Bonding, Structure and Energy AS 91164

Achievement Criteria

Bonding and structure are limited to:

- Lewis structures, shape and polarity of simple molecules.
- Intermolecular forces (the distinction between the different types of intermolecular forces is not required)
- Ionic, covalent and metallic bonding
- Molecular, ionic, metallic and covalent network substances
- Properties are limited to hardness (including malleability and ductility), electrical conductivity, melting and boiling points and solubility.

Energy changes are limited to:

- exothermic and endothermic reactions including energy (enthalpy) changes associated with differing amounts of substances and changes of state and enthalpy changes associated with the making and breaking of chemical bonds
- calculations of energy changes using $\Delta_r H$ and reaction stoichiometry, and bond enthalpy

Introduction

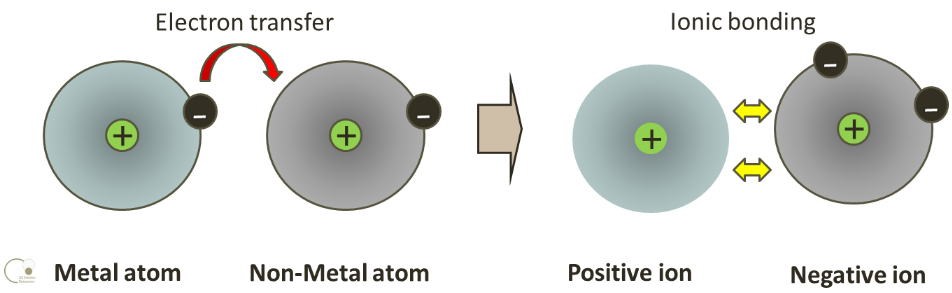
Chemistry is the study of matter and energy and the interaction between them. The elements are the building blocks of all types of matter in the universe. Each element is made up of only one type of atom, each with its specific number of protons known as its atomic number.

A large amount of energy is required to break an atom down into smaller particles. The elements occur in widely varying quantities on earth. The ten most abundant elements make up 98% of the mass of earth. Many elements occur only in traces, and a few elements are synthetic and highly unstable.

Ionic Bonding

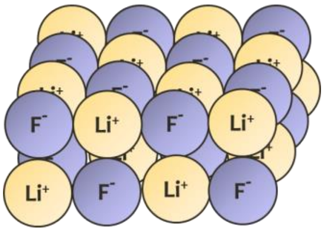
Ionic Bonding holds together oppositely charged ions due to electrostatic attraction. This type of bonding occurs when metal and non-metal atoms react and there is a complete transfer of electrons to form negative (anion) and positive (cation) ions.

The ions then combine in a set ratio to form a neutral compound (usually) with negative and positive charges balanced out.



Ionic compounds are the product of chemical reactions between metal and non-metal ions

Some compounds are ionic compounds, since they are made up of cations and anions.



The Anion (F^-) takes an electron from the Cation (Li^+) so their outer energy levels have a stable 8 electrons each. Anions and Cations have a strong <u>electrostatic attraction</u> for each other, so they bond together as a compound.

Compounds are neutral substances. For ionic compounds, the charges of the positive ions are balanced by the charges of the negative ions.

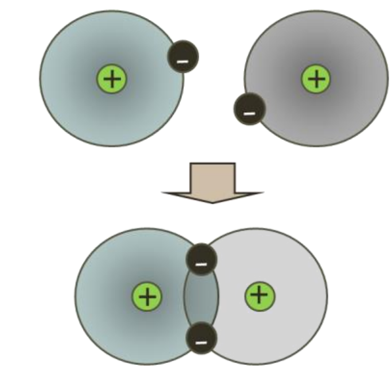
Metallic solids also involve strong electrostatic attraction, but between ions and free moving valence electrons (this will be explained in detail later)

Covalent Bonding

Covalent Bonding occurs when electrons are 'shared' between neighbouring atoms. This often occurs when two or more non-metals react. No ions are formed and there is no transfer of electrons. The compound formed is neutral with no charge.

The valance electrons (electrons in outside energy level) are involved in bonding. These electrons orbit in pairs. The negative charge of the electron pair will attract the positively positive nucleus of other atoms, and this holds the atoms together in a molecule.

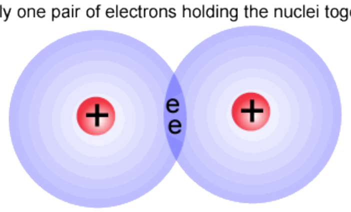
Covalent bonding occurs in both molecular solids, just within the molecules, and in covalent network solids, between each and every individual atom in a solid.



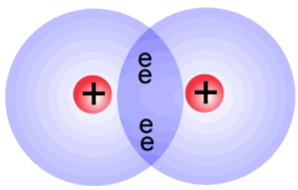
covalent bonding

The electron pair must lie between the nuclei for the attraction to outweigh the repulsion of the two nuclei. This 'sharing' of electrons between atoms creates a covalent bond – giving both atoms the stability of a full outer shell. Covalent bonds are normally formed between pairs of non-metallic atoms. Some covalent bonds involve only one pair of electrons and are known as single bonds. Other covalent bonds can involve two pairs of electrons; double bonds and three pairs of electrons; triple bonds.

Only one pair of electrons holding the nuclei together



Two pair of electrons hold the nuclei tighter and closer

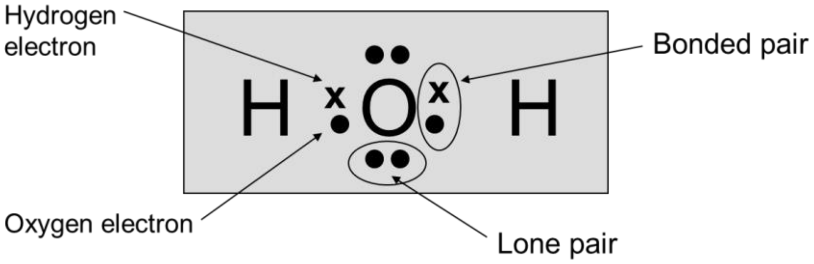


GZ Science Resources

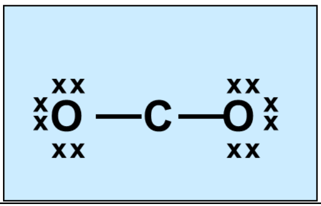
Drawing molecular compounds – Lewis Structures

G Lewis devised a system of drawing covalent molecules showing arrangement of atoms and valence electrons – both those involved in bonding and those that are not (called lone pairs). Electrons in inner shells are <u>not</u> involved in bonding. These diagrams are called Lewis structures. (or diagrams) The Lewis structure is drawn so that each atom has eight electrons associated with it (except for hydrogen, which has two). This is the *octet rule*.

Lewis structure of H_2O (water)

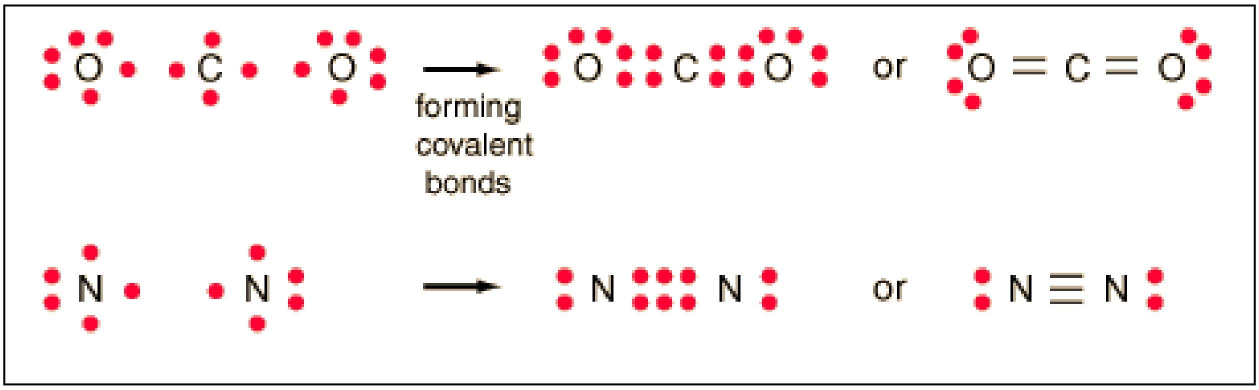


Drawing Lewis Structures

1. Calculate valence electrons of all atoms. If the molecule is an ion, then subtract the charge from the total electrons and place the charge outside of square brackets of the Lewis structure at the end. *Example carbon dioxide.* C = 4 O = 6 O = 6 16 CO_2	2. Write down number of pairs of electrons. 16 / 2 = 8 pairs
3. Place atom with least filled valence shell in the centre with the other atoms arranged around the outside (periphery) **O C O**	4. Bond all atoms together (either - or x or = one pair of electrons) **O—C—O** 8 pairs – 2 pairs = 6 pairs remaining
5. Place remaining e- pairs around the periphery atoms so each has 4 pairs (including bond pair) around it.  6 pairs – 6 pairs = 0 pairs remaining	6. If there any remaining pairs place them around the outside of the central atom.
7. Rearrange lone pairs (pairs not bonded) into bonded pairs if the central atom does not have 4 pairs around it.	

