

STRUCTURE & BONDING

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

TYPES OF BOND

CHEMICAL BONDS

(strong bonds)

- **IONIC** (or electrovalent)
- **COVALENT**
- **DATIVE COVALENT** (or COORDINATE)
- **METALLIC**

PHYSICAL BONDS

(weak bonds)

- **induced dipole-dipole interactions** (London forces)
- **permanent dipole-dipole interactions**
(both the above are examples of **van der Waals' forces**)
- **hydrogen bonds**

weakest
↓
strongest

FORMATION OF IONS FROM ATOMS

- Positive ions**
- known as **cations**
 - formed when electrons are removed from atoms
 - are smaller than the original atom
 - the energy associated with the process is known as the ionisation energy (IE).

1st I.E. The energy required to remove one mole of electrons (to infinity) from 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. $\text{Mg}^{\text{+}}(\text{g}) \longrightarrow \text{Mg}^{\text{2+}}(\text{g}) + \text{e}^{-}$ and so on

Notes

- successive ionisation energies get larger as the proton : electron ratio increases.
3rd ionisation energy > 2nd ionisation energy > 1st ionisation energy

- big jumps in value occur when electrons are removed from shells nearer the nucleus - **less shielding** so **more energy** is needed to overcome the attraction.

1st I.E 500 kJmol⁻¹ 2nd I.E 900 kJmol⁻¹ 3rd I.E 6000 kJmol⁻¹

The 3rd electron must have been in a shell nearer the nucleus - In Group 2

- if the **IE values are very high, covalent bonding is favoured** (e.g. *beryllium*).

- Negative ions**
- known as **anions**
 - **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 (ENC) 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 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

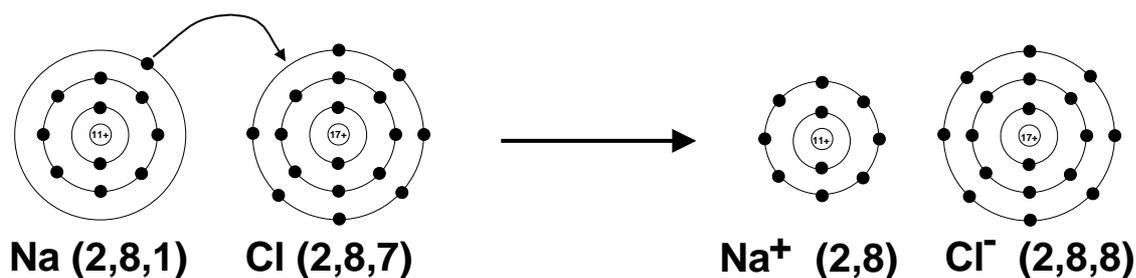
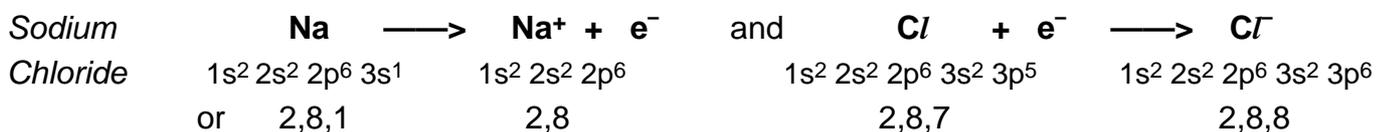
Q.3 In which group would you find elements with the following successive I.E.'s ?

