3. STRUCTURE AND BONDING

IONIC (ELECTROVALENT) BONDING

Noble gases like neon or argon have eight electrons in their outer shells (or two in the case of helium). These noble gas structures are thought of as being in some way a "desirable" thing for an atom to have. When other atoms react, they try to organise electrons such that their outer shells are either completely full or completely empty. Chemical reactions occur so that atoms attain inert gas configuration by either losing valency electrons as in the case of metals, or gaining electrons as in the case of non metals.

Ionic bonding in sodium chloride

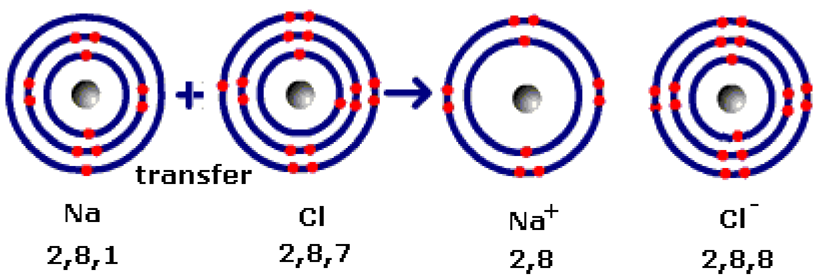
Sodium (2,8,1) has 1 electron more than a stable noble gas structure (2,8). If it gave away that electron it would become more stable. Chlorine (2,8,7) has 1 electron short of a stable noble gas structure (2,8,8). If it could gain an electron from somewhere it too would become more stable.

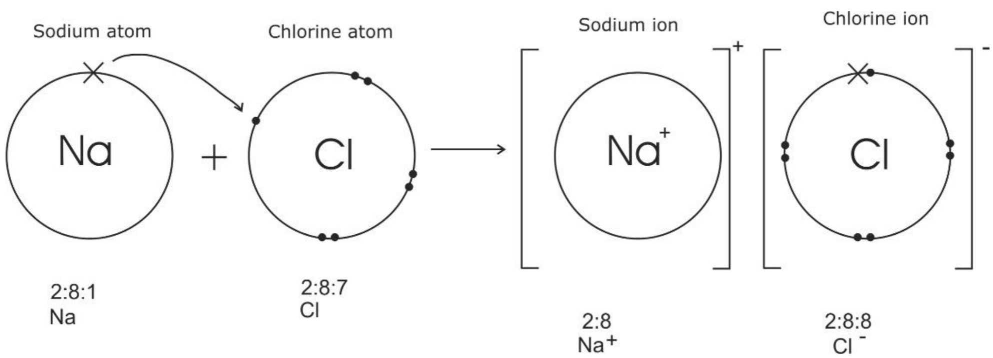
If a sodium atom gives an electron to a chlorine atom, both become more stable.

$$Na \xrightarrow{-1e} Na^+$$

$$Cl + 1e \rightarrow Cl^-$$

$$Na^+ + Cl^- \rightarrow [Na^+ - Cl^-]$$





The sodium has lost an electron, so it no longer has equal numbers of electrons and protons. Because it has one more proton than electron, it has a charge of 1+. If electrons are lost from an atom, positive ions are formed. Positive ions are sometimes called cations because they move to the cathode during electrolysis.

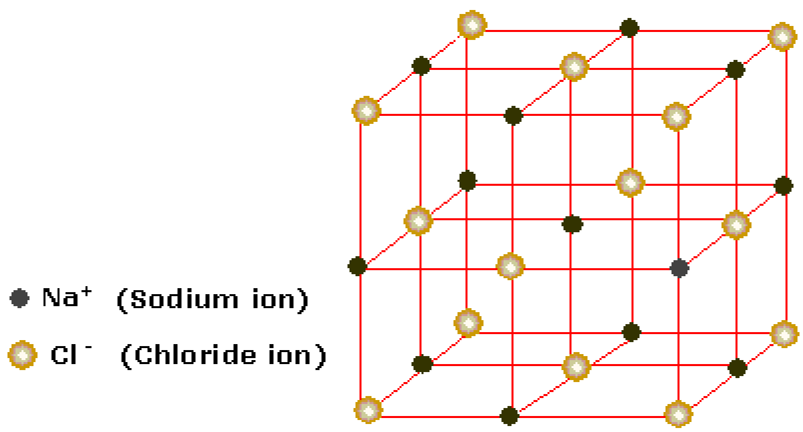
The chlorine has gained an electron, so it now has one more electron than proton. It therefore has a charge of 1-. If electrons are gained by an atom, negative ions are formed. A negative ion is sometimes called an anion since it drifts to the anode during electrolysis.

