high melting point because it takes a lot of energy to overcome the attractive forces between the ions - the ionic bonds. i.e they are in solid state
- In solid ionic compound does not conduct electricity as ions are fixed (not movable) When molten, or dissolved in water, ionic compounds will conduct electricity because the charged particles (ions) are free to move and carry the electric current.

Ionic compounds are brittle as when mechanical pressure is applied to an ionic crystal then ions of similar charges may be forced to get closer to each other.

Now, by doing so, the electrostatic repulsion can be enough to split or disorient completely the lattice infrastructure. Thus imparting the brittle character.



In ionic compounds, ions are surrounded on all sides by oppositely charged ions forming a **giant ionic lattice**.

2

Compound	Ions	Formation of ions	Dot and cross diagram
Sodium chloride (NaCl)	$\text{Na}^+$ and $\text{Cl}^-$		
Magnesium oxide (MgO)	$\text{Mg}^{2+}$ and $\text{O}^{2-}$		
Calcium fluoride (CaF <sub>2</sub> )	$\text{Ca}^{2+}$ and $\text{F}^-$		





### 3.3 Metallic bonding

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#### **Metallic bonding**

In metals, positive metal ions (cations) are fixed in a **lattice** and surrounded by mobile **delocalised electrons**. The strong electrostatic attraction between the positive metal ions and negative electrons hold the metal together.

### 3.4 Covalent bonding

A covalent bond is a chemical bond where electron pairs are shared between atoms. A covalent bond is the strong electrostatic attraction between a **shared pair of electrons** and the nuclei of the bonding atoms. This is because the negative electrons are attracted to the positive protons in the nuclei and this overcome the repulsion between the two nuclei.

Similarly to ionic bonding, dot and cross diagrams can be used to represent covalent bonding. The circles (or outer shells) must overlap and this overlap must contain a dot and cross to represent the shared pair of electrons.

Below are examples of covalent compounds:

Compound	Dot and cross diagram
Hydrogen ( $H_2$ )	
Hydrogen chloride ( $HCl$ )	
Methane ( $CH_4$ )	

Compound	Dot and cross diagram
Oxygen ( $O_2$ )	
Carbon dioxide ( $CO_2$ )	
Ethene ( $C_2H_4$ )	



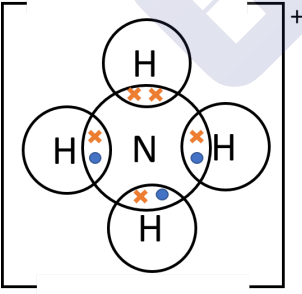
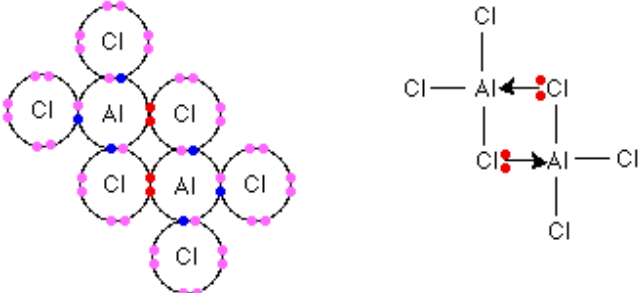
b

The elements in period 3 can expand their octet  
eg. sulfur dioxide, phosphorous pentachloride, sulfur hexafluoride

3.4

### Coordinate (dative covalent) bonding

- c A dative covalent bond has **one atom which supplies both of the shared electrons**. In the dative covalent bond  $A \rightarrow B$ , A donates a pair of electrons to B. Examples are shown below:

Compound	Dot and cross diagram
Ammonium ion ( $\text{NH}_4^+$ )	
$\text{Al}_2\text{Cl}_6$	 <a href="#">'Coordinate (dative covalent) bonding'. Chemguide</a>

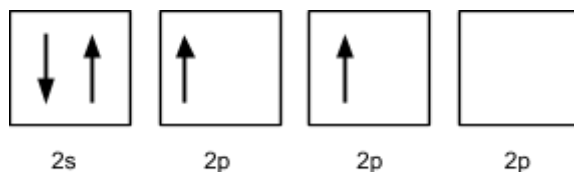




## 2 Sigma Bond ( $\sigma$ )

- (a) A sigma bond is a **single covalent bond** formed when **two orbitals overlap end-to-end**. The pair of electrons are found between the two nuclei.

Below is a diagram showing the electrons in the second shell of carbon:



Carbon forms 4 covalent bonds rather than 2 because this releases more energy and makes the molecule more stable. A small amount of energy is used to **promote** one of the 2s electrons to the empty 2p orbital (as these have a similar energy) to give 4 unpaired electrons. The carbon atom is now in an excited state. **Hybridisation** occurs when the electrons are rearranged again into four identical  $sp^3$  hybrids. The sigma bond forms when two orbitals from different atoms **overlap end-to-end**.

The process of promoting an electron, hybridisation and formation of the molecular orbitals follows the same pattern in all covalently-bound molecules.