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

THE IONIC (OR ELECTROVALENT) BOND

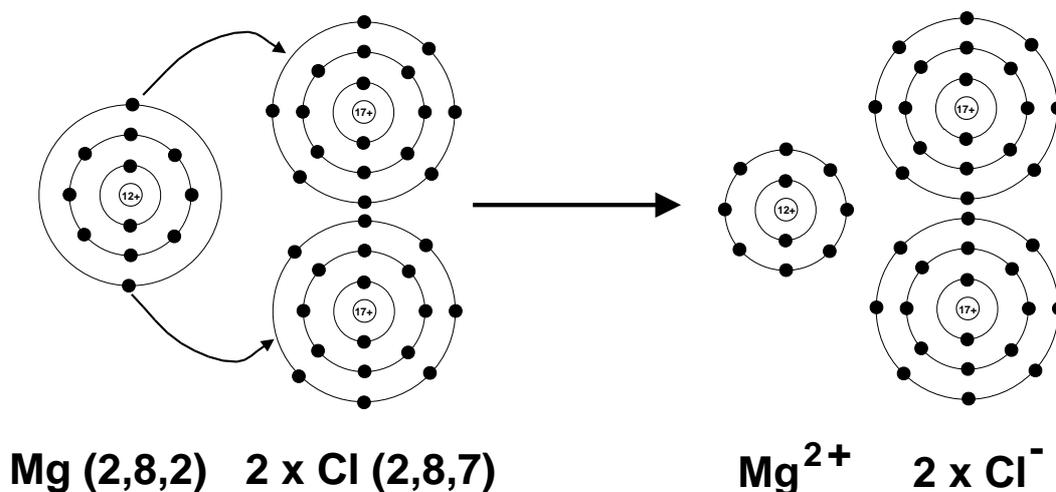
'An electrostatic attraction between positive and negative ions'

Formation Ionic bonds tend to be formed between elements whose atoms need to "lose" electrons to gain the nearest noble gas electronic configuration (nhec) and those needing to gain electrons. **Electrons are transferred** from one atom to the other.



- 1 electron is **transferred** from the 3s orbital of sodium to the 3p orbital of chlorine
- both species end up with an 'octet' of electrons in their outer shell
- the resulting ions are held together in a crystal lattice by **electrostatic attraction**

MgCl₂ 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 Mg²⁺ 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

Predicting the charge on an ion

Simple ions

s and *p* block elements

Can be predicted from their position in the Periodic Table

Group	electrons in outer shell	charge on ion
1	1	+
2	2	2+
3	3	3+
6	6	2-
7	7	-

d block elements

Transition elements (eg iron) can have more than one ion. The use of a Roman numeral identifies which ion is present.

iron(II) **Fe²⁺** *iron(III)* **Fe³⁺**

Complex ions

Some groups possess a charge.

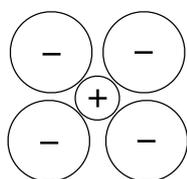
nitrate **NO₃⁻** *sulphate* **SO₄²⁻**
carbonate **CO₃²⁻** *ammonium* **NH₄⁺**

SOME COMMON IONS

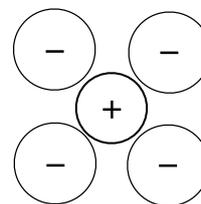
1	hydrogen	H ⁺	chloride	Cl ⁻
	sodium	Na ⁺	bromide	Br ⁻
	potassium	K ⁺	iodide	I ⁻
	lithium	Li ⁺	hydroxide	OH ⁻
	rubidium	Rb ⁺	nitrate	NO ₃ ⁻
	caesium	Cs ⁺	nitrite	NO ₂ ⁻
	copper(I)	Cu ⁺	hydrogencarbonate	HCO ₃ ⁻
	silver(I)	Ag ⁺	hydrogensulphate	HSO ₄ ⁻
	ammonium	NH ₄ ⁺		
	2	calcium	Ca ²⁺	sulphate
barium		Ba ²⁺	sulphite	SO ₃ ²⁻
magnesium		Mg ²⁺	sulphide	S ²⁻
zinc		Zn ²⁺	oxide	O ²⁻
iron(II)		Fe ²⁺	carbonate	CO ₃ ²⁻
cobalt		Co ²⁺	copper(II)	Cu ²⁺
manganese(II)		Mn ²⁺		
3	aluminium	Al ³⁺	phosphate	PO ₄ ³⁻
	iron(III)	Fe ³⁺		

GIANT IONIC LATTICES

- bonding*
- oppositely charged ions held in a regular 3-d lattice by electrostatic attraction
 - ions pack together in the most efficient way so there is little wasted space
 - the arrangement of ions in a lattice depends on the relative sizes of the ions



NaCl



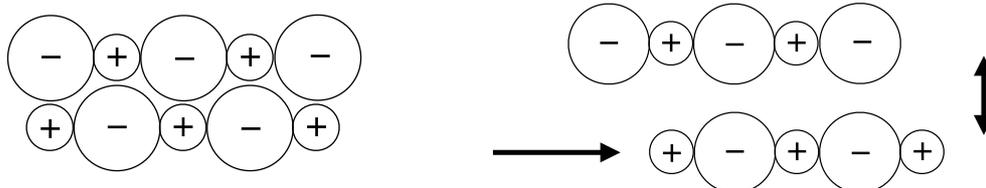
CsCl

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 pt* **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 layers moving and similarly charged ions being next to each other. The repulsion splits the crystal.