The nature of ionic bond

The sodium ions and chloride ions are held together by the strong electrostatic attractions between the positive and negative charges. You need one sodium atom to provide the extra electron for one chlorine atom, so they combine together 1:1. The formula is therefore NaCl.

Properties of ionic compounds

- ✓ All compounds with ionic bonding produce giant ionic structures.
- ✓ Consist of oppositely charged ions arranged in an ionic lattice, the ions are held together by strong ionic bonds. e.g. NaCl is composed of Na^+ ions and Cl^- ions.



- ✓ These bonds are hard to break, therefore ionic substances have very high melting and boiling points.
- ✓ All exist as solids.
- ✓ They conduct electricity when molten, because the ions are free to move, but do not conduct when solid.
- ✓ They conduct electricity in the aqueous state because the ions are free to move.
- ✓ Most ionic substances are soluble in water because the polar water molecules can accommodate the charged ions.

COVALENT BONDING - SINGLE BONDS

As well as achieving noble gas structures by transferring electrons from one atom to another as in ionic bonding, it is also possible for atoms to reach these stable structures by sharing electrons to give covalent bonds.

Depending on the number of electron pairs shared between atoms which participate in bonding, covalent bonds are classified as follows:

1) Single covalent bond [•—•] - one pair of electrons shared.

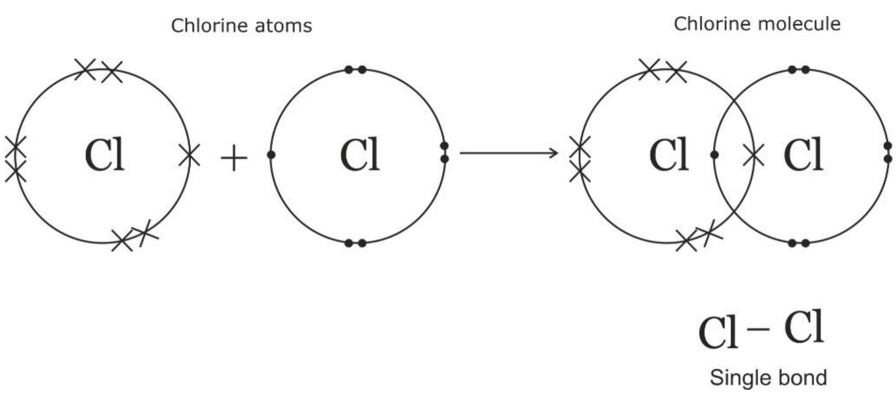
2) Double covalent bond [═] - two pairs of electrons shared.

3) Triple covalent bond [≡] - three pairs of electrons shared.

Some simple covalent molecules

Chlorine

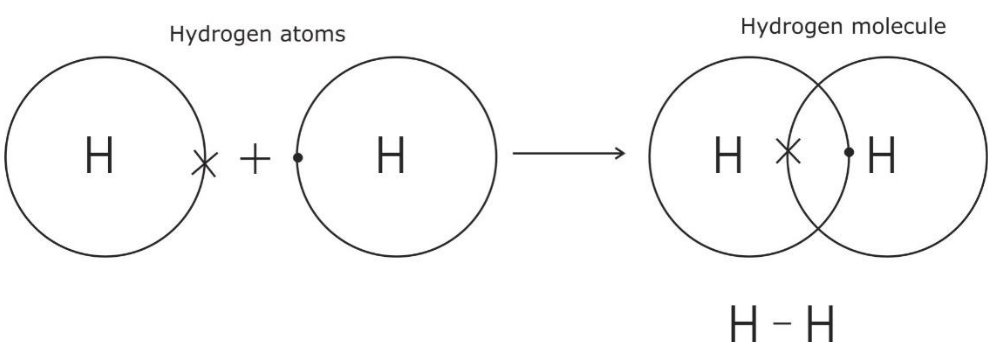
For example, two chlorine atoms could both achieve stable structures by sharing their single unpaired electron as in the diagram. The fact that one chlorine has been drawn with electrons marked as crosses and the other as dots is simply to show where all the electrons come from. In reality there is no difference between them.