## Pi Bond ( $\pi$ )

A pi bond is a covalent bond formed when **2 orbitals overlap sideways**. The pi bond is the region **above and below a sigma bond** where this pair of electrons can be found.

When a pi bond forms between two carbons, first a 2s electron is **promoted** to the empty 2p orbital to give 4 unpaired electrons. The carbon atom is now in an excited state. **Hybridisation** of three orbitals (rather than 4 when forming a sigma bond) forms  $sp^2$  hybrids. **End-to-end overlap** of two  $sp^2$  hybrids from different carbon atoms forms a sigma bond. The p orbital in each carbon contains an unpaired electron. These orbitals **overlap sideways** to form a pi bond.

**Greatest repulsion**    Lone pair - lone pair

Lone pair - bonding pair

**Lowest repulsion**    Bonding pair - bonding pair







### 3 Reactivity

The reactivity of covalent compound is affected by three factors:

- (a)
- **Bond energy**: the amount of energy needed to break one mole of a given gaseous covalent bond to produce gaseous atoms. Bond energies given in the data book are an average and don't consider the specific molecule the bond is found in.
  - **Bond length**: the distance between two nuclei in a covalent bond. A longer bond means the shared pair of electrons is further from at least one nucleus so the attraction and bond strength decreases with increasing bond length.
  - **Bond polarity**: if the electronegativities of the bonding atoms are different, the bond will be polar and the bonding atoms will have partial charges.

The strength of a bond rather than polarity typically determines the rate of a reaction. A stronger bond means the compound is less reactive. Polarity may mean molecules are attracted to each other which triggers the reaction.

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#### Shapes of molecules

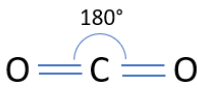
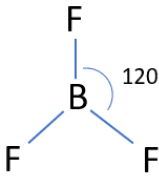
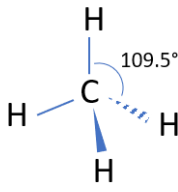
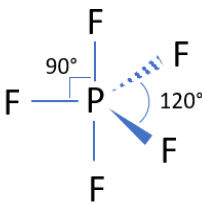
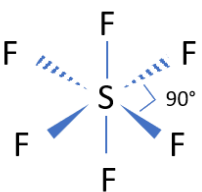
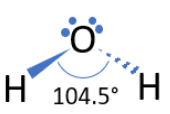
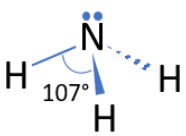
- 3.5 The shape of a molecule is determined by the **arrangement of electrons** around the central atom. Electron pairs are regions of negative charge so they repel each other and arrange themselves as far apart as possible. **Lone pairs offer more repulsion than bonding pairs** so the order of repulsion is:

repulsion : lone pair-lone pair > lone pair -bond pair > bond pair -bond pair

When drawing the shapes of molecules, a bond in the plane of the paper is a normal line. A bold wedge shows the bond is coming towards you and a dotted wedge shows the bond is going away from you. Dots are used to represent electrons in a lone pair.



The shape of molecules are shown in the table below:

Number of lone pairs (lp) and bonding pairs (bp)	Shape name	Bond angle	Example compound and diagram
2 bp	Linear	180°	CO <sub>2</sub> 
3 bp	Trigonal planar	120°	BF <sub>3</sub> 
4 bp	Tetrahedral	109.5°	CH <sub>4</sub> 
5 bp	Trigonal bipyramidal	90° and 120°	PF <sub>5</sub> 
6 bp	Octahedral	90°	SF <sub>6</sub> 
2 bp, 2 lp	Non-linear or V-shaped	104.5°	H <sub>2</sub> O 
3 bp, 1 lp	Pyramidal	107°	NH <sub>3</sub> 



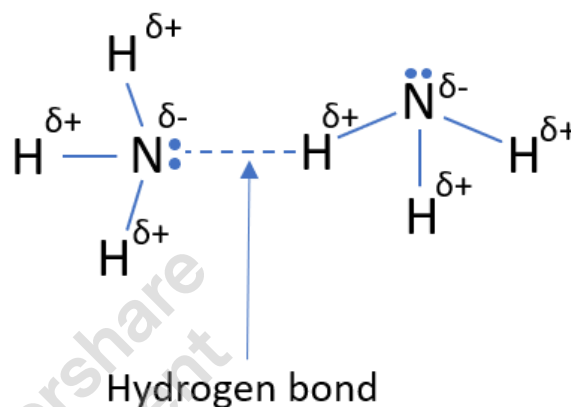
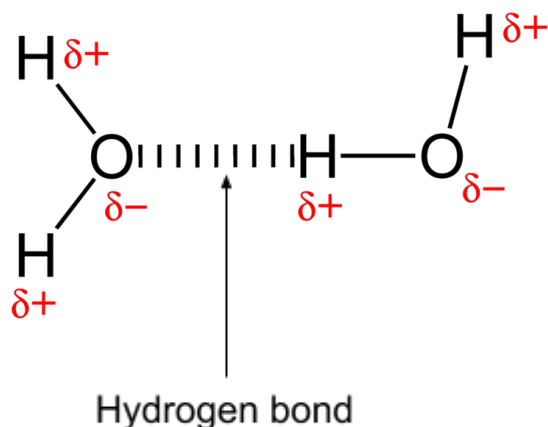


