

STRUCTURE & BONDING

Introduction The physical properties (e.g. boiling point, conductivity, strength) of a substance depend on its structure and type of bonding present. Bonding determines the type of structure.

TYPES OF BOND

Basic theory

- noble gases (He, Ne, Ar, Kr, Xe and Rn) are all relatively, or totally, inert
- this is due to their electronic structure which **appears to** confer stability
- atoms without the electronic structure of a noble gas try to gain one
- various methods are available according to an element's position in the periodic table.

<i>Bond types</i>	CHEMICAL BONDS (<i>strong bonds</i>)	<ul style="list-style-type: none"> • ionic (or electrovalent) • covalent • dative covalent (or co-ordinate) • metallic
	PHYSICAL BONDS (<i>weak bonds</i>)	<ul style="list-style-type: none"> • van der Waals' forces - weakest • dipole-dipole interaction • hydrogen bonds - strongest

Formation of ions

Positive ions

- also known as cations; they are smaller than the original atom.
- formed when electrons are removed from atoms.
- the energy associated with the process is known as the ionisation energy (I.E.).

1st I.E. The energy required to remove one mole of electrons (to infinity) from the one mole of gaseous atoms to form one mole of gaseous positive ions.



There are as many ionisation energy steps as there are electrons in the atom.

2nd I.E. $\text{Mg}^+_{(g)} \longrightarrow \text{Mg}^{2+}_{(g)} + \text{e}^-$ and so on

Other points

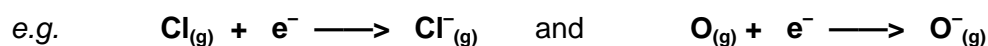
- successive ionisation energies get larger as the proton : electron ratio increases.
- large jumps in value occur when electrons are removed from shells nearer the nucleus because there is less shielding and more energy is required to overcome the attraction.
- if the I.E. values are very high, covalent bonding will be favoured (e.g. *beryllium*).

Negative ions

- known as anions
- are larger than the original atom due to electron repulsion in outer shell
- formed when electrons are added to atoms
- energy is released as the nucleus pulls in an electron
- this energy is the **electron affinity**.

Electron Affinity

The energy change when one mole of gaseous atoms acquires one mole of electrons (from infinity) to form one mole of gaseous negative ions.



The greater the effective nuclear charge (E.N.C.) the easier an electron is pulled in.

Q.1 Write out equations representing the

- 1st I.E. of Li
- 1st I.E. of Al
- 1st I.E. of F
- 2nd I.E. of Na
- 2nd I.E. of Al
- 2nd I.E. of F
- 3rd I.E. of Li
- 4th I.E. of Al
- 21st I.E. of Rb

Q.2 Write out equations representing the

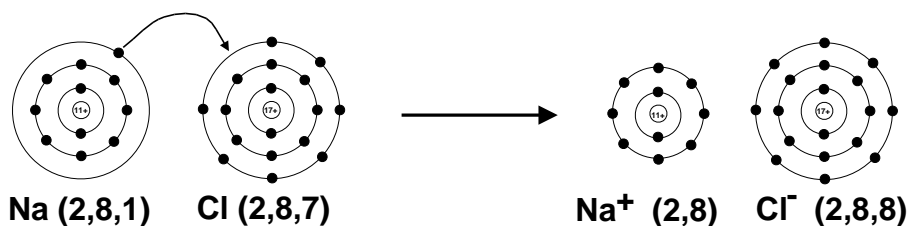
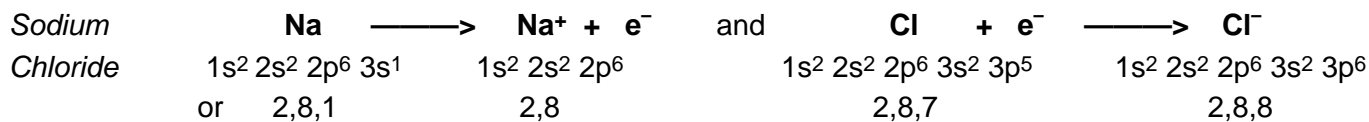
- 1st E.A. of Br
- 2nd E.A. of Br
- 1st E.A. of N

Q.3 In which group would you find elements with the following successive I.E.'s ?