The two chlorine atoms are said to be joined by a covalent bond. The reason that the two chlorine atoms stick together is that the shared pair of electrons is attracted to the nucleus of both chlorine atoms.

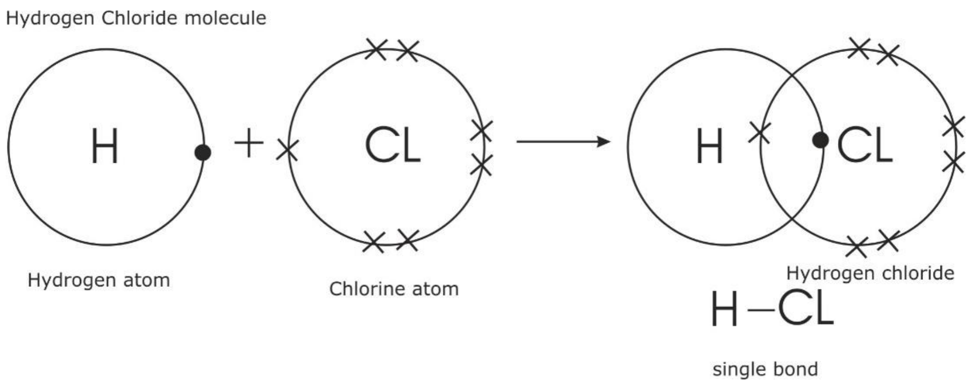
Hydrogen

Hydrogen atoms only need two electrons in their outer level to reach the noble gas structure of helium.



Once again, the covalent bond holds the two atoms together because the pair of electrons is attracted to both nuclei. This is another single bond.

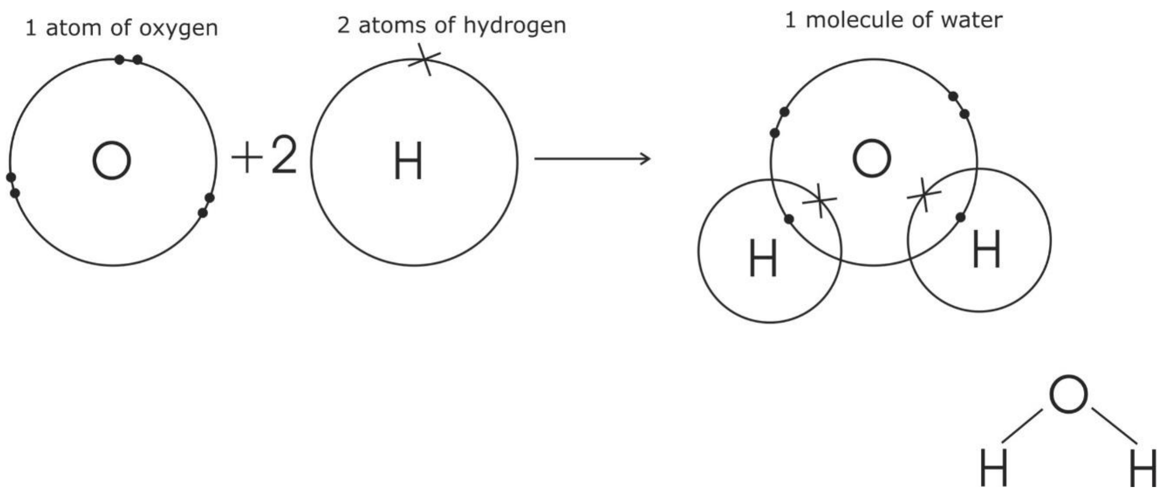
Hydrogen chloride



The hydrogen has a helium structure, and the chlorine an argon structure.