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

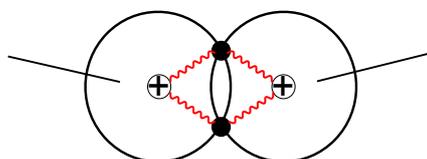
- solubility*
- **insoluble in non-polar solvents**
 - **soluble in water** as it is a polar solvent and stabilises the separated ions
 - energy is needed to overcome the electrostatic attraction and separate the ions
 - stability is achieved by polar water molecules surrounding the ions

Diagram

COVALENT BONDING

- Definition*
- consists of a **shared pair of electrons**; each atom supplies one electron
 - atoms are held because their nuclei are attracted to the shared electrons

*positive nucleus
attracts shared pair*

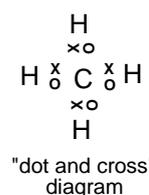
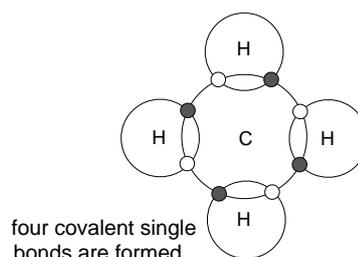
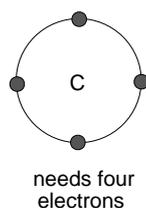
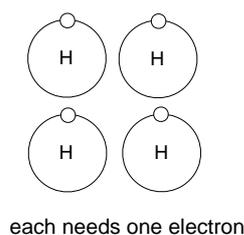


*nucleus of other atom
is also attracted to the
shared pair*

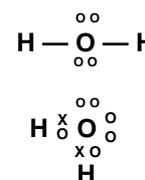
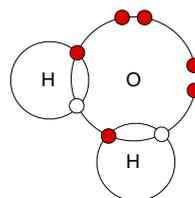
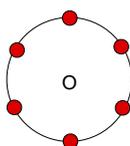
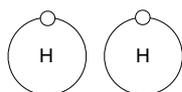
- **Average bond enthalpy** is a measurement of the strength of a covalent bond the stronger the bond, the higher its value (see later work)

- Formation*
- between atoms of the same element; (N_2 , O_2 , diamond and graphite)
 - between atoms of different elements on RHS of the periodic table; (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 complete their 'octet' of electrons
- some don't achieve an 'octet' as they haven't enough electrons - **Al** in $AlCl_3$
- others share only some - if they share all their 'octet' is exceed - **NH₃** and **H₂O**
- atoms of elements in the 3rd period onwards can exceed their 'octet' because they are not restricted to eight electrons in their 'outer shell' - **S** in SF_6

Q.5 Show how the covalent bonding is arranged in the following molecules

- a) H_2 b) Cl_2 c) O_2 d) N_2 e) NH_3
f) $SiCl_4$ g) BF_3 h) SF_6 i) PCl_5 j) CO_2

Structures containing covalent bonds

1. Simple molecules

<i>bonding</i>	Atoms are joined together within the molecule by covalent bonds.
<i>electrical</i>	Don't conduct electricity as they have no mobile ions or electrons .
<i>solubility</i>	Tend to be more soluble in organic solvents than in water; some are hydrolysed
<i>boiling pt</i>	Low - the forces between molecules (intermolecular forces) are weak (known as van der Waals forces - see below)

Attractions between molecules increases as the molecules get more electrons.

e.g. CH_4 -161°C C_2H_6 -88°C C_3H_8 -42°C

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

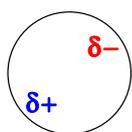
boiling points are LOW

Dipole-dipole interactions (van der Waals' forces)