- 577 1820 2740 11600 14800
- 418 3070 4600 5860 7990
- 736 1450 7740 10500 13600

THE IONIC (OR ELECTROVALENT) BOND

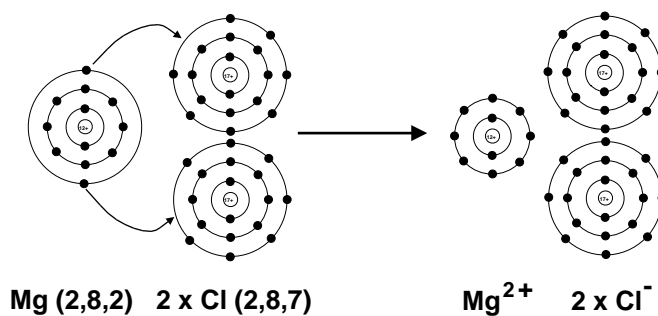
Formation Ionic bonds tend to be formed between elements whose atoms need to “lose” electrons to gain the nearest noble gas electronic configuration (n.g.e.c.) and those which need to gain electrons. The **electrons are transferred** from one atom to the other.



- an electron is **transferred** from the 3s orbital of sodium to the 3p orbital of chlorine
- both species end up with the electronic configuration of the nearest noble gas
- the resulting ions are held together in a crystal lattice by electrostatic attraction

MgCl_2

Because magnesium atoms have two outer shell electrons they can combine with two chlorine atoms by the transfer of one electron to each atom to form one Mg^{2+} and two Cl^- ions



Q.4 Show how the following combine to form ionic compounds.

- a) Na and O b) Mg and O c) Mg and F d) Al and O

Giant ionic lattices

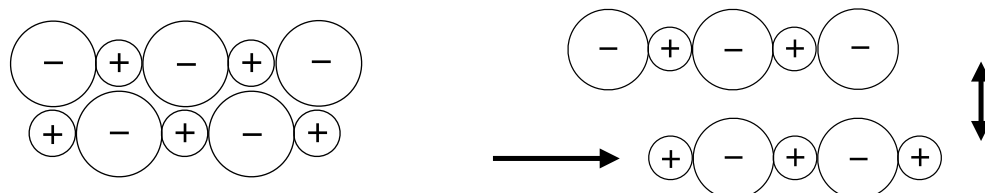
- bonding*
- oppositely charged ions held in a regular 3-dimensional lattice by electrostatic attraction
 - ions try to pack together in the most efficient form so there is little wasted (empty) space
 - the arrangement of ions in a crystal lattice depends on the relative sizes of the ions



The Na^+ ion is small enough relative to the Cl^- ion to fit in the spaces so that both ions occur in every plane. Each Na^+ is surrounded by 6 Cl^- (co-ordination number = 6) and each Cl^- is surrounded by 6 Na^+ (co-ordination number = 6).

Physical properties of ionic compounds

- melting point* **Very high** A large amount of energy must be put in to overcome the strong electrostatic attractions and separate the ions.
- strength* **Very brittle** Any dislocation leads to the layers moving and similarly charged ions being next to each other. The ensuing repulsion splits the crystal.



- electrical*
- **do not conduct electricity when solid** - as the ions are held strongly in the lattice.
 - **Conduct electricity when molten or in aqueous solution** - the ions become mobile and conduction takes place.