Lewis Structures and Diagrams

- The number of covalent bonds an atom forms is called its *valence*.
- Some atoms have *fixed valence*. E.g.: H = 1, C = 4, F = 1. (most halogens = 1)
- Some atoms have *variable valence*. For example:
  O = 2 (sometimes 3), B, N = 3 (sometimes 4).
- An atom bonded to only one other atom is *peripheral* (monovalent atoms such as H and F are always peripheral).
- An atom bonded to two or more other atoms is *central*.
- Often, the formula is written to indicate connectivity. For example: HCN = H bonded to C, C bonded to N, H and N are not bonded.



Valence-shell electron-pair repulsion (VSEPR) theory

Sidgewick and Powell devised a theory to predict the shapes molecule formed. It is based on the following ideas:

Electron pairs form regions of negative charge

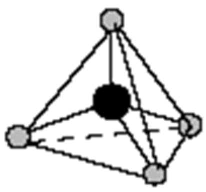
Negative charges repel each other

Regions of negative charge will be spaced as far apart as possible around a central atom.

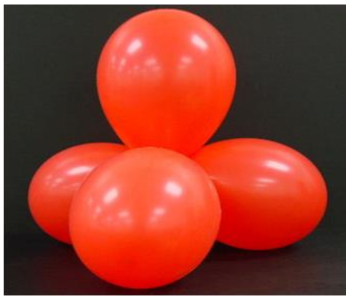
This theory is called valence-shell electron-pair repulsion (VSEPR) theory

The shapes of molecules are determined by the way the regions of negative charge are arranged around the central atom in the molecule. A region may consist of one non-bonded pair of electrons <u>or</u> one bonded pair <u>or</u> two bonded pairs <u>or</u> three bonded pairs. All of these electron arrangements occupy the same region of space.

Three pairs



Four pairs

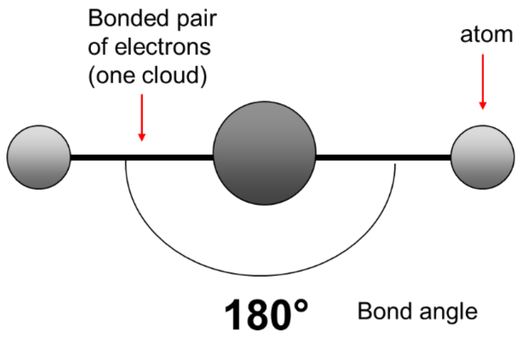


Molecular Shapes – two regions of negative charge

Since regions of electrons are negatively charged, they repel each other as far apart as possible (VSEPR) into a linear geometry / arrangement. Two negative regions arrange themselves on opposite sides of the central atom.

The bond angle will be 180°.

The shape name is linear.

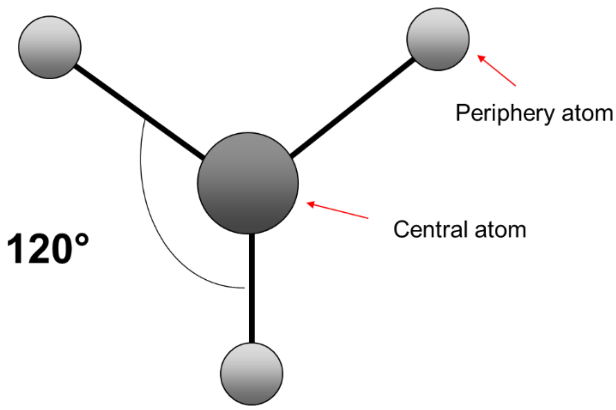


Molecular Shapes – three regions of negative charge (0 non-bonded pairs)

Three regions of negative charge will cause a bond angle of 120° as they repel each other into a trigonal planar geometry / arrangement.

All the atoms still lie on a flat plane (like a sheet of paper).

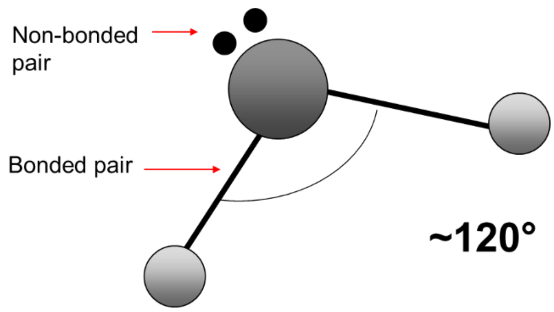
As there are no non-bonded pairs of electrons, the final shape is also a trigonal planar. (or triangular planar)



Molecular Shapes – three regions of negative charge (1 non-bonded pair)

The regions of negative charge repel to a trigonal planar geometry. The bond angle between the remaining pairs is approximately 120°. As there is one non-bonded pair of electrons, the final shape formed by the atoms is called bent.

When one of the regions of electrons is a *non-bonding pair*, it will have a slightly greater push to the bonded pairs. This is because the non-bonding pair is only orbiting around one positive nucleus and their negative charge is less 'neutralised' than if they had another nucleus to orbit around.

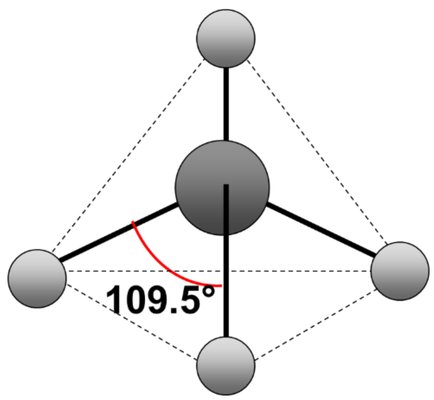


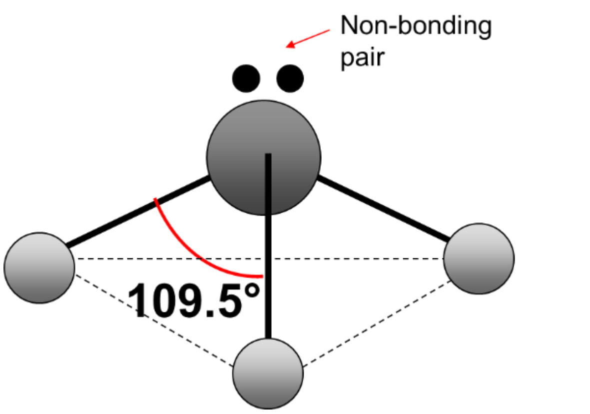
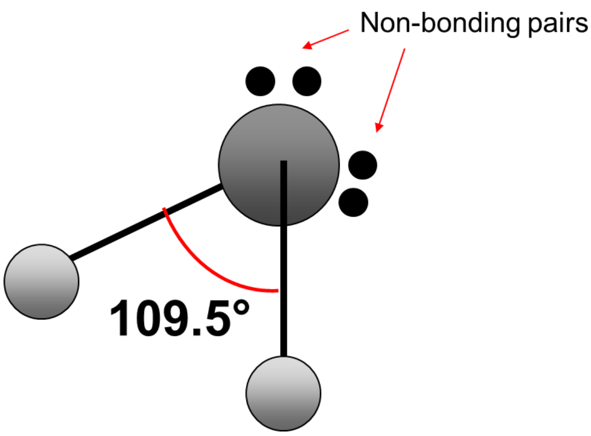
Molecular Shapes – four regions of charge (0 non-bonding pairs)

When four regions of negative charge are around a central atom, they repel each other into a 3-dimensional tetrahedral geometry / arrangement.