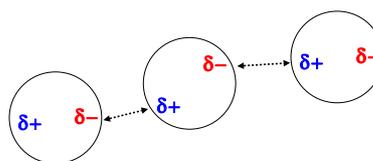
- Types**
- **Induced** dipole-dipole interactions - London (or Dispersion) Forces
 - **Permanent** dipole-dipole interactions

1. Induced dipole-dipole interactions

- 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
 - this forms a dipole where one side is slightly negative; 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

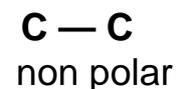
- Examples*
- layers in graphite are held together by weak van der Waals's forces so it is soft
 - the boiling point of noble gases increases down the group

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

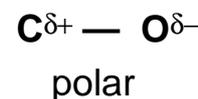
HOWEVER Some molecules have boiling points much higher than one would expect!

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

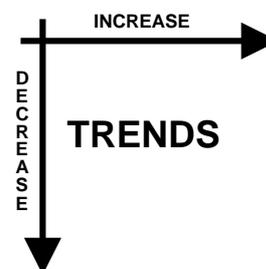


- Polar bond*
- different atoms have different electronegativities
 - one will pull the electron pair closer to its end
 - it will be slightly more negative than average, δ^-
 - other will be slightly less negative, or more positive, δ^+
 - a dipole is induced and the bond is said to be polar
 - the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



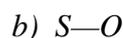
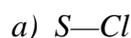
Pauling Scale

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



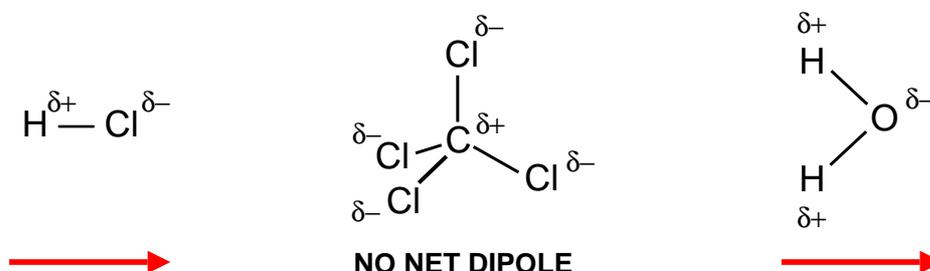
H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K						Br
0.8						2.8

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

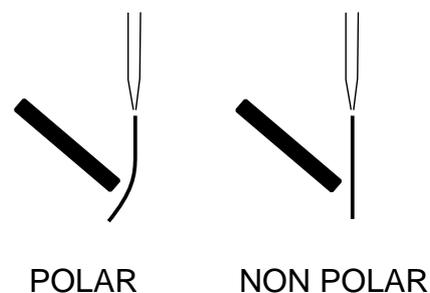


Polar**molecules**

- 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'
- **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

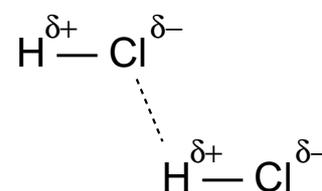


Q.7 Which of the following molecules are polar?

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

2. Permanent dipole-dipole interaction

- Occurrence**
- between molecules containing polar bonds **in addition to** the basic induced 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 even higher boiling points**
 - bonds between **H** and the three most electronegative elements, **F, O and N** are extremely polar
 - the **small sizes of H, F, N and O** concentrates the partial charges in a small volume thus leading to a **high charge density**
 - intermolecular attractions are greater, leading to even higher boiling points

Hydrogen fluoride (HF)

WATER

- Ice*
- each water molecule is **hydrogen bonded to 4 others** in a tetrahedral formation
 - ice has a “diamond-like” structure
 - it is a **simple molecular lattice**
 - its volume is larger than the liquid water making it
 - when ice melts, the structure collapses slightly and molecules close 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 the surface gives a **high surface tension** and causes the meniscus to be the shape it is