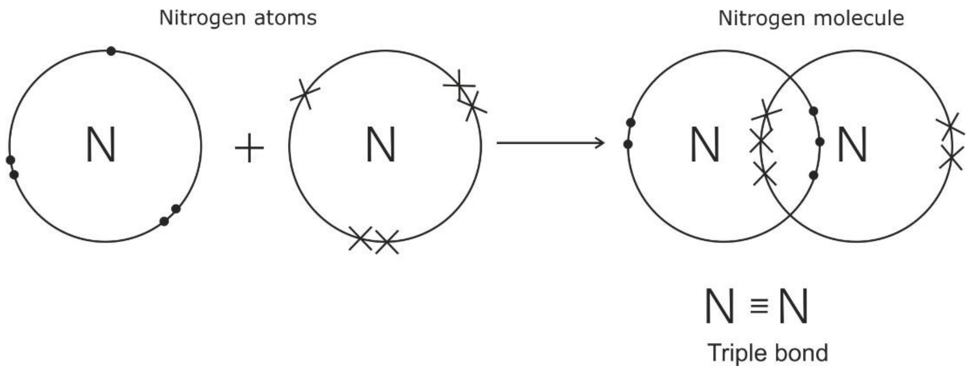
Water

Oxygen atom has six electrons in the outer shell, while each of the two hydrogen atoms has one each. After bonding, oxygen has 8 electrons while each hydrogen atom has two as shown by the molecule.



NITROGEN GAS

Each nitrogen atom has five electrons in the outer shell. Each needs 3 electrons to complete the outer shell. In the formation of the molecule, each nitrogen atom contributes three electrons and a triple bond is formed



Characteristics of Covalent Compounds

1) Covalent compounds consist of molecules and not ions. The molecules do not have any electric charge on them. The molecules are held together by weak forces called **Van der Waal's forces**.

2) Covalent compounds are gases, volatile liquids or soft solids. As there are weak, Van der Waal's forces between the molecules, they are not held in rigid position. The state depends on the bond energy. If the bond energy is very low, they stay as gases, if it is appreciable they are volatile liquids. If very high, they exist as soft solids.

3) Covalent compounds generally have low melting and boiling points. As Van der Waal's forces are weak, a very small amount of energy is required to break the bond between the molecules corresponding to low melting point and boiling point.

4) Covalent compounds dissolve in organic solvents. As they do not contain ions, solvation does not take place when water is added to the compound. Hence they do not dissolve in water.

5) Covalent compounds are bad conductors of electricity. They do not contain ions in the fused state, nor do ions migrate on application of an electric potential. Hence, there is no conduction of current.

6) Covalent compounds are less dense when compared to water. Very weak Van der Waal's forces hold the molecules together, hence there are large inter molecular spaces. Consequently less number of molecules per unit volume, which means mass per unit volume is also less. Hence they have a low density.

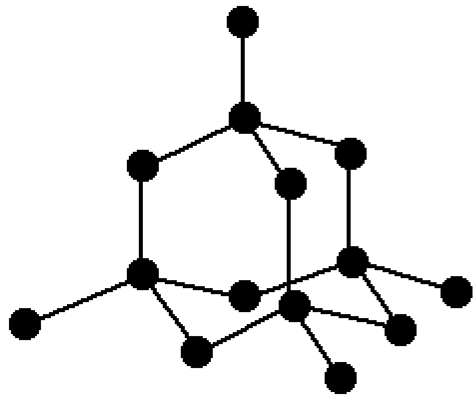
Exceptions

- Diamond and graphite, the allotropes of carbon have high melting point.
- Hydrogen chloride in the aqueous state conducts electricity.

The giant covalent structure of diamond

Carbon has an electronic arrangement of 2, 4. In diamond, each carbon shares electrons with four other carbon atoms - forming four single bonds.