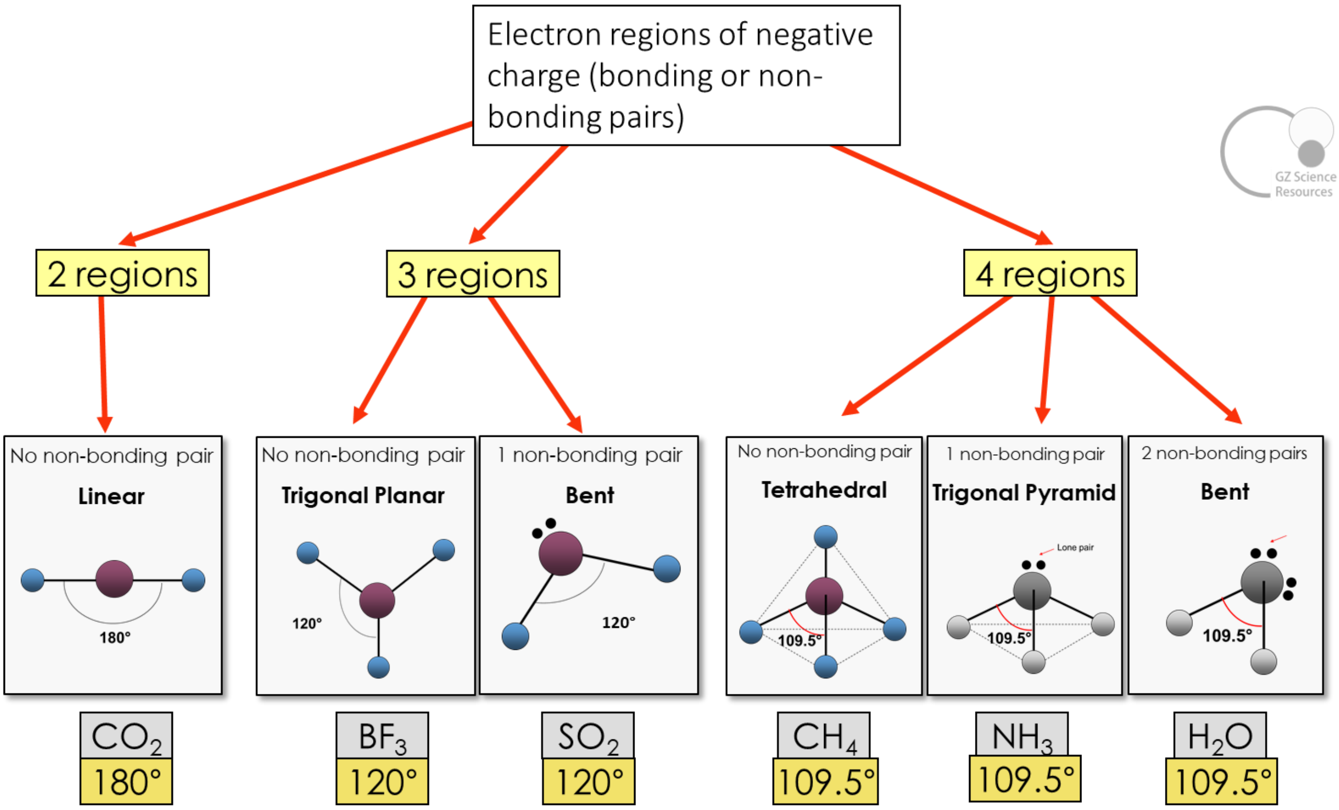
The bond angle is now 109.5°. This is because it is a 3-dimensional sphere divided into 4 rather than a circle.

This final shape is tetrahedral.



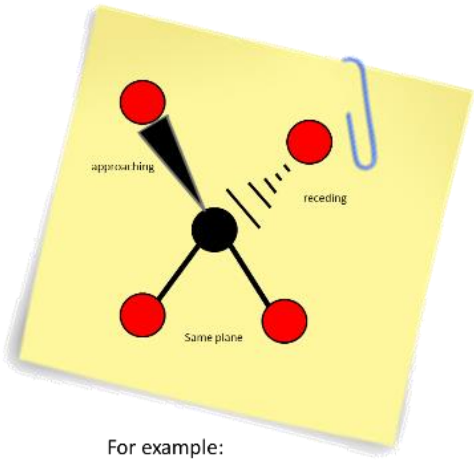
Molecular Shapes – four regions of negative charge (1 non-bonding pair) The four regions of negative charge still occupy a 3-dimensional tetrahedral geometry / arrangement. (The lone pair, however, exerts a stronger repulsion to the remaining bonded pairs). The bond angle is approximately 109.5°. The final shape the bonded atoms form, due to one non-bonded pair, s a trigonal pyramid (or a triangular pyramid)	
Molecular Shapes – four negative regions of charge (2 non-bonding pairs) The 4 regions of negative charge repel each other to a (warped) tetrahedral geometry / arrangement. However, the two non-bonding pairs create a much stronger repulsion than one non-bonding pair and the bond angle between the remaining bonded pairs is smaller again at approximately 109.5° (compared to 120 ° of the bent shape with only 3 regions of negative charge). The final shape the bonded atoms form is called Bent.	

Determining Molecular Shapes



Drawing Molecular Shapes

1. Atom on same plane as central atom – straight solid line
2. Atom receding from central atom – lines starting large and getting smaller
3. Atom approaching from central atom – solid triangle starting small and getting larger



For example:
Tetrahedral shape

Discussing shapes questions – NCEA example

Explain why the shape of the CO_2 molecule is linear but the shape of H_2O is bent?

1. The C (central atom) of CO_2 has 2 regions of negative charge around it in the form of double bonds connected to an O atom. (draw Lewis structure)

2. Each of the regions of negative charge repel each other the furthest away from each other in 3-dimensional space into a linear geometry / arrangement

3. There are no non-bonding pairs, so the CO_2 molecule therefore also forms a *linear shape*

1. The O molecule (central atom) of H_2O has 4 regions of negative charge around it in the form of two single bonds connected to a H atom and two non-bonding pairs. (draw Lewis structure)

2. Each of the regions of negative charge repel each other the furthest away from each other in 3-dimensional space and form a tetrahedral geometry / arrangement.

3. However with only 2 of the regions bonded to atoms the shape the H_2O molecule forms is a *bent shape*.

Electronegativity

Electronegativity is the attraction that an atom has towards electrons from another atom. The greater the electronegativity the stronger the pull it has towards other electrons.

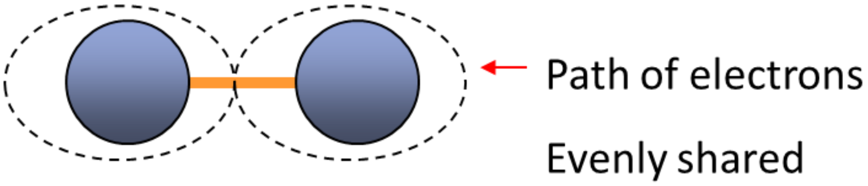
Trends in the periodic table

- The larger the nucleus (with the positive protons) the stronger the electronegativity, this means it increases from left to right.
- The further the valence electrons are from the nucleus the less the electronegativity, therefore the electronegativity decreases down a group.

Non – Polar Bonds in covalent molecules

If two identical atoms are covalently bonded together then there will be exactly the same amount of attraction between the shared valence electrons to the nuclei of each atom in the bonded pair. This is because there is no electronegativity difference between atoms, and the valence electrons 'orbit' each atom evenly. This becomes a non-polar molecule with non-polar bonds.

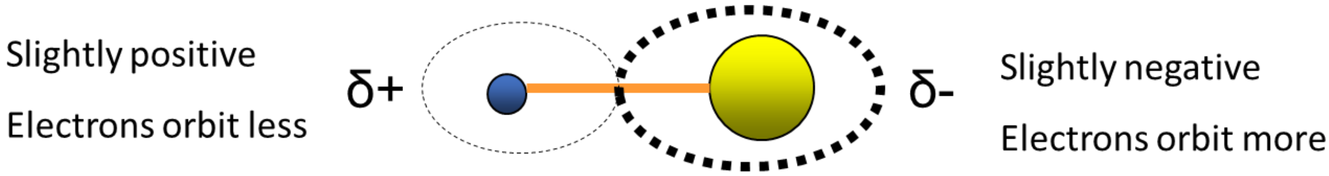
Example - Iodine molecule I_2



Polar Molecules

If two different types of atoms are bonded together then they will exert different levels of attraction for the orbiting electrons. That is because they may have different numbers of electron shells and different numbers of protons in their nucleus. This will cause an electronegativity difference. These bonds become polar bonds, creating a dipole, as there is an electronegativity difference and the valence electrons spend more time around the atom with the higher electronegativity value (that atom becomes slightly negative). The atom that the valence electrons spend less time around becomes slightly positive.

Example – hydrochloric acid HCl

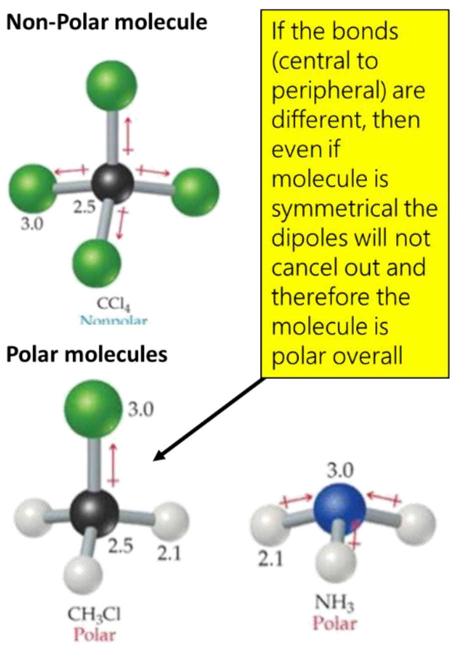


Symmetry and Polarity

The **overall polarity** of a molecule with polar bonds depends upon whether the molecule is symmetrical or not and if all bonds are the same.

A symmetrical molecule (one where the centres of peripheral atoms coincide) becomes a **non-polar molecule** (only if all bonds are the same) – as the bond dipoles cancel out.

An unsymmetrical molecule (one where the centre of peripheral atoms do not coincide) is a **polar molecule**, – as the bond dipoles **do not** cancel out.