- solubility*
- Insoluble in non-polar solvents.
 - Soluble in water as it is a polar solvent and stabilises the separated ions.
 - much energy is needed to overcome the electrostatic attraction and separate the ions
 - stability attained by being surrounded by polar water molecules compensates for this

Diagram

COVALENT BONDING

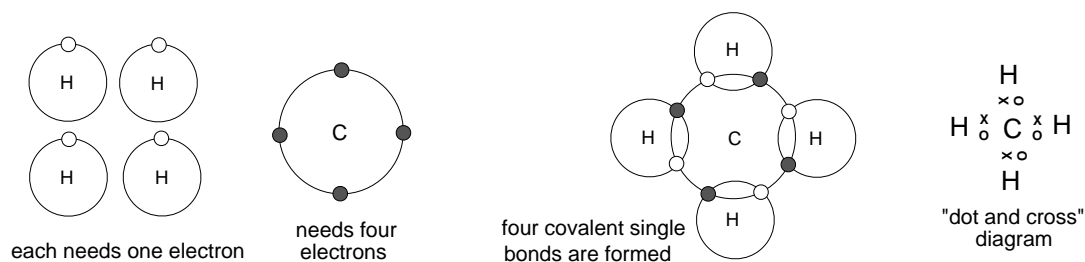
Definition

- consists of a **shared pair of electrons, one electron being supplied by each atom** either side of the bond. (*compare with dative covalent bonding*)
- atoms are held together because their nuclei are attracted to the shared electrons

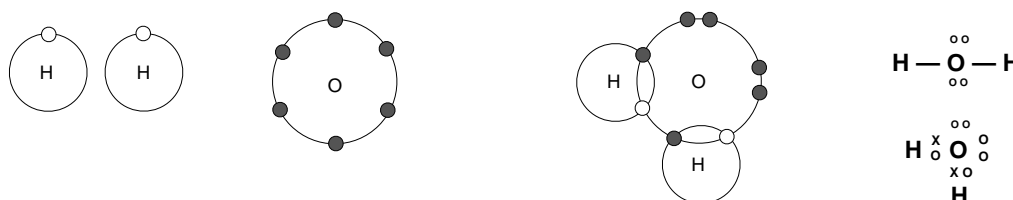
Formation

- between atoms of the same element; (e.g. in N_2 , O_2 , diamond and graphite)
- between atoms of different elements on the RHS of the periodic table; (e.g. CO_2 , SO_2).
- when one of the elements is in the middle of the table; (e.g. C, Si)
- head-of-the-group elements with high ionisation energies, (e.g. Be in $BeCl_2$)

METHANE



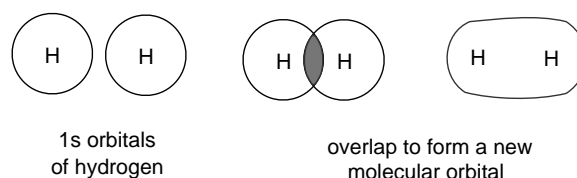
WATER



- atoms share electrons in order to get the nearest noble gas electronic configuration
- some don't achieve an "octet" as they haven't got enough electrons - Al in $AlCl_3$
- others share only some - if they share all they will exceed their "octet" - NH_3 and H_2O
- atoms of elements in the 3rd period onwards can exceed their "octet" if they wish
- they are not restricted to eight electrons in their "outer shell"

Orbital theory

Covalent bonds are formed when orbitals, each containing one electron, overlap. This forms a region in space where an electron pair can be found; new molecular orbitals are formed.



The greater the overlap the stronger the bond.