In the diagram some carbon atoms only seem to be forming two bonds (or even one bond), but that's not really the case. We are only showing a small bit of the whole structure.



This is a giant covalent structure - it continues on and on in three dimensions. It is not a molecule, because the number of atoms joined up in a real diamond is completely variable - depending on the size of the crystal.

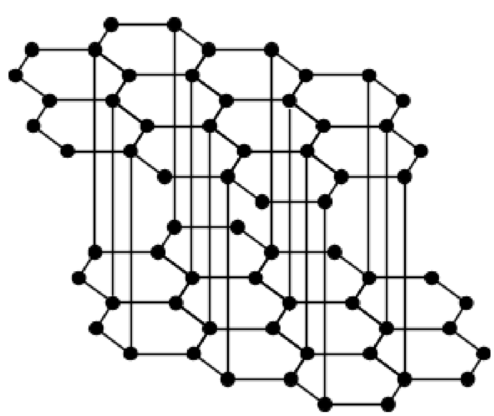
The physical properties of diamond

Diamond

- Has a very high melting point (almost 4000°C). Very strong carbon-carbon covalent bonds have to be broken throughout the structure before melting occurs.
- Is very hard. This is again due to the need to break very strong covalent bonds operating in 3-dimensions.
- Doesn’t conduct electricity. All the electrons are held tightly between the atoms, and aren't free to move.
- Is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and carbon atoms which could outweigh the attractions between the covalently bound carbon atoms.

The giant covalent structure of graphite

Graphite has a **layer structure** which is quite difficult to draw convincingly in three dimensions. The diagram below shows the arrangement of the atoms in each layer, and the way the layers are spaced.



The bonding in graphite

Each carbon atom uses three of its electrons to form simple bonds to its three close neighbours. That leaves a fourth electron in the bonding level. These "spare" electrons in each carbon atom become delocalised over the whole of the sheet of atoms in one layer. They are no longer associated directly with any particular atom or pair of atoms, but are free to wander throughout the whole sheet. The important thing is that the delocalised electrons are free to move anywhere within the sheet - each electron is no longer fixed to a particular carbon atom. There is, however, no direct contact between the delocalised electrons in one sheet and those in the neighbouring sheets.

The atoms within a sheet are held together by strong covalent bonds - stronger, in fact, than in diamond because of the additional bonding caused by the delocalised electrons. So what holds the sheets together?

In graphite you have the ultimate example of van der Waals dispersion forces. As the delocalised electrons move around in the sheet, very large temporary dipoles can be set up which will induce opposite dipoles in the sheets above and below - and so on throughout the whole graphite crystal.

The physical properties of graphite

Graphite

- Has a high melting point, similar to that of diamond. In order to melt graphite, it isn't enough to loosen one sheet from another. You have to break the covalent bonding throughout the whole structure.
- Has a soft, slippery feel, and is used in pencils and as a dry lubricant for things like locks. You can think of graphite rather like a pack of cards - each card is strong, but the cards will slide over each other, or even fall off the pack altogether. When you use a pencil, sheets are rubbed off and stick to the paper.
- Has a lower density than diamond. This is because of the relatively large amount of space that is "wasted" between the sheets.
- Is insoluble in water and organic solvents - for the same reason that diamond is insoluble. Attractions between solvent molecules and carbon atoms will never be strong enough to overcome the strong covalent bonds in graphite.
- Conducts electricity. The delocalised electrons are free to move throughout the sheets. If a piece of graphite is connected into a circuit, electrons can fall off one end of the sheet and be replaced with new ones at the other end.