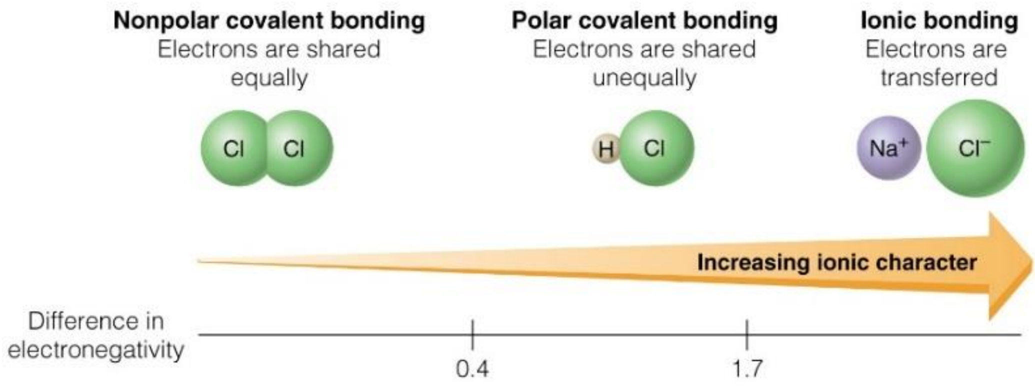


Ionic – covalent bond continuum due to electronegativity

Bond types between atoms can depend on the electronegativity of the atoms. Rather than discrete categories, molecules fall along a continuum

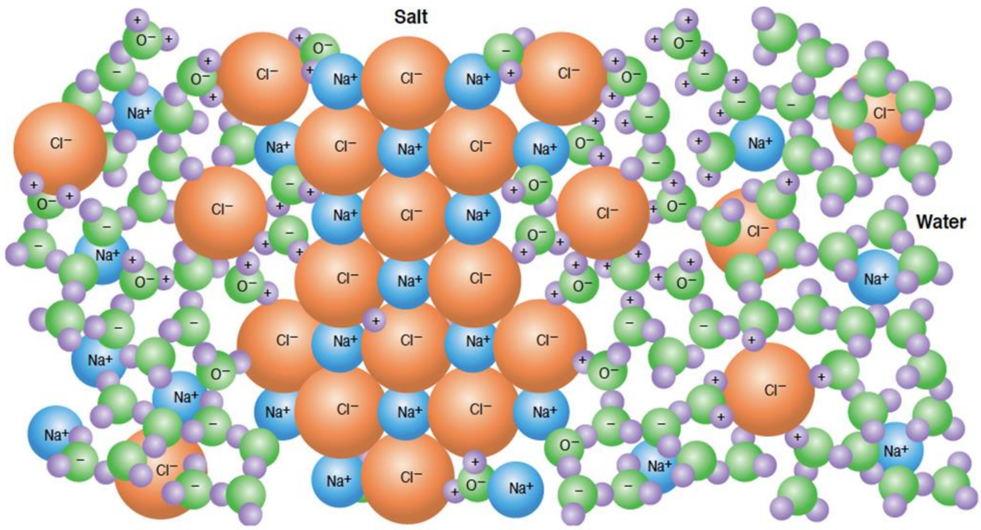
If there is little difference in electronegativity between two atoms then they tend to form a covalent bond with no polarity difference. A greater electronegativity difference creates a polar bond with uneven "sharing" of valance electrons.

If the electronegativity is even greater then there will be a complete transfer of electron from one atom (Metal) to another atom (non-metal) and ions will form that are held together with an ionic bond.



Solutions form when a solute is dissolved in a solvent

When a solid mixes into a liquid and can longer be seen it has dissolved. The liquid is called the solvent and it pulls apart the bonds between the solid particles, called the solute, and they diffuse. A solution is then created when the solvent particles (often water) are mixed up with the broken apart solute particles.



For a solute to dissolve, the solvent particles must form bonds with the solute particles. Water, being polar attracts ions because of their dipoles, and so dissolve many ionic substances.

Solubility

The solubility of a substance is the amount of that substance that will dissolve in a given amount of solvent. Solubility is a quantitative term. Solubility will vary depending on the solvent and the solute. The terms soluble and insoluble are relative. Some substances can be sparingly soluble where only the minutest percentage dissolves. For a solute to dissolve the attraction to the solvent molecules must be stronger than the bonds holding the atoms/molecules of the solute together.

Dissolving and Polarity

Polar substances dissolve polar substances.

e.g. Water, being polar attracts the molecules of other polar substances (e.g. HCl) and will dissolve them.

Polar substances will not dissolve non-polar substances.

e.g. Water, (polar) has a stronger attraction to itself than to non-polar molecules (e.g. cyclohexane) and will not dissolve them.

Non-polar substances dissolve non-polar substances.

e.g. Non-polar solvents (like cyclohexane) attract non-polar solutes (like napthalene) by the same weak molecular forces they attract themselves by and so will dissolve non-polar solutes.

Water as a Solvent

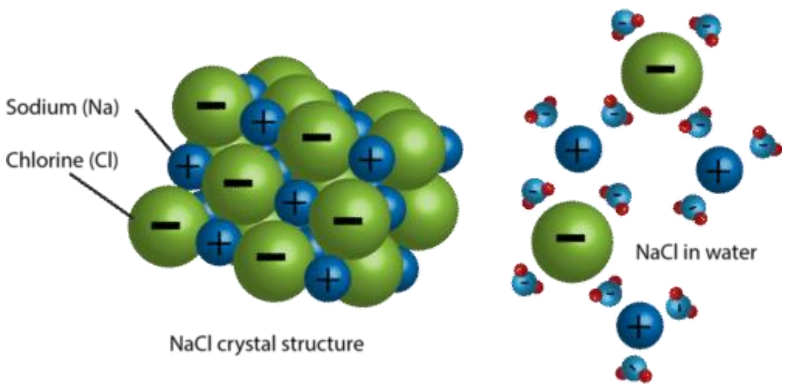
The water molecule has dipoles, caused by the separation of charge (δ+ - δ-). Due to the asymmetry of the molecule, their dipoles reinforce making the oxygen side of the molecule partially negative (δ-) and the hydrogen side partially positive (δ+). Such molecules are called 'polar'. Polarity causes a stream of water molecules to attract to a charged plastic pen.

Common Polar and Non-polar molecular substances

Polar	Non-Polar
water methanol ethanol acetic acid hydrogen chloride	cyclohexane benzene hydrocarbons (e.g. petrol) iodine

Solubility and dissolving

When a soluble salt, such as sodium chloride is dissolved in water the attractions between the polar water molecules and between the ions in the salt are replaced by attractions between the water molecules and the ions. The negative charges on the oxygen ends of the water molecules are attracted to the positive Na^+ ions, and the positive hydrogen ends of the water molecules are attracted to the negative Cl^- ions.

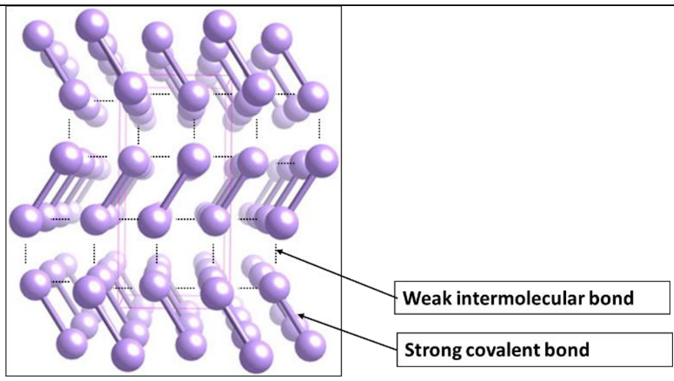
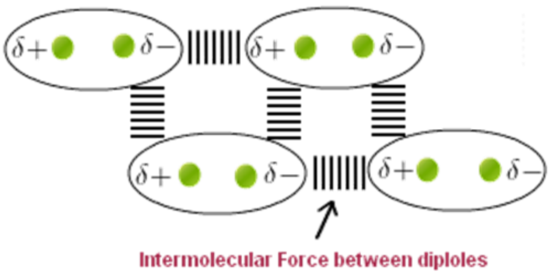


Groups of substances

Substances are grouped together according to the type of bonds they have between particles, and consequently the structure they form.

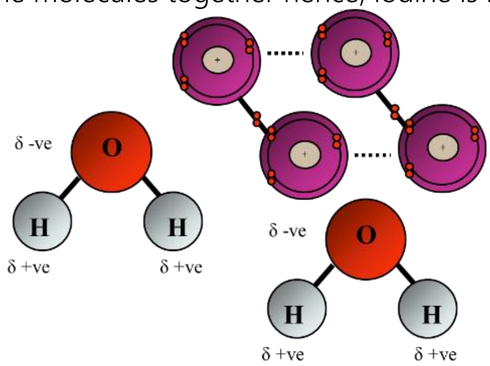
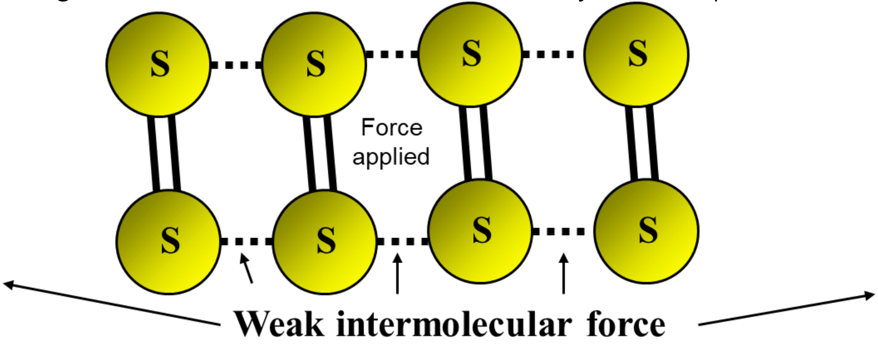
L2 will cover four groups of substances; Molecular, metallic, ionic and covalent network. The physical properties of these groups will be linked to their structure.