Viscosity

The greater the hydrogen bonding in alcohols, the greater the viscosity

propan-1-ol

propan-1,2-diol

propan-1,2,3-triol

CH₃CH₂CH₂OH

CH₃CH(OH)CH₂OH

CH₂(OH)CH(OH)CH₂OH

————— INCREASING VISCOSITY —————>

2. GIANT COVALENT LATTICES (covalent networks) - DIAMOND, GRAPHITE and SILICA

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

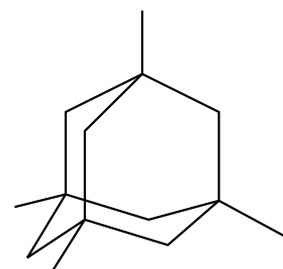
Diamond each carbon atom is joined to four others - **Co-ordination No. = 4**

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

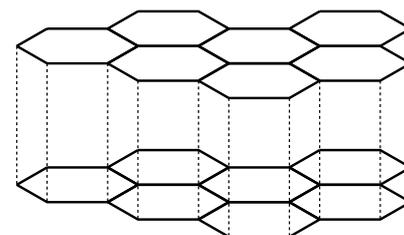


Graphite

soft consists of layers which are attracted by weak induced dipole-dipole interactions

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 atoms
- 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 ones

3. MOLECULAR SOLIDS

Iodine At room temperature, iodine is a grey solid. However, on gentle warming it produces a purple vapour. This is because iodine is **composed of diatomic molecules (I₂)** existing in an ordered molecular crystal. Each molecule is independent and attracted by weak induced dipole-dipole interactions.

Therefore, little energy is required to separate the iodine molecules.

DATIVE COVALENT (CO-ORDINATE) BONDING

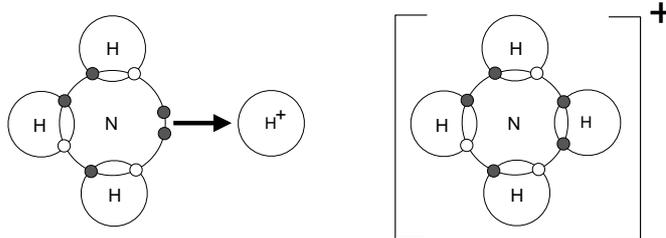
Theory

- 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

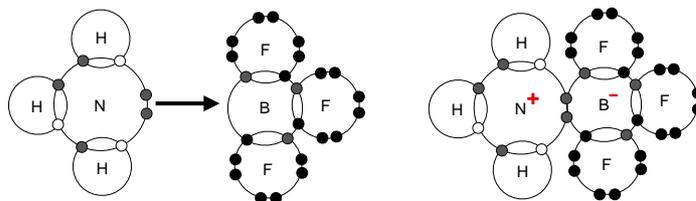
Formation ammonium ion, NH_4^+

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 ?

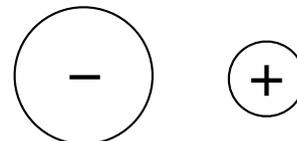
Q.10 Show the formation of dative covalent bonds between

- a) H_2O and H^+ b) AlCl_3 and Cl^- c) PCl_5 and Cl^-

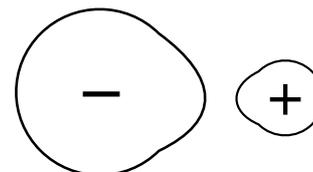
Fajan's Rules

- not all ionic compounds have high melting points
- some covalently bonded compounds have higher than expected boiling points 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 is predicted using **Fajan's Rules**.

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

CATION	small size high charge	"highly polarising"	attracts electrons in the anion
ANION	large size high charge	"highly polarisable"	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.

Examples Changes in bond type of chlorides 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⁺
d) F⁻ and I⁻

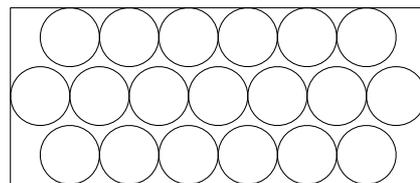
- b) Li⁺ and Be²⁺
e) C and Pb

- c) B³⁺ and Al³⁺
f) Sn²⁺ and Sn⁴⁺

METALLIC BONDING

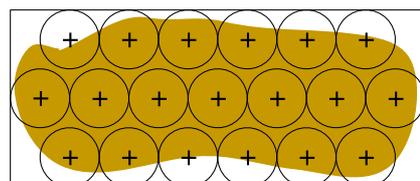
Involves a lattice of positive ions surrounded by delocalised electrons

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**

- **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 pt. **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