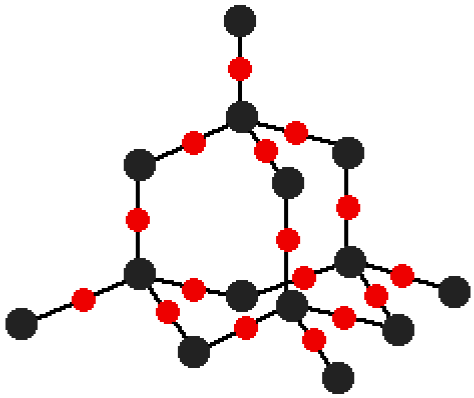
The structure of silicon dioxide, SiO_2

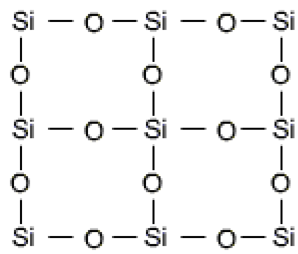
Silicon dioxide is also known as silicon (IV) oxide.

The giant covalent structure of silicon dioxide

There are three different crystal forms of silicon dioxide. The easiest one to remember and draw is based on the diamond structure.

Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, all you need to do is to modify the silicon structure by including some oxygen atoms.





Notice that each silicon atom is bridged to its neighbours by an oxygen atom. Don't forget that this is just a tiny part of a giant structure extending on all 3 dimensions.

<u>The physical properties of silicon dioxide</u>

Silicon dioxide

- Has a high melting point - varying depending on what the particular structure is (remember that the structure given is only one of three possible structures), but around 1700°C. Very strong silicon-oxygen covalent bonds have to be broken throughout the structure before melting occurs.
- Is hard. This is due to the need to break the very strong covalent bonds.
- Doesn’t conduct electricity. There aren't any delocalised electrons. All the electrons are held tightly between the atoms, and aren't free to move.
- Is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and the silicon or oxygen atoms which could overcome the covalent bonds in the giant structure.

Uses of Silica

i) Quartz glass is used for manufacturing optical instruments.

ii) Colored quartz is used for manufacturing gems.

iii) Sand is used in manufacture of glass, porcelain, sand paper and mortar etc.

iv) Sand stone is used as a building material.

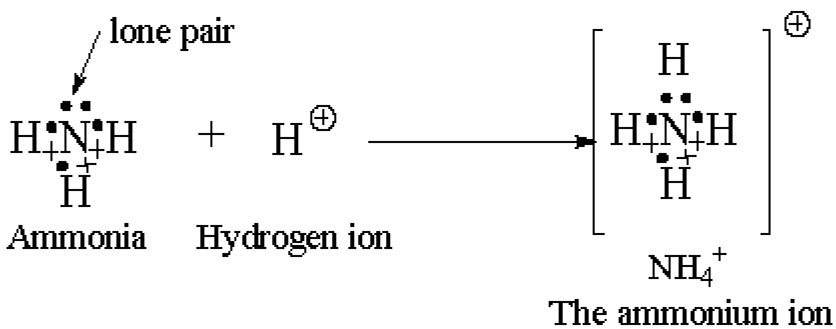
<u>CO-ORDINATE (DATIVE COVALENT) BONDING</u>

<u>Co-ordinate (dative covalent) bonding</u>

A covalent bond is formed by two atoms sharing a pair of electrons. The atoms are held together because the electron pair is attracted by both of the nuclei. In the formation of a simple covalent bond, each atom supplies one electron to the bond - but that doesn't have to be the case. A co-ordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom.

<u>The reaction between ammonia and hydrogen chloride</u>

If these colourless gases are allowed to mix, a thick white smoke of solid ammonium chloride is formed. Ammonium ions, NH_4^+, are formed by the transfer of a hydrogen ion from the hydrogen chloride to the lone pair of electrons on the ammonia molecule.



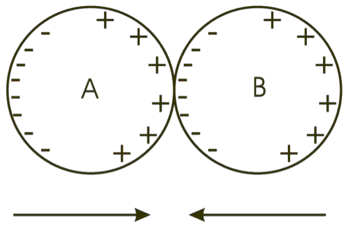
When the ammonium ion, NH_4^+, is formed, the fourth hydrogen is attached by a dative covalent bond, because only the hydrogen's nucleus is transferred from the chlorine to the nitrogen. The hydrogen's electron is left behind on the chlorine to form a negative chloride ion.