Molecular solids Non-metals forming molecules **S_2** sulfur **HCl** Hydrogen chloride **I_2** iodine	**Ionic solids** Non-metals and metals together forming a ionic compound **KI** Potassium iodide **$CuSO_4$** Copper sulfate **NaCl** Sodium chloride
Metallic solids Elements that are metals **Fe** iron **Al** aluminium **Cu** copper	**Covalent network solids** Carbon and silicon dioxide **SiO_2** Silicon dioxide **C** diamond **C** graphite

Non-polar Molecular solids non-metal + non-metal Molecules are held together by weak intermolecular bonding caused by temporary dipoles only. These are induced (created) by electrons randomly spending more time around one nucleus than the other. Within the Molecules, the atoms are held together by strong covalent bonds.	
Polar Molecular solids Polar molecules are held together by weak intermolecular forces, the δ –ve end of one molecule is attracted to the δ +ve end of another. This is due to both temporary and permanent dipoles (which tend to be stronger). Permanent dipoles are induced by electrons spending more time around one nucleus in the molecule that has greater electronegativity than the other. Note the distinction: Intra-molecular Forces: the strong bonding forces within a molecule. i.e. the covalent bonds holding the molecule together. Inter-molecular Forces: the weak bonding forces between molecules due to the attractions between partial charges. i.e. permanent dipole	

Three steps to answering structure and physical properties questions.

- ❑ The first is state the name of the solid.
- ❑ The second is describe the structure of the solid.
- ❑ The third is link the structure of the solid to the physical property discussed.

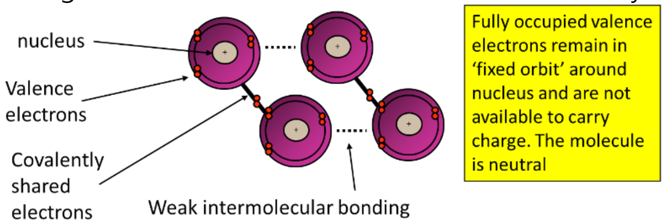
Polar Molecular solids – solubility 1. Hydrogen chloride (HCl) is a molecular solid 2. Hydrogen chloride is composed of covalently bonded atoms to form molecules 3. These molecules are held together by weak intermolecular forces 4. These molecules are <u>polar</u> therefore, the electrostatic attractions of water molecules (which is stronger than the weak intermolecular forces) have sufficient strength to pull the molecules apart hence, hydrogen is soluble	Non-polar Molecular solids – solubility Non-polar molecular solids are insoluble in water EXAMPLE: 1. Iodine is a molecular solid. 2. Iodine is composed of covalently bonded atoms to form molecules 3. These molecules are held together by weak intermolecular forces 4. Iodine is <u>non-polar</u> therefore, the electrostatic charges of the water do not have sufficient strength to overcome the weak intermolecular forces holding the molecules together hence, iodine is insoluble 
Molecular solids – Melting point Molecular solids have a low melting point. Many molecular solids are only solid at temperatures well below 0◦C and at room temperature, they are gases <u>For example:</u> 1. Carbon dioxide is a molecular solid (at low temperatures below -56◦C 2. Carbon dioxide is composed of covalently bonded atoms to form molecules 3. These molecules are held together by weak intermolecular forces 4. These forces require small amounts of energy to break apart the solid (but not the individual molecules, which are held together by strong covalent bonds) therefore, carbon dioxide has low melting point	Molecular solids - hardness <u>For example:</u> 1. Sulfur is a molecular solid 2. Sulfur is composed of covalently bonded atoms to form molecules 3. These molecules are held together by weak inter molecular forces 4. These forces require small amounts of energy to break apart the solid (but not the individual molecules which are held together by strong covalent bonds) therefore, sulfur is easily broken up 

Molecular solids - Conductivity

Molecular solids do not conduct electricity. In order for a substance to be electrically conductive there must be free moving charged particles

For example:

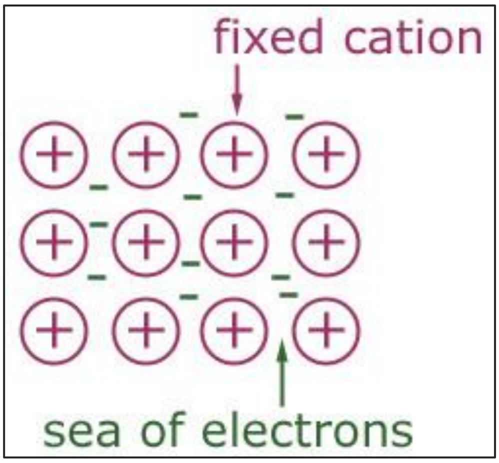
1. Iodine is a molecular solid
2. Iodine is composed of covalently bonded atoms to form molecules; weak intermolecular forces hold these molecules together
3. There are no free moving charges therefore iodine cannot conduct electricity



Metallic Solids - structure

Metals atoms are arranged as positive ions held in place in ordered layers by strong attractive non-directional bonding, forming a lattice. - this gives metals strength.

Metal atoms are held together in a 3–D lattice by metallic bonding in which valence electrons are attracted to the nuclei of neighbouring atoms. The attraction of the metal atoms for the valence electrons is not in any particular direction; therefore, metal atoms can move past one another without disrupting the metallic bonding, therefore metal is ductile and malleable. The atoms are packed tightly together - this makes metals dense



Metallic Solids – Conductivity

Metallic solids are conductive. Free moving charged particles are required to carry a charge and for a substance to be electrically conductive. Electrons from the outer shells of the metal atoms move freely throughout the lattice. - This makes metals excellent conductors of heat and electricity

For example:

1. Copper is a metallic solid
2. copper is arranged as positive ions held in place in ordered layers by strong attractive non-directional forces, in a sea of de-localised electrons
3. Electrons are free moving hence can carry a charge
4. Therefore, copper can conduct electricity

Metallic Solids - Solubility

Metallic solids are not soluble. In order for substance to dissolve in water (a polar liquid) the attraction between the particles in a substance must be less than the attraction towards water molecules

For example:

1. Lead is a metallic solid
2. Lead is arranged as positive ions held in place in ordered layers by strong attractive non-directional forces, in a sea of de-localised electrons
3. These forces require a large amount of energy to break therefore the electrostatic attractions of water molecules do not have sufficient strength to pull the atoms apart
4. Therefore, lead is insoluble

Metallic Solids – Malleability and ductility

Metallic solids are malleable and ductile. Layers of ions can slide over each other without breaking- this makes metals hard and also malleable and ductile

<u>For example:</u>

1. Iron is a metallic solid
2. Iron is arranged as positive ions held in place in ordered layers - a lattice, by strong attractive non-directional forces, in a sea of de-localised electrons
3. These forces require large amounts of energy to break apart the solid therefore aluminium is not easily broken up
4. However when pressure is applied layers can slide over each other, and as the attractive forces are non-directional the metallic particles remain strongly bonded. – This gives the metallic solids the properties of being malleable (moulded into flat sheets) and ductile (drawn out to thin wires)

Metallic Solids – Melting Point

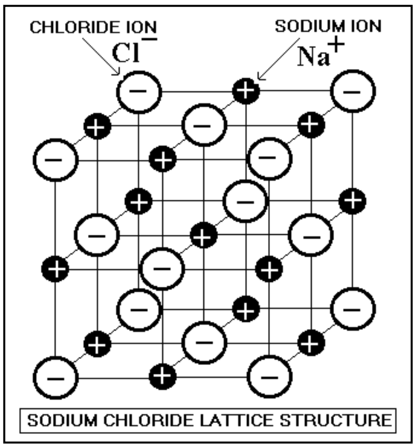
Metallic solids have a high melting point. The strength of the bonds between particles determines the energy required to break them, and therefore the amount of energy to change a solid into a liquid (the melting point) where the bonds are somewhat broken. Metals in general, have very strong bonds, which makes them solid at room temperature (Mercury is the exception)

<u>For example:</u>

1. Aluminium is a metallic solid
2. Aluminium is arranged as positive ions held in place in ordered layers by strong attractive non-directional forces, in a sea of de-localised electrons
3. These forces require a large amount of energy (high temperature) to break apart the metallic solid therefore the melting point is very high.

Ionic Solids – structure

Metal + Non-Metal. An ionic solid is composed of ions held together by strong directional electrostatic forces (ionic bonding) between +ve (cations) and –ve (anions) ions in a 3-dimensional lattice.