Q.5

Show how the covalent bonding is arranged in the following molecules

- a) H_2 b) F_2 c) O_2 d) N_2 e) NH_3 f) $SiCl_4$
 g) BF_3 h) H_2SO_4 i) CH_3OH j) IF_7 k) PCl_5 l) CO_2

Structures containing covalent bonds

1. Simple molecules

bonding Atoms are joined together **within** the molecule by covalent bonds.

electrical **Don't conduct** electricity as they have **no mobile ions or electrons**.

solubility Tend to be more soluble in organic solvents than in water; some are hydrolysed

boiling point **Low** - the forces between molecules (intermolecular forces) are weak known as **van der Waals forces** - see below

These arise from attractions between instantaneous dipoles caused by the varying position of electrons in molecules. They increase as molecules get more electrons.

e.g. CH₄ -161°C C₂H₆ - 88°C C₃H₈ -42°C

as forces are weak, little energy is required to separate molecules from each other so

boiling points are low

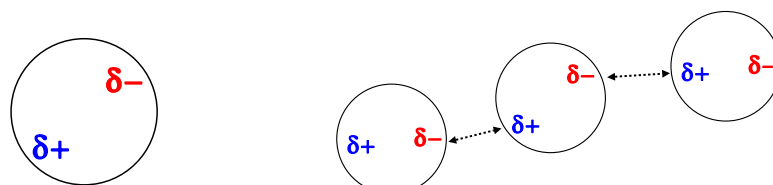
some boiling points are higher than expected

due to additional forces of attraction

Instantaneous dipole-induced dipole forces (van der Waals' forces)

Origin

- electrons in atoms or molecules are moving at high speeds in orbitals
- it is possible for more electrons to be on one side of an atom/molecule than the other
- this forms a dipole where one side is slightly negative and the other slightly positive
- a dipole in one atom/molecule can then induce a dipole in a neighbouring one



For an instant there are more electrons on the right side of the atom - a dipole is formed

The dipole on one atom induces (causes) dipoles to form on other atoms. The atoms are then attracted to each other by their oppositely charged ends

Result

- atoms/molecules become attracted to each other
- this makes them harder to separate and gives them higher boiling points

Trends

- the more electrons there are in an atom/molecule the bigger the effect

Examples

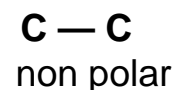
- layers in graphite are held together by weak van der Waals's forces so it is soft
- the boiling point of noble gases increases down the group

Element	He	Ne	Ar	Kr	Xe
No. of Electrons	2	10	18	36	54
Boiling point / °C	-269	-246	-186	-152	-108

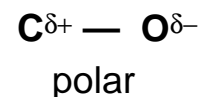
HOWEVER Some molecules have boiling points which are higher than one would expect!

Electronegativity "The ability of an atom to attract the pair of electrons in a covalent bond to itself."

- Non-polar bond*
- similar atoms have the same electronegativity
 - they will both pull on the electrons to the same extent
 - the electrons will be equally shared

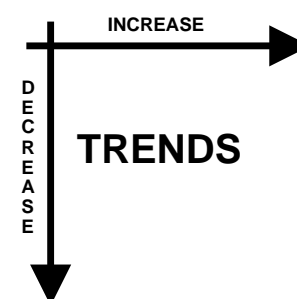


- Polar bond*
- different atoms have different electronegativities
 - one will pull the electron pair closer to its end
 - it will be slightly more negative than average, δ^-
 - other will be slightly less negative, or more positive, δ^+
 - a dipole is induced and the bond is said to be polar
 - the greater the difference in electronegativity, the greater the polarity of the bond.



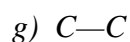
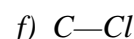
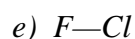
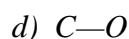
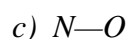
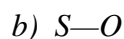
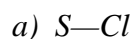
Pauling Scale

- a scale for measuring electronegativity
- values increase across periods
- values decrease down groups
- fluorine has the highest value