Once the ammonium ion has been formed it is impossible to tell any difference between the dative covalent and the ordinary covalent bonds. Although the electrons are shown differently in the diagram, there is no difference between them in reality.

INTERMOLECULAR BONDING - VAN DER WAALS FORCES

(a) VAN DER WAALS FORCES

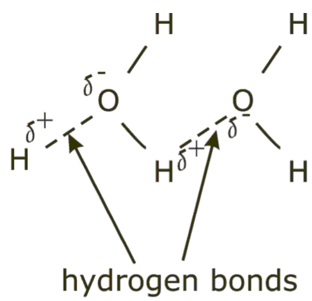
Intermolecular attractions are attractions between one molecule and a neighbouring molecule. The forces of attraction which hold an individual molecule together (for example, the covalent bonds) are known as **intramolecular** attractions. All molecules experience intermolecular attractions, although in some cases those attractions are very weak. Even in a gas like hydrogen, H_2, if you slow the molecules down by cooling the gas, the attractions are large enough for the molecules to stick together eventually to form a liquid and then a solid.



In hydrogen's case the attractions are so weak that the molecules have to be cooled to (-252°C) before the attractions are enough to condense the hydrogen as a liquid. Helium's intermolecular attractions are even weaker - the molecules won't stick together to form a liquid until the temperature drops to (-269°C).

HYDROGEN BONDING

Polar molecules, such as water molecules, have a weak, partial negative charge at one region of the molecule (the oxygen atom in water) and a partial positive charge elsewhere (the hydrogen atoms in water).



Hydrogen bonds between water molecules

Thus when water molecules are close together, their positive and negative regions are attracted to the oppositely-charged regions of nearby molecules. The force of attraction, shown here as a dotted line, is called a **hydrogen bond**. Each water molecule is hydrogen bonded to four others.

The hydrogen bonds that form between water molecules account for some of the essential — and unique — properties of water.

- The attraction created by hydrogen bonds keeps water liquid over a wider range of temperature than is found for any other molecule its size.
- The energy required to break multiple hydrogen bonds causes water to have a high heat of vaporization; that is; a large amount of energy is needed to convert liquid water, where the molecules are attracted through their hydrogen bonds, to water vapor, where they are not.

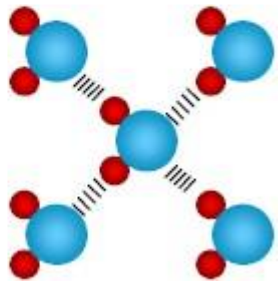
Liquid Water and Hydrogen Bonding

Why water is a liquid?

In many ways, water is a miracle liquid. Since the hydrogen and oxygen atoms in the molecule carry opposite (though partial) charges, nearby water molecules are attracted to each other like tiny little magnets. Hydrogen bonding makes water molecules "stick" together. This makes water have high melting and boiling points compared to other covalent compounds such as ammonia (NH_3) which have similar molecular mass but are gases

Ice and Hydrogen Bonding

The structure that forms in the solid ice crystal actually has large holes in it. Therefore, in a given volume of ice, there are fewer water molecules than in the same volume of liquid water. In other words, ice is less dense than liquid water and will float on the surface of the liquid.

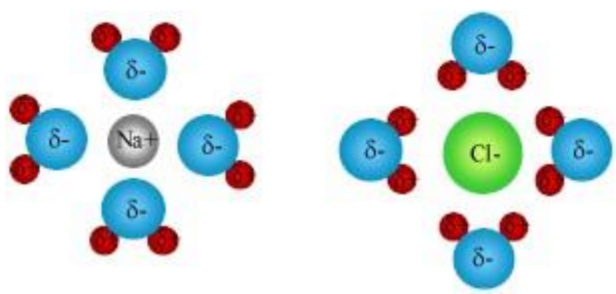


Surface Tension and hydrogen bonding

As we just discussed, neighboring water molecules are attracted to one another. Molecules at the surface of liquid water have fewer neighbors and, as a result, have a greater attraction to the few water molecules that are nearby. This enhanced attraction is called **surface tension**. It makes the surface of the liquid slightly more difficult to break through than the interior.