Ionic Solids - Solubility

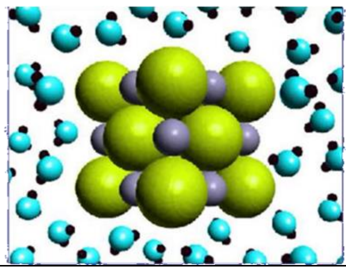
Ionic solids are soluble in solution. In order for substance to dissolve in water (a polar liquid), the attraction between the particles in a substance must be less than the attraction towards water molecules

<u>For example:</u>

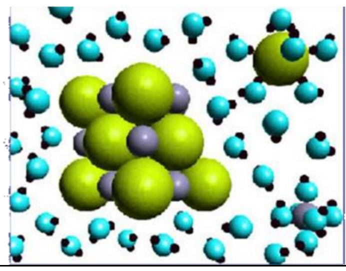
1. Sodium chloride (NaCl) is an ionic solid
2. Sodium chloride is composed of ions held together by strong directional electrostatic attractions between +ve and –ve ions in a lattice
3. The electrostatic attractions of water molecules have sufficient strength to pull the ions apart
4. Therefore, the solid will dissolve and is soluble

The positive hydrogen end of water is attracted to the anions and the negative oxygen end of water is attracted to the cations.

NaCl first placed in water



Na^+ and Cl^- ions breaking apart



Ionic Solids - Conductivity
Ionic solids are conductive when in solution or molten only. Free moving charged particles are required to carry a charge and for a substance to be electrically conductive

<u>For example:</u>

1. Sodium chloride is an ionic solid
2. Sodium chloride is composed of ions held together by strong directional electrostatic forces between +ve and –ve ions in a 3-d lattice
3. When solid the ions are not free to move therefore it does not conduct electricity
4. However, when molten, or dissolved in solution, the bonds are broken, and the ions are free to move therefore, sodium chloride can conduct electricity

Ionic Solids – Hardness and brittleness
Ionic solids are hard but brittle

<u>For Example:</u>

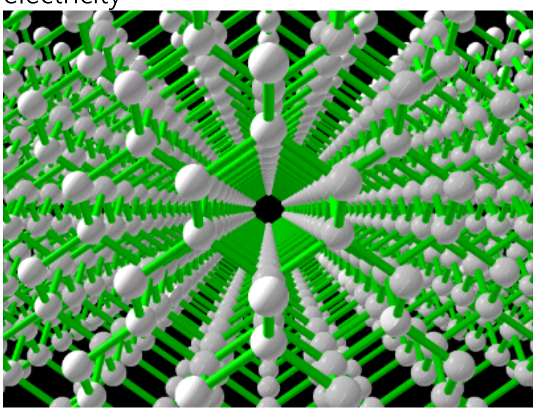
1. Sodium chloride is an ionic solid
2. Sodium chloride is composed of ions held together by strong directional electrostatic attractions between +ve and –ve ions in a 3-d lattice so requires a lot of energy to break the bonds
3. However, because the ionic bonding is directional, if sideways force is applied and a sheet of the lattice slides then ions of the same charge may come in close contact with each other and repel hence the ionic solid is brittle (and can break into pieces)

Covalent Network Solids - structure
All atoms are held together by strong covalent bonds
Diamond (C) is a 3-dimensional covalent network structure where atoms are held together by strong covalent bonds in all planes
Graphite (C) is a covalent network structure that is in 2-dimensional sheets (graphite). Between the layers are free moving electrons from the valance electrons of the carbon atoms.
Silicon dioxide (SiO_2) is a 3-dimensional covalent network structure

Covalent Network (3D) - Conductivity of diamond
3D Covalent network solids are not conductive

<u>For example:</u>

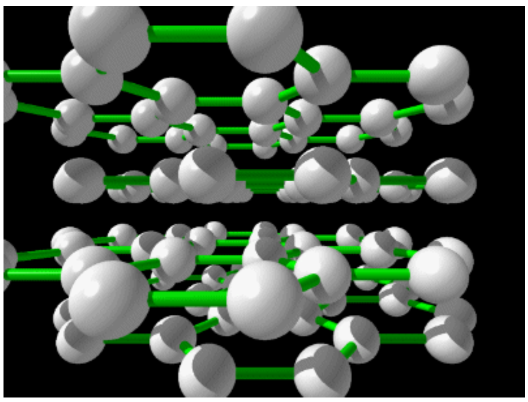
1. Diamond is a 3-dimensional covalent network structure (diamond)
   2. All atoms are held together by strong covalent bonds
   3. There are no free moving charged particles
   4. Therefore, diamond cannot conduct electricity



Covalent Network (2D) - Conductivity of graphite
2D Covalent network solids are conductive.

<u>For example:</u>

1. Graphite is a covalent network that is in 2-dimensional sheets
   2. Between the layers are free moving electrons from the valance electrons of the carbon atoms. 3. The free moving electrons can carry a current
   4. Therefore, graphite can conduct electricity



Covalent Network Solids – Solubility Covalent network solids are not soluble <u>For example:</u> 1. Silicon Dioxide is a 3-dimensional (or 2-dimensional) covalent network structure 2. All atoms are held together by strong covalent bonds 3. These forces require a large amount of energy to break therefore; the electrostatic attractions of water molecules do not have sufficient strength to pull the ions apart 4. Hence, silicon dioxide will not dissolve in water and is insoluble	Covalent Network Solids - Melting Point Covalent network solids have a high melting point <u>For example:</u> 1. Diamond is a 3-dimensional (or 2-dimensional) covalent network structure 2. All atoms are held together by strong covalent bonds 3. These forces require a large amount of energy to break 4. Therefore, diamond has a very high melting point.
Covalent Network Solids (3-D) – Hardness 3-dimensional covalent network solids are hard <u>For example:</u> 1. Diamond is a 3-dimensional covalent network structure 2. All atoms are held together by strong covalent bonds 3. These forces require a large amount of energy to break 4. Therefore, diamond is very hard.	Covalent Network Solids (2-D) - Hardness 2-dimensional covalent network solids are soft <u>For example:</u> 1. Graphite is a 2-dimensional covalent network structure 2. Atoms are held together by strong covalent bonds in 2-dimensional layers 3. However, the attractive forces holding the layers together are very weak and are broken easily, so the layers easily slide over one another, but the attraction is not strong enough to hold the layers together 4. Therefore, graphite is considered soft.

Solids Summary

Name of solid substance	Type of particle in solid	Attractive force broken when solid melts	Attractive force between particle – weak or strong (hardness)	Relative melting point	solubility	Electrical conductivity	Malleable
Molecular	molecules	Weak inter molecular	weak	low	Yes if polar No if non-polar	no	no
Metallic	atoms	Metallic bonding	strong	high	no	yes	yes
Ionic	ions	Electrostatic Ionic bonding	strong	high	Yes	Only if molten or in solution	No - brittle
Covalent Network 3-D	atoms	Covalent bonding	strong	high	no	no	no
Covalent Network 2-D	atoms	Covalent bonding	Strong (but weak between layers)	high	no	yes	no

Substance summary chart

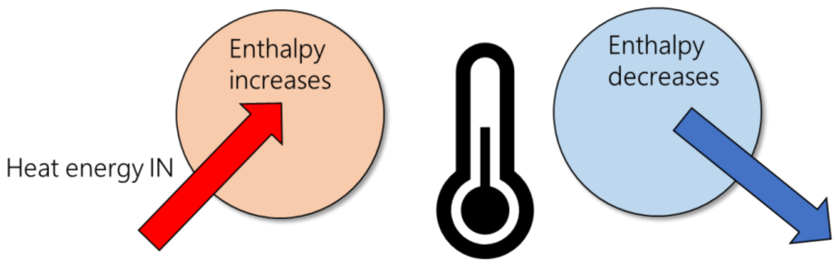
This chart needs to be learnt. There will not necessarily be one example for each group but information from this chart MUST be used in following questions about solids

Substance (for example)	Type of substance	Type of particle	Attractive forces between particles
$C_{(s)}$ Graphite	Covalent network	Atom	Covalent (and weak intermolecular forces)
$Cl_{2\ (s)}$ chlorine	Molecular	Molecules	Weak intermolecular forces
$CuCl_{2(s)}$ copper chloride	Ionic	Ion	Ionic bonds / electrostatic attraction
$Cu_{(s)}$ copper	Metal	Atom / cations and electrons	Metallic bonds / electrostatic attraction

Enthalpy and Enthalpy Change ΔH

Enthalpy (or Heat Content) is the energy in a substance due to kinetic energy of particles and potential energy in chemical bonds.