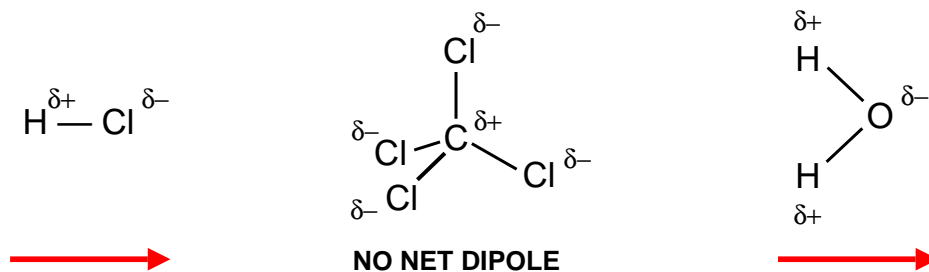
H							
2.1							
Li	Be	B	C	N	O	F	
1.0	1.5	2.0	2.5	3.0	3.5	4.0	
Na	Mg	Al	Si	P	S	Cl	
0.9	1.2	1.5	1.8	2.1	2.5	3.0	
K							Br
0.8							2.8

Q.6 Predict the polarity in the following bonds; where applicable, draw in the δ^+ and δ^-



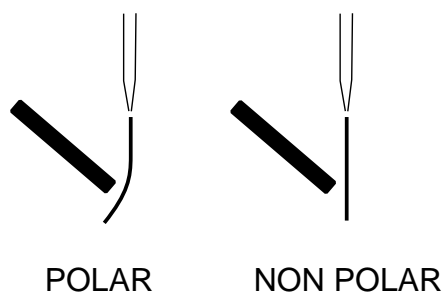
Polar molecules

- some molecules are polar if they contain polar bonds
- the **molecules will be polar if they have a NET DIPOLE MOMENT**
- it is a bit like balanced forces
- non-polar molecule dipoles in bonds within the molecule 'cancel each other out'
- polar molecule dipoles do not 'cancel each other out'



Experiment

- place a liquid in a burette
- allow a narrow stream to run out
- place a charged rod next to the flow
- polar molecules will be attracted

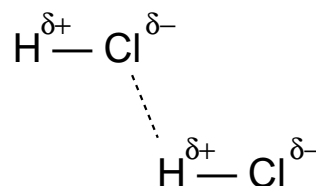


Q.7 Which of the following molecules are polar?

- a) F_2 b) CH_3Cl c) H_2S d) C_2H_5OH e) NH_3

Dipole-dipole interaction

- Occurrence**
- between molecules containing polar bonds
in addition to the basic van der Waals' forces
 - the extra attraction between dipoles means that more energy must be put in to separate molecules
 - get higher boiling points than expected for a given mass



Q.8 Find the boiling points of the hydrides of elements in Groups 4,5,6, and 7. Plot four lines (one for each group) on a graph of boiling pt. v. molecular mass. On the graph, state what is unusual about the values for NH_3 , H_2O and HF ?

Hydrogen bonding

- Formation*
- an extension of dipole-dipole interaction **giving rise to even higher boiling points**
 - bonds between **H** and the three most electronegative elements, **F, O and N** are extremely polar
 - because of the **small sizes of H, F, N and O** the partial charges are concentrated in a small volume thus leading to a **high charge density**
 - makes the intermolecular attractions greater and leads to even higher boiling points

Hydrogen fluoride

WATER

- Ice*
- each water molecule is **hydrogen bonded to 4 others** in a tetrahedral formation
 - ice has a “diamond-like” structure
 - its volume is larger than the liquid water making it
 - when ice melts, the structure collapses slightly and the molecules come closer together
 - they then move a little further apart as they get more energy (warmer)
 - this is why water has a maximum density at 4°C and ice floats.