Water as a Solvent

The partial charge that develops across the water molecule helps make it an excellent solvent. Water dissolves many substances by surrounding charged particles and "pulling" them into solution. For example, common table salt, sodium chloride, is an ionic substance that contains alternating sodium and chlorine ions. When table salt is added to water, the partial charges on the water molecule are attracted to the Na^+ and Cl^- ions.



Why does ethanol have a higher boiling point than methoxymethane?

Ethanol, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, C_2H_6O.

They have the same number of electrons, and a similar length to the molecule. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be much the same.

However, ethanol has a hydrogen atom attached directly to oxygen - and that oxygen still has exactly the same two lone pairs as in a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient $\delta+$ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens aren't sufficiently $\delta+$ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur.

The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)	78.5°C
methoxymethane (without hydrogen bonding)	-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C.It is important to realise that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two are much the same length. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.

4. BONDING IN METALS

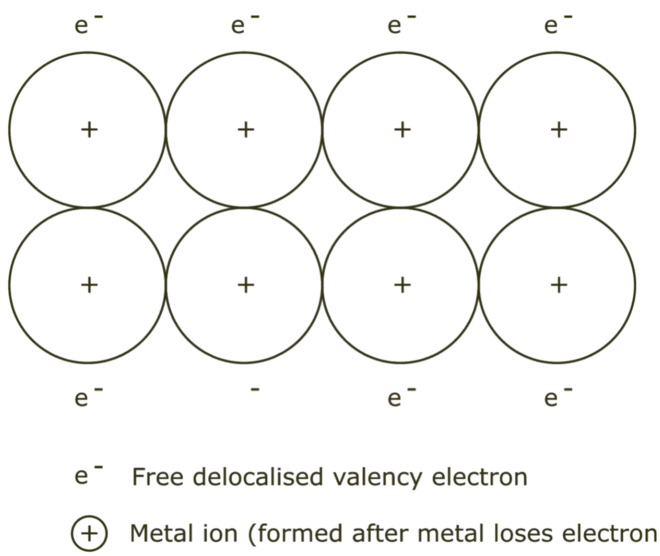
Bonding in metals

Metal atoms have relatively few electrons in their outer shells. When they are packed together, each metal atom loses its outer electrons into a ‘sea’ of free electrons (or mobile electrons). Having lost electrons, the atoms are no longer electrically neutral. They become positive ions because they have lost electrons but the number of protons in the nucleus has remained unchanged.

Therefore the structure of a metal is made up of positive ions packed together. These ions are surrounded by electrons, which can move freely between the ions.

- An ion is a charged particle made from an atom by the loss or gain of electrons.
- Metal atoms most easily lose electrons, so they become positive ions. In doing so they achieve a more stable electron arrangement, usually that of the nearest noble gas.

These free electrons are **delocalized** (not restricted to orbiting one positive ion) and form a kind of electrostatic ‘glue’ holding the structure together. In an electrical circuit, metals can conduct electricity because the mobile electrons can move through the structure carrying charge. His type of bonding (called **metallic boding**) is present in alloys as well. Alloys, for example solder and brass, will conduct electricity.



The physical properties of metals:

This strong bonding generally results in dense, strong materials with high melting and boiling points. Usually a relatively large amount of energy is needed to melt or boil metals.

a. Metals are good conductors of electricity because these 'free' electrons carry the charge of an electric current when a potential difference (voltage!) is applied across a piece of metal.
b. Metals are also good conductors of heat. This is also due to the free moving electrons. Non-metallic solids conduct heat energy by hotter more strongly vibrating atoms, knocking against cooler less strongly vibrating atoms to pass the particle kinetic energy on. In metals, as well as this effect, the 'hot' high kinetic energy electrons move around freely to transfer the particle kinetic energy more efficiently to 'cooler' atoms.
c. Typical metals also have a silvery surface but remember this may be easily tarnished by corrosive oxidation in air and water.
d. Unlike ionic solids, metals are very malleable, they can be readily bent, pressed or hammered into shape.