Enthalpy change ΔH is the difference in enthalpy of products H_P and reactants H_R



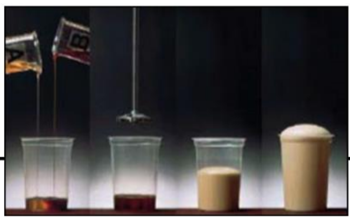
The unit for Enthalpy is kilojoules (kJ)

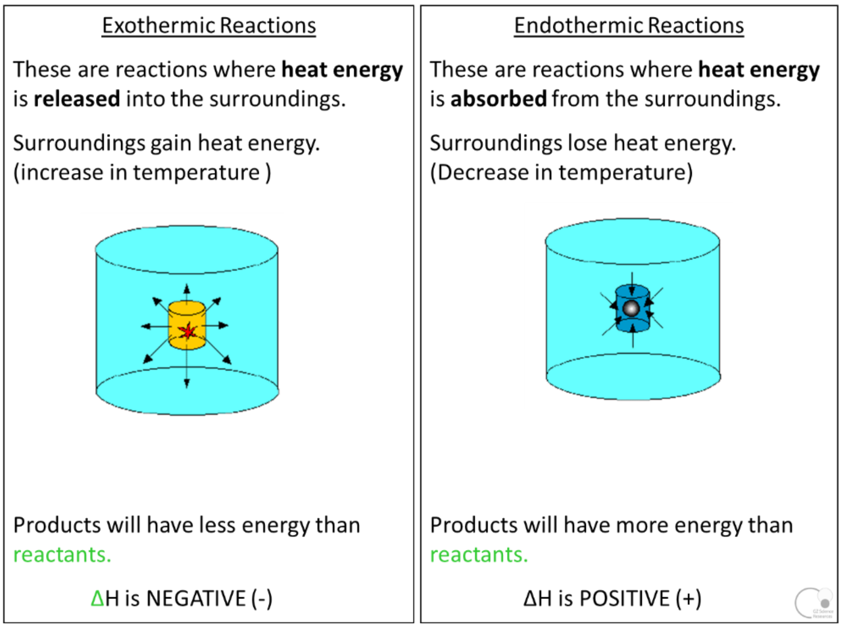
$$\Delta H = H_P - H_R$$

Enthalpy Change

H_P (products) and H_R (reactants) cannot be measured directly.

We can measure Enthalpy change (ΔH) by measuring energy

Released to surroundings (Exothermic Reactions)	Absorbed from surroundings (Endothermic Reactions)
	



Endothermic reactions

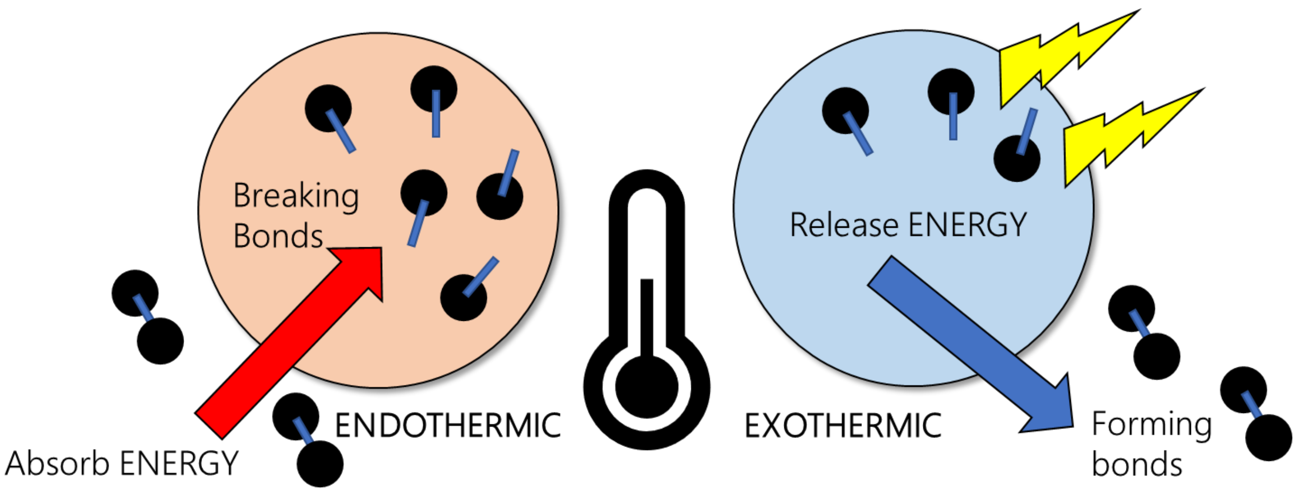
Any combustion reaction is exothermic. The bonds holding the atoms of fuel molecules together (usually consisting of carbon and hydrogen atoms) release a lot of energy in the form of light and heat when they are broken. The total energy holding the bonds together in the products are less than the total energy in the reactions and the difference is released.

Melting ice is an example of an endothermic reaction. The solid ice (water) atoms, that are in a fixed pattern, are barely moving and need to absorb energy in order to move faster and break the bonds to form water in a liquid state.

Forming and breaking Bonds

Bonds forming between atoms and molecules release energy therefore bond forming is an exothermic reaction. Bonds are formed to form a stable molecule.

Bonds breaking between atoms and molecules require energy therefore bond breaking is an endothermic reaction. The input of energy (usually light or heat energy) cause the atoms and molecules to move faster and 'pull away' from each other. Each type of bond has its own specific amount of energy, called *bond enthalpy* measured in kJ, required to break its bond.



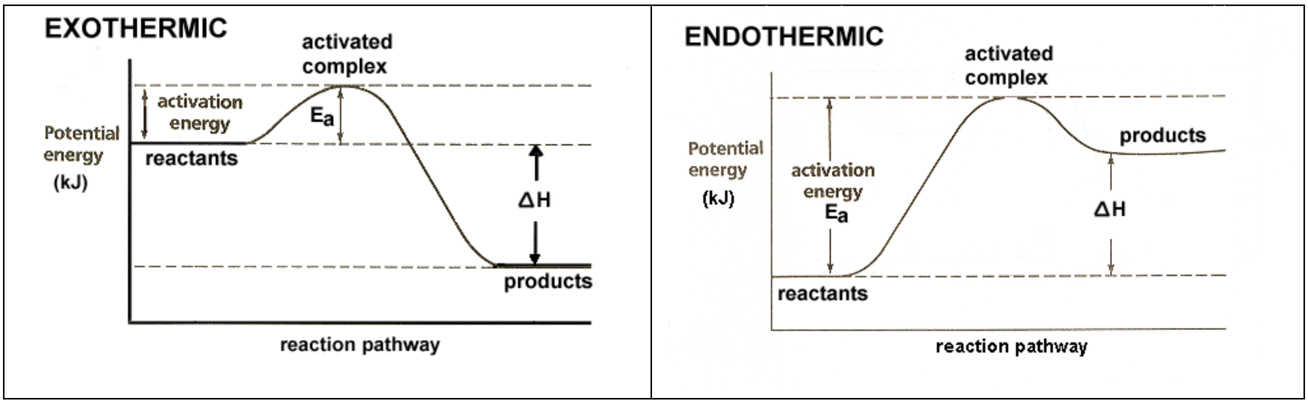
Enthalpy in Dissolving

If more energy is released when water bonds to the solute than it takes to separate the solute, the dissolving is exothermic and the temperature increases. An example is adding a strong acid (such as sulfuric acid) or base (such as sodium hydroxide)

However, for some substances dissolving the reaction is endothermic, for example Potassium chloride in water. More energy is needed to break the bonds between this ionic salt than released when new bonds are formed with the ions and water molecules.

Enthalpy Diagrams

Enthalpy Diagrams can be used to show the relative amounts of enthalpy of the reactants and products in a reaction as well as the direction and relative size of enthalpy change. In endothermic reactions, the enthalpy change will be positive and in exothermic reactions, the enthalpy change will be negative.



Enthalpy Change

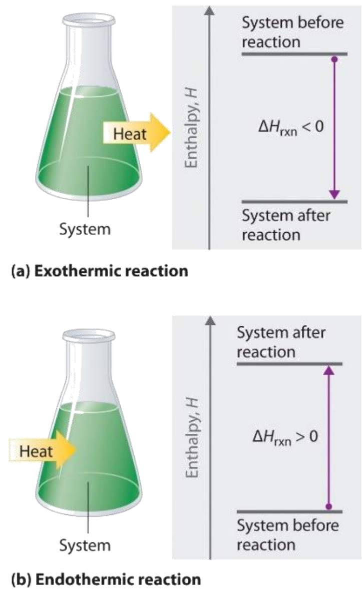
An exothermic reaction will release energy and the products will be at a lower enthalpy level than the reactants.

The reaction system will feel will feel hot to the touch as the energy is released as heat energy.

An endothermic reaction will absorb energy and the products will be at a higher enthalpy than the reactants.

The reaction system will feel cool to the touch as heat energy is taken from the surroundings, including your skin, and used to break bonds in the molecules.

$\Delta_r H$ is the enthalpy of a reaction and is measured in $kJmol^{-1}$



Standard conditions

Measurements depend on conditions. When measuring an enthalpy change you will get different values under different conditions. For example, the enthalpy change of a particular reaction will be different at different temperatures, different pressures or different concentrations of reactants.

The values for enthalpy are given for standard conditions, indicated by the superscript θ

Standard conditions include:

Temperature of 25°C
Atmospheric pressure conditions of 1 ATM (sea level)
Concentration of 1mol per Litre

Thermochemical Calculations and stoichiometry

You can perform stoichiometry calculations using energy changes from thermochemical equations. Using a balanced chemical equation to calculate amounts of reactants and products is called *stoichiometry*. Energy released or absorbed can be calculated per amount of substance.

Exothermic	Endothermic
$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	$CH_4 + H_2O \longrightarrow CO + 3H_2$
$\Delta H = -888 kJmol^{-1}$	$\Delta H = 206 \ kJmol^{-1}$
This thermochemical equation reads; 888kJ of heat is released when 1 mole of CH_4 reacts with 2 moles of O_2 to produce 1 mole of CO_2 and 2 moles of H_2O	This thermochemical reaction reads; 206kJ of heat is absorbed when 1 mole of CH_4 reacts with 1 mole of H_2O to produce 1 mole of CO and 3 moles of H_2.