Liquid water

- intermolecular hydrogen bonding gives **higher than expected boiling point**
- extra attraction between molecules just below surface give **high surface tension** and causes the meniscus to be the shape it is

2. Covalent networks (Macro (or giant) molecules) - DIAMOND, GRAPHITE and SILICA

bonding Many atoms are joined together in a regular array by a large number of covalent bonds

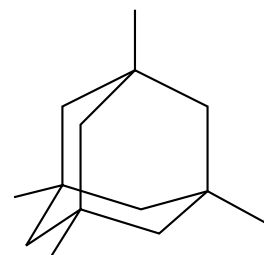
Diamond each carbon atom is joined to four others - **Co-ordination No 4**

Graphite each carbon atom is joined to three others - **Co-ordination No 3**

melting point **Very high** - structures are made up of a large number of covalent bonds, all of which need to be broken if the atoms are to be separated.

strength **Diamond and silica (SiO₂)**

hard exists in a rigid tetrahedral structure

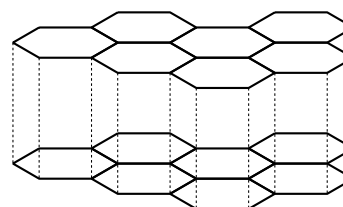


Graphite

soft consists of layers which are only attracted by weak van der Waals' forces

layers can slide over each other

it used as a lubricant and in pencils



electrical Do not conduct electricity as they have no mobile ions or electrons.

BUT Graphite conducts electricity

- each atom only uses three of its outer shell electrons for bonding to other carbon atoms
- the remaining electron can move through layers allowing the conduction of electricity
- carbon atoms in diamond use all four electrons for bonding so have no free electrons

3. Molecular solids

Iodine At room temperature and pressure, iodine is a greyish solid. However it doesn't need to be warmed much in order to produce a purple vapour. This is because iodine is **composed of diatomic molecules (I₂)** which exist in an ordered molecular crystal in the solid state. Each molecule is independent of the others, only being attracted by van der Waals' forces. Therefore, little energy is required to separate the iodine molecules.

Structure of iodine

DATIVE COVALENT (CO-ORDINATE) BONDING

Theory

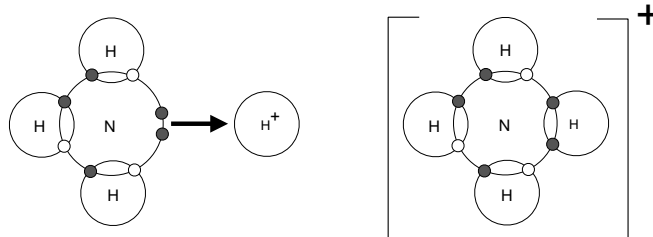
- dative covalent (or co-ordinate) bond differs from a covalent bond only in its formation
- both electrons of the shared pair are provided by one species (donor) and it shares the electrons with the acceptor
- donor species will have lone pairs in their outer shells
- acceptor species will be short of their "octet" or maximum.

Lewis Base :- a lone pair donor Lewis Acid :- a lone pair acceptor

Formation

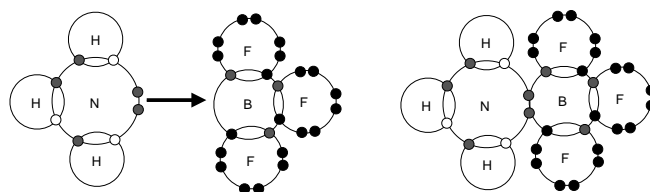
ammonium ion, NH_4^+

The lone pair on N is used to share with the hydrogen ion which needs two electrons to fill its outer shell. The N now has a +ive charge as it is now sharing rather than owning two electrons.



Boron trifluoride-ammonia NH_3BF_3

Boron has an incomplete shell in BF_3 and can accept a share of a pair of electrons donated by ammonia. The B becomes -ive as it is now shares a pair of electrons (i.e. it is up one electron) it didn't have before.



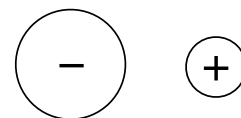
Q.9 Why does BF_3 react with NH_3 but not with CH_4 or AlH_3 ?