### 3.6 Intermolecular forces

**Intermolecular forces** of attraction occur **between** neighbouring molecules.

#### Hydrogen bonding

Molecules containing **N-H**, **O-H** or **F-H** bonds can form hydrogen bonds. This is because oxygen, nitrogen and fluorine are **very electronegative** meaning they draw the bonding electrons towards them to create a strong dipole (a charge difference across the bond). A hydrogen bond is the attraction between the partially positive hydrogen ( $H^{\delta+}$ ) and a lone pair on  $O^{\delta-}$ ,  $N^{\delta-}$ , or  $F^{\delta-}$ . Water ( $H_2O$ ) and ammonia ( $NH_3$ ) are examples of compounds that form hydrogen bonds:



- b The hydrogen bonding in water causes water molecules in ice to align in an **open lattice structure**. This means water expands as it freezes so **ice is less dense than water**.





### 3.6 intermolecular forces ,

- 2 A polar bond is a bond with a **permanent charge difference** (or permanent dipole). This occurs when the two bonding atoms in a covalent bond are different because one atom is more electronegative than the other so it will attract the bonding electrons towards itself. If two atoms in a covalent bond are exactly the same, the electronegativity of both atoms will be the same so the bond will be non-polar.
- A polar molecule must contain **polar bonds** and be **non-symmetrical**. If a polar molecule is symmetrical, the dipoles will cancel each other out.





### 3 Van der Waals forces

Dispersion forces, also known as London forces, are a type of van der Waals force found between **symmetrical, non-polar molecules**. There are no permanent dipoles but electrons are mobile and in an instant, they may be **unevenly distributed**. This creates a **temporary dipole**, with the side containing more electrons becoming partially negative. The temporary dipole can **induce dipoles in neighbouring molecules** as the partial negative charge repels electrons. These opposite partial charges will remain attracted to each other.

Permanent dipole-dipole forces are another type of van der Waals forces found between **polar molecules**. The permanent dipole in these molecules means the partial charges are more strongly attracted to one another. Molecules with permanent dipole-dipole forces usually have higher boiling points than those which only have London forces between them. However,  $\text{CCl}_4$  has a higher boiling point than  $\text{CHCl}_3$  because  $\text{CCl}_4$  is a bigger molecule with more electrons so the increased London forces compensate for the lack of permanent dipole-dipole forces.

Elements in group 18 exist as single atoms so the only forces between the atoms are London forces. These forces are **relatively weak** so require little energy to break meaning group 18 elements have low boiling points. Boiling point increases down the group because the **number of electrons and atomic radius increases** meaning there are stronger temporary dipole and stronger London forces between the atoms.

$\text{Br}_2$  is liquid at room temperature because although it only has London forces between molecules, it contains lots of electrons meaning strong temporary dipoles between molecules.

4 strength of bonding in general : metallic > ionic > covalent > intermolecular forces





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## Bonding and physical properties

The physical properties of a substance are affected by the types of bonding it contains:

- Covalent (giant structures only):
  - High melting and boiling points - strong covalent bonds require a large amount of energy to break.
  - Mostly non-conductors - don't contain mobile charged particles (except graphite which contains delocalised electrons).
  - Insoluble - covalent bonds in the lattice are too strong to be broken.
- Ionic:
  - High melting and boiling points - strong electrostatic attraction between oppositely charged ions requires a lot of energy to break.
  - Electrical conductor - when aqueous or molten, the ions are free to move and conduct electricity. When solid, the ions are fixed in an ionic lattice so can't conduct electricity.
  - Soluble in polar solvent - charged parts of the solvent are attracted to the oppositely charged ions.
- Metallic:
  - High melting and boiling point - the attraction between the ions and delocalised electrons is strong so a lot of energy is needed to overcome the metallic bonding.
  - Good electrical conductor - contains mobile delocalised electrons which can conduct electricity as a solid.
  - Malleable and ductile - the regular structure and delocalised electrons allow the uniform layers of ions to slide over one another.
- Hydrogen bonds:
  - High boiling point - The melting and boiling points are greater than those of molecule with only van der Waals forces between them because hydrogen bonds are stronger.
  - Soluble in water - strong permanent dipoles allow the formation of hydrogen bonds with water.
  - Non-conductors - no mobile charges so are unable to conduct electricity.
- Van der waals forces:
  - Low boiling point - forces are weak so require little energy to break. Larger molecules have more van der Waals forces so have higher melting and boiling points.
  - Solubility - unless they react with water, most molecular compounds are insoluble in water because they release too little energy when they dissolve. They are often soluble in organic solvents because they both contain van der Waals forces.
  - Non-conductors - no mobile charges so are unable to conduct electricity.