Use thermochemical equations to find ΔH, n and m.

$$n = m/M$$

n = moles (6.02×10^{23} particles) m = mass (grams) M = Molar Mass ($gmol^{-1}$)

The mole, abbreviated mol, is an SI unit, which measures the number of particles in a specific substance. One mole is equal to $6.02214179 \times 10^{23}$ atoms

Thermochemical Equation Example

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta_r H = -888 kJmol^{-1}$

Use the equation above to find heat released if 2.5 moles of CH_4 burns.

ANSWER:
1 mole of CH_4 releases 888kJ
2.5 moles CH_4 releases x kJ
x = 2.5 x 888 = 2220kJ

An equation is a mole ratio – the number in front of each substance tells you how many moles of that there is to any other substance.

For example there is 1 mole of CH_4 to every 2 moles of O_2
The enthalpy of the equation shows you the amount of energy per unit of substance.
888 = $1CH_4$ 888 = $2O_2$ (444 = $1O_2$)

Thermochemical Equation Example 2

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta_r H = -888 kJmol^{-1}$

Calculate the amount (in moles) of H_2O produced when the reaction above releases 10,000kJ.

Amount of mols in equation

2 moles H_2O when 888kJ released

x moles H_2O when 10000kJ released

$x = \frac{2 \times 10000}{888} = 22.5$ moles

Amount energy per unit of substance

Total energy released

An **alternative method** is to find out how much energy is released per mole first
2 moles H_2O = 888kJ
Therefore 1 mole H_2O = 444kJ

10,000kJ/444kJ = 22.5

So 22.5 moles of water are produced at 444kJ to reach 10,000kJ
(22.5 x 444 = 10,000)

Thermochemical Equation Example 3

$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta_rH = 206kJmol^{-1}$

$M(C) = 12gmol^{-1} \quad M(O) = 16gmol^{-1}$

Calculate the energy required to produce 1kg of CO gas from the reaction above

Step one
moles of CO produced
M = 1000g M(CO) = $28gmol^{-1}$
n = m/M
n = 1000/28 = 35.7 moles

Step two
1 mole CO produced requires 206kJ (as per the equation above)
35.7 mols CO produced so.....
enthalpy = 35.7 x 206 = 7354kJ

1kg = 1000g. Must be converted to grams first. If Molar mass is not given then use the periodic table. The units are kJ not $kJmol^{-1}$ as it is total amount not amount per mole.

Thermochemical Experimental data

Enthalpy change (Δ_rH) for a reaction, can be collected from a thermochemical investigation.

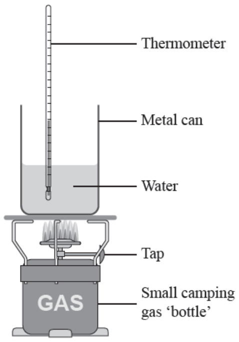
Values required are masses of water in which the reaction takes place, temperature change (in °C) and the specific heat capacity value for water. (These calculations will be done in Level 3)

Often questions will ask why a particular investigation set up does not provide the same thermochemical data as the accepted enthalpy change.

Reasons can include errors such as:

- Some energy is used to heat the metal can and the air surrounding the experiment / the experiment was not conducted in a closed system
- Incomplete combustion of butane.
- Some butane may have escaped before being ignited.
- The butane in the gas canister was impure.
- Some water evaporated
- Some energy was converted to light and sound
- Not carried out under standard conditions

Therefore, not all of the energy released by the combustion of butane was transferred to heating the water



Bond Enthalpy

Bond enthalpy (also known as bond energy) is defined as the amount of energy required to break one mole of the stated bond.

The high values for bond enthalpy explains why some substances are very resistant to chemical attack and form very stable molecules

In a polyatomic (more than one atom) molecule, the bond strength between a given pair of atoms can vary slightly from one compound to another. The value given for bond enthalpy is the average of all these variations.

A multiple bond (double/triple) is always stronger than a single bond because more electrons bind the multiple bonded atoms together.

The table below shows some common average bond enthalpies.

Bond enthalpy /kJ mol^{-1}	**Bond enthalpy /kJ mol^{-1}**	**Bond enthalpy /kJ mol^{-1}**
H - H 436	C - H 412	C = C 612
H - O 463	C - Cl 338	C o C 837
H - N 388	C - F 484	C = O 743
H - Cl 431	C - O 360	O = O 496
H - F 565	C - C 348	N ≡ N 944
F - F 158	O – O 146	
Cl - Cl 242		

Bond Enthalpy calculations

Bonds Broken – Endothermic Bonds formed – Exothermic

$\Delta_r H° = \sum$ (energy of bonds broken) - $\sum$(energy of bonds formed)

Note: Bond energies calculated for gases. Convert using $\Delta_{vap}H°$ or $\Delta_{sub}H°$ if in solid or liquid state.

$$CO_{(g)} + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{2(g)} \qquad \Delta_r H° = -1.0\ Kjmol^{-1}$$

Bonds Broken		Bonds formed	
C≡O	995kJ	C=O x 2	2(743)kJ
H-O x 2	2(463)kJ	H-H	436kJ
	1921kJ		1922kJ

$\Delta_r H°$ = 1921kJmol^{-1} – 1922kJmol^{-1}

$\Delta_r H°$ = -1.0 kJmol^{-1}

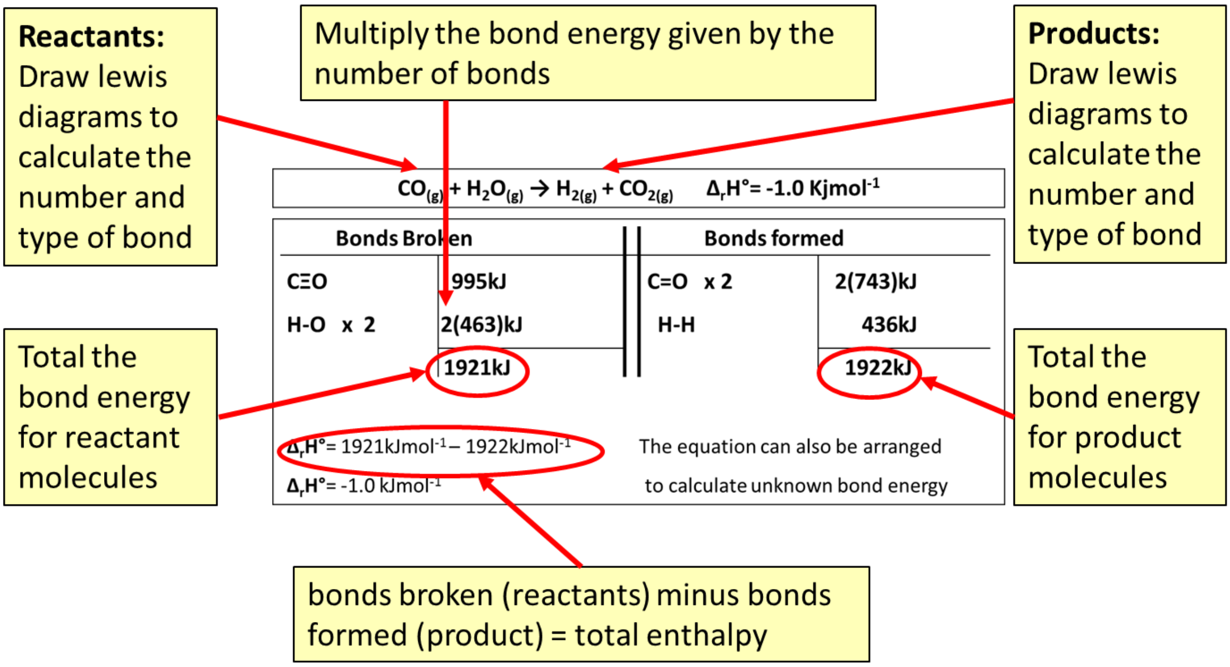
The equation can also be arranged to calculate unknown bond energy

Enthalpy of fusion ($\Delta_{fus}H°$) 1 mol solid to liquid state

Enthalpy of vaporisation ($\Delta_{vap}H°$) 1 mol liquid to gas state

Enthalpy of sublimation ($\Delta_{sub}H°$) 1 mol solid to gas state

Bond Enthalpy calculations



Using Bond Enthalpy to calculate $\Delta_r H°$

Bond enthalpy is the change in enthalpy when the covalent bond, in a gaseous molecule, is broken. It is always a positive value because bond breaking always requires an input of energy.

Making bonds releases energy so the more bonds a substance can form the more stable it will be.

The strength of a covalent bond depends on the electrostatic attraction between the positive nuclei and the shared electron pair. The larger the atomic radius of an atom (which increases down a group) the further the shared electron pair from the positive nucleus – which creates decreasing electrostatic attraction. Therefore the weaker the covalent bond and the lower the value of bond enthalpy.

The stronger a covalent bond, the higher the value of the bond enthalpy. The units are kJ mol^{-1}