Q.10 Show the formation of dative covalent bonds between
 a) H_2O and H^+ b) AlCl_3 and Cl^- c) PCl_5 and Cl^-

Fajan's Rules

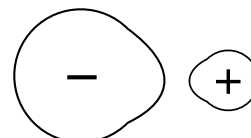
- Not all ionic compounds have high melting points
- Some covalently bonded compounds have higher than expected b.pts
this is due to dipoles in their structure
- Reason :- in many substances the bonding is not 100% ionic or covalent

The ideal ionic compound has completely separate, spherical ions and the electron densities are apart from each other.



If the positive ion has a **high charge density** it can distort the negative ion by attracting the outer shell electrons to give an area of electron density between the two species ...

- a bit like a covalent bond



The feasibility of formation of covalent bonds can be predicted using **Fajan's Rules**.

The rules A compound is more likely to be covalent if the ...

CATION has a **small size** and **high charge** it is "highly polarising" and attracts electrons in the anion

ANION has a **large size** and **high charge** it is "highly polarisable" and will be easily distorted

N.B. Just because a substance is less likely to be covalent according to Fajan's Rules doesn't mean it will be ionic; it will remain covalent but have some ionic character (or vice versa).

Examples Chlorides can be used to demonstrate changes in bond type as the positive charge density increases due to higher charge (across Period 3) or larger size (down Group 1)

		charge	ionic rad.	m.pt./°C	solubility	bonding
Period 3	NaCl	1+	0.095nm	808	soluble	ionic
	MgCl ₂	2+	0.065nm	714	soluble	ionic
	AlCl ₃	3+	0.050nm	180	hydrolysed	covalent
	SiCl ₄	4+	0.041nm	-70	hydrolysed	covalent
Group 1	LiCl	1+	0.060nm		soluble	some cov. character
	NaCl	1+	0.095nm		soluble	ionic
	KCl	1+	0.133nm		soluble	ionic
	RbCl	1+	0.148nm		soluble	ionic

Q.11 Which ion / species in each pair favours covalency ?

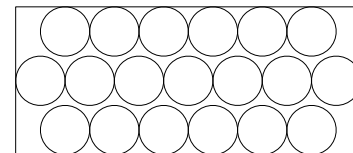
- a) Li⁺ and Na⁺ b) Li⁺ and Be²⁺ c) B³⁺ and Al³⁺
 d) F⁻ and I⁻ e) C and Pb f) Sn²⁺ and Sn⁴⁺

METALLIC BONDING

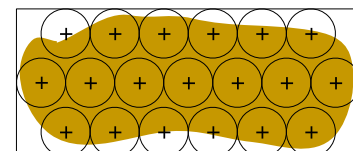
involves a lattice of positive ions surrounded by delocalised electrons

Formation Metal atoms achieve stability by “off-loading” electrons to attain the electronic structure of the nearest noble gas. These electrons join up to form a **mobile cloud** which prevents the newly-formed positive ions from flying apart due to repulsion between similar charges.

Atoms arrange themselves in regular close packed 3-dimensional crystal lattices.



The outer shell electrons of each atom leave to join a mobile “cloud” or “sea” of electrons which can roam throughout the metal. The electron cloud binds the newly-formed positive ions together.



Metallic bond strength depends on the

- number of outer electrons donated
- the size of the metal atom/ion.

The melting point is a measure of the attractive forces within the metal.

electrical Conduct electricity as there are mobile electrons.

strength The delocalised electron cloud binds the “ions” together making metals ...

- **malleable** can be hammered into sheets
- **ductile** can be drawn into rods

melting point

High. Ease of separation depends on the - density of the electron cloud and - ionic size/charge.

Periods	Na (2,8,1)	<	Mg (2,8,2)	<	Al (2,8,3)
m.pt	98°C		650°C		659°C
b.pt	890°C		1110°C		2470°C

reason

Groups	Li (2,1)	>	Na (2,8,1)	>	K (2,8,8,1)	>	Rb	>	Cs
m.pt	181°C		98°C		63°C				
b.pt	1313°C		890°C		774°C				

reason