Anderson Serangoon Junior College 2024 JC1 H2 Chemistry Chemical Bonding

Content

- Ionic bonding, metallic bonding, covalent bonding and co-ordinate (dative covalent) bonding
- Shapes of simple molecules and bond angles
- Bond polarities and polarity of molecules
- Intermolecular forces, including hydrogen bonding
- Bond energies and bond lengths
- Lattice structure of solids
- Bonding and physical properties

Learning Outcomes

Candidates should be able to:

- (a) show understanding that all chemical bonds are electrostatic in nature and describe:
 - (i) ionic bond as the electrostatic attraction between oppositely charged ions
 - (ii) covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei
 - (iii) metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons
- (b) describe, including the use of 'dot-and-cross' diagrams,
 - (i) ionic bonding as in sodium chloride and magnesium oxide
 - (ii) covalent bonding as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene
 - (iii) co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al₂Cl₆ molecule
- (c) describe covalent bonding in terms of orbital overlap (limited to s and p orbitals only), giving σ and π bonds
- (d) explain the shapes of, and bond angles in, molecules such as BF₃ (trigonal planar); CO₂ (linear); CH₄ (tetrahedral); NH₃ (trigonal pyramidal); H₂O (bent); SF₆ (octahedral) by using the Valence Shell Electron Pair Repulsion theory
- (e) predict the shapes of, and bond angles in, molecules analogous to those specified in (d)
- explain and deduce bond polarity using the concept of electronegativity
 [quantitative treatment of electronegativity is not required]
- (g) deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d));
- (h) describe the following forces of attraction (electrostatic in nature):
 - (i) intermolecular forces, based on permanent and induced dipoles, as in CHCl₃(I); Br₂(I) and the liquid noble gases
 - (ii) hydrogen bonding, using ammonia and water as examples of molecules containing -NH and -OH groups
- (i) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water
- (j) explain the terms bond energy and bond length for covalent bonds
- (k) compare the reactivities of covalent bonds in terms of bond energy, bond length and bond polarity
- (I) describe, in simple terms, the lattice structure of a crystalline solid which is:
 - (i) ionic, as in sodium chloride and magnesium oxide
 - (ii) simple molecular, as in iodine
 - (iii) giant molecular, as in graphite and diamond
 - (iv) hydrogen-bonded, as in ice
 - (v) metallic, as in copper
 - [the concept of the 'unit cell' is not required]
- (m) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances
- (n) suggest the type of structure and bonding present in a substance from given information

References

- 1 Peter Cann and Peter Hughes. Chemistry for Advanced level.
- 2 Brown, LeMay, Bursten. Chemistry, The Central Science.
- 3 E. N. Ramsden. A-Level Chemistry
- 4 Jeanne Tan and Kim Seng Chan, Understanding Advanced Physical Inorganic Chemistry

1. INTRODUCTION

All chemical bonds are <u>electrostatic</u> in <u>nature</u> which involve **attractions** between a positive charge and a negative charge.

Strong forces of attraction

Type of chemical bond	Electrostatic attraction between		
(i) metallic bond	metal ions and 'sea' of delocalised electrons		
(ii) ionic bond cations and anions			
(iii) covalent bond shared pair of electrons and positively charged nu			

The type of chemical bond in a substance is primarily determined by the outer-shell electronic structure of its atoms where atoms lose, gain or share valence electrons to achieve the stable noble gas configuration.

Weak forces of attraction

Some atoms are bonded together as a group by covalent bonds to form discrete molecules. Weak forces of attraction exist <u>between</u> these molecules. These are called <u>intermolecular forces</u> of attraction which include:

- (i) Instantaneous dipole-induced dipole attraction
- (ii) Permanent dipole-permanent dipole attraction
- (iii) Hydrogen bonding

All these strong and weak electrostatic forces of attraction between particles bind them together to form matter.

Lattice structures

There are two major types of solid: **crystalline** and **non-crystalline solids**. In non-crystalline (or amorphous) solids, the particles are not arranged in any order (i.e. fixed in random positions). In crystalline solids, the particles are arranged in a regular three-dimensional pattern. This regular arrangement of points in space, occupied by the particles such as atoms, ions or molecules, is called a **lattice**.

The different types of structures include:

- (i) **giant** metallic
- (ii) giant ionic
- (iii) simple molecular
- (iv) giant molecular

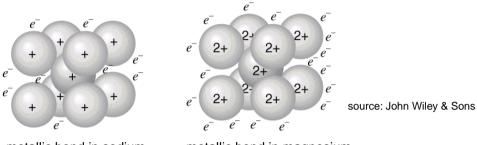
The different types of structure and bonding present in substances largely determine the properties of the substances.

2. GIANT METALLIC LATTICE

2.1 Metallic Bond

Metallic bonds are **strong electrostatic attractions** that exist <u>between the metal ions and the 'sea' of delocalised electrons</u> in a giant metallic structure.

• Metallic bonds are formed when each metal atom (e.g. Mg) contributes its valence electrons to form a 'sea' of electrons that are *delocalised* throughout the lattice of metal ions (Mg²⁺).



metallic bond in sodium

metallic bond in magnesium

2.2 Physical properties of metallic elements

Generally high melting points

Strong electrostatic forces of attraction exist between the metal ions and 'sea' of delocalised electrons. Large amount of energy is required to break the strong metallic bonds.

High electrical conductivity

Presence of **delocalised valence electrons** that are small and move fast gives rise to its high electrical conductivity.

Malleable and ductile

These properties are related to the ability of the cations to move over one another without breaking of metallic bonds.

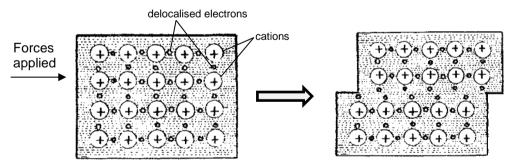


Diagram showing how the structure in metal changes when pressure is applied

When stress is applied to the metal, the metal structure can change its shape without fracturing. The layers of metal ions are still held together by the negative sea of electrons without breaking the metallic lattice.

The metal ions between the layers are not pushed apart by the repulsion as they are shielded by the delocalised electron cloud between them.

2.3 Factors affecting the strength of metallic bond

a) No. of valence electrons available for (metallic) bonding

Greater the number of such electrons, the stronger the metallic bonds.

Useful in explaining increasing MP across period

b) Ionic radius of the metal cation

Smaller the ionic radius of the cation, the stronger the metallic bonds.

Useful in explaining decreasing MP down the group

Note: When you are asked to compare 2 metals with contradicting effects from the two factors above (e.g. one metal has more valence electrons but also larger ionic radius than the other metal), see melting point data given by the question to decide which factor is more predominant.

Checkpoint 1

metal	Na	Mg	Al
melting point / °C	98	650	660
no. of delocalised valence electrons	1 (Group 1)	2 (Group 2)	3 (Group 13)
cationic charge, q+	+1	+2	+3
cationic radius, r+ / nm (data can be found in Data Booklet)	0.095	0.065	0.050
metallic bond strength		Na < Mg < Al	

(a) Why is the melting point of K (64 °C) lower than that of Na (98 °C)?

- K⁺ has a larger ionic radius than Na⁺ due to an additional quantum shell.
- Weaker electrostatic forces of attraction exist between the K⁺ ions and its sea of delocalised electrons.
- Less energy required to break weaker metallic bond, resulting in lower melting point.

(b) Why is the melting point of Al (660 °C) higher than that of Na (98 °C)?

- Each A*l* atom can delocalise 3 electrons while each Na atom can delocalise 1 electron, to the sea of electron cloud.
- At the same time, Al³⁺ ion has smaller ionic radius compared to Na⁺.
- Both factors contribute to <u>stronger electrostatic forces of attraction</u> between <u>Al³⁺ ions</u> and its sea
 of delocalised electrons.
- More energy required to break stronger metallic bond, resulting in higher melting point.

3. GIANT IONIC LATTICE

3.1 Ionic Bond (electrovalent bonds)

lonic bonds are **strong electrostatic attractions** that exist <u>between the **cations** and **anions**</u> in the crystal lattice of an ionic solid.

- In an ionic solid, the strong electrostatic forces hold <u>infinite</u> number of regularly arranged cations and anions together to form a giant ionic crystalline lattice.
- An ionic bond forms when elements have <u>large differences in their *electronegativity</u>, where electron transfer tends to occur.
 - *refer to page 14 for the definition of 'electronegativity'
- Electron transfer results in formation of cations (positive ions) and anions (negative ions) such that each ion achieves a stable noble gas configuration.

Example of formation of ions by electron transfer to form NaCl

Na
$$\xrightarrow{\text{lose electron from 3s}}$$
 Na⁺ + e⁻
1s²2s²2p⁶**3s**¹ 1s²2s²2p⁶

$$Cl + e^{-} \xrightarrow{gain 6 concer} Cl^{-}$$

 $1s^{2}2s^{2}2p^{6}3s^{2}3p^{5}$ $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$

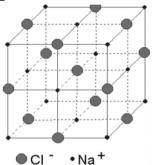


Diagram showing a NaCl crystal lattice

3.2 Dot-and-cross diagram of ionic compounds

- Show valence electrons only.
- Only dots () and crosses (x) are accepted.
- Enclose the symbol for each element in square (not round) brackets.
- The number of each ion present in one formula unit should be written as a coefficient outside the square brackets, not as a subscript.



<u>Do not</u> use concentric circles for dot–and–cross diagrams because the idea of electrons orbiting around the nucleus in circles is a myth! (Recall the concept of orbitals in 'Atomic Structure')

Example

(a) MgO

(b) CaF₂

$$Mg^{2+} \left[\begin{array}{c} xx \\ xx \\ xx \end{array} \right]^{2-}$$

$$Ca^{2+}$$
 $2\begin{bmatrix} x^{x} \\ x^{x} \end{bmatrix}^{-}$

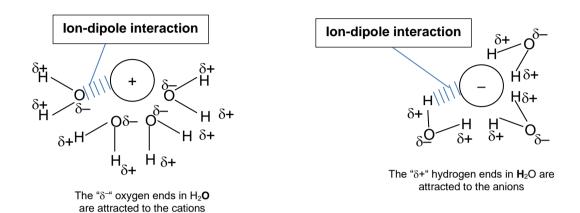
3.3 Physical properties of ionic compounds

High melting point and high boiling point

Strong electrostatic forces of attraction exist between the oppositely charged ions. Large amount of energy is required to break these ionic bonds.

Soluble in water and other polar solvents

strong ion-dipole interactions are formed between the ions and water/polar solvent molecules.

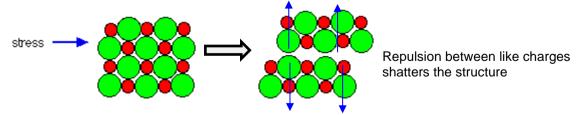


Diagrammatic representation of ion-dipole interactions

For full answer in terms of energy changes during the process of dissolving ionic salts: formation of ion-dipole interactions between the ions and water molecules releases sufficient energy to overcome the electrostatic forces of attraction between the oppositely charged ions in the ionic salt and the hydrogen bonds between water molecules.

(Note that the concept of "hydrogen bonds" will be covered later in this topic.)

- Good electrical conductors when in molten state or when dissolved in aqueous solutions due to the presence of mobile ions.
 - electrical conductivity increases with increasing concentration of the ions in the solution
- Non-electrical conductors in solid state as ions can only vibrate about fixed positions and hence are not mobile to conduct electricity.
- Brittle and fractures under stress



lonic compound comprises a lattice of alternating positive and negative ions. When stress is applied, the ions will be displaced and this leads to contact between the like charges. The **repulsion between the like charges** causes the (crystal) lattice to break apart.

3.4 Factors affecting the strength of ionic bond

- For solids with the same lattice type, the strength of ionic bonds depends mainly on the <u>charge</u> <u>size</u> and the <u>ionic radius</u>.
- The larger the **charge size** and the **smaller the ions** (as seen from the ionic radius), the stronger the electrostatic forces of attractions.
- Charge density of ions, $\frac{q_+}{r_+}$, is irrelevant in the comparison of melting point for giant ionic lattice since $\left|\text{Lattice Energy}\right| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$ (You will learn more about this in Chemical Energetics)

Checkpoint 2

The melting point of MgO (2852 °C) is higher than Na₂O (1132 °C). Explain.

- Mg²⁺ has a <u>higher charge</u> and <u>smaller ionic radius</u> than Na⁺.
- Stronger electrostatic forces of attraction between Mg²⁺ and O²⁻.
- More energy required to break stronger ionic bonds and therefore higher melting point.

CsCl (645 °C) has a lower melting point than NaF (993 °C). Explain.

- Cs⁺ and Cl⁻ have <u>larger ionic radius</u> than Na⁺ and F⁻ respectively.
- Weaker electrostatic forces of attraction between Cs⁺ and Cl⁻.
- Less energy required to break weaker ionic bonds and therefore lower melting point.

3.5 Coordination number in an ionic compound (SDL)

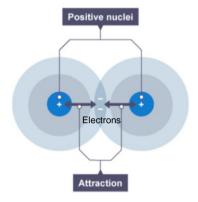
- The number of nearest ions that surround another ion of the opposite charge in an ionic lattice is called the <u>coordination number</u> of that central ion.
- Factors that affect coordination number are:
 - (i) Relative size of the ions
 - (ii) Relative charge
- Refer to page 43 and 44 for more information on 'coordination number'.

4. SIMPLE MOLECULAR

4.1 Covalent Bond

A covalent bond is the strong electrostatic attraction between a shared pair of electrons and two positively charged nuclei.

- A covalent bond forms between atoms that have similar ability to attract the electrons in a covalent bond to itself. In other words, it forms between atoms of <u>similar *electronegativity</u>.
 *refer to page 14 for the definition of 'electronegativity'
- The shared electrons are <u>localised between the two nuclei</u>, and are called <u>bonding electrons</u>.



4.2 Modern theory on covalent bonding

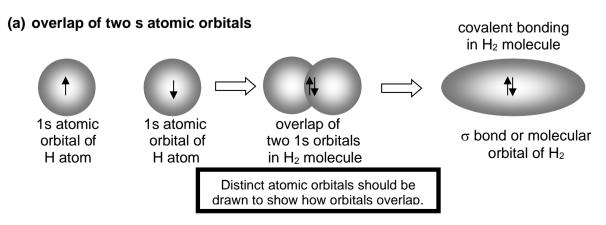
A covalent bond is formed by the <u>overlap of two valence atomic orbitals</u> (one from each atom). Each orbital must be occupied by a <u>single</u> electron, so that when the orbitals overlap the bond contains two electrons.

Two types of orbital overlap result in two different types of covalent bond formed:

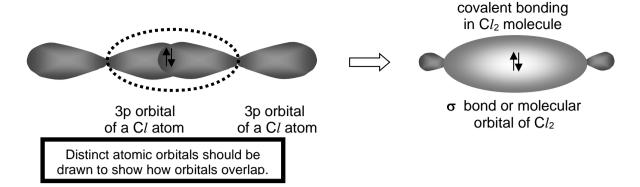
- head—on overlap of orbitals forms σ (sigma) bond
- side—on overlap of orbitals forms π (pi) bond

What is a σ (sigma) bond?

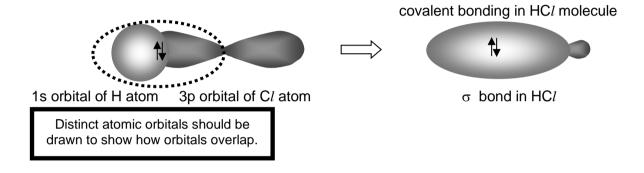
- When a valence orbital overlaps with another valence orbital <u>along the inter-nuclear axis</u>, a single region of overlap is produced. This region of overlap results in a σ bond.
- The electron density is concentrated between the nuclei of the atoms.
- There are **3** possible ways to form a sigma bond:



head-on overlap of two p atomic orbitals

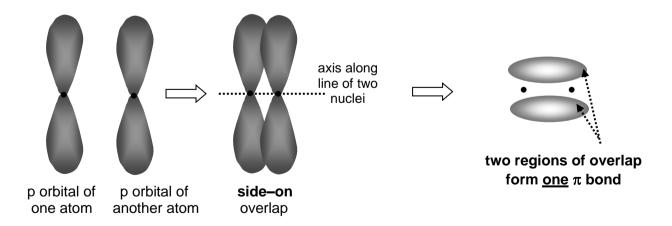


(b) overlap of one s and one p atomic orbital



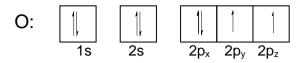
What is a π (pi) bond?

- After a σ bond is formed between two atoms, it is possible to have the valence p orbitals of these atoms overlap in a side—on manner.
- The side—on overlap of p orbitals will result in **two regions** of overlap; above and below the plane of the inter—nuclear axis. These two regions of overlap result in a π bond.
- Only 1 way to form a pi bond: two p orbitals overlap



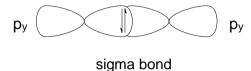
Example: Bonding in the oxygen molecule, O₂

1. Electronic configuration of O: 1s²2s²2p⁴

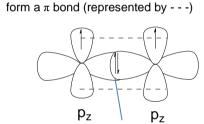


Based on the configuration, there are two unpaired electrons in the 2p subshell of O atom.

2. When two oxygen atoms approach each other, the $2p_y$ orbitals of each O atom will overlap head—on and a σ bond is formed.



3. The σ overlap brings the two atoms <u>close enough</u> for the $2p_z$ orbitals of each O atom to overlap side–on.



Two pz orbitals overlap side-on to

σ bond formed from head-on overlap of p_V orbitals

This is a fully labelled diagram that shows the orbitals used to form a double bond.

This (NOT the molecular orbitals below) should be drawn to show how π bonds are formed.

Diagram showing the two types of molecular orbitals in the double bond of O₂ molecule:



This diagram shows the eventual molecular orbitals after the formation of both σ and π bonds, **but this is not the diagram to draw** when asked in tutorial or examination as it does not show the atomic orbitals used for the overlap.

Why is the π bond weaker than σ bond?

- In a π bond, the overlapping region of valence orbitals <u>lies above and below the plane of the inter–nuclear</u> axis. (For σ bond: the region of overlap <u>lies in the inter–nuclear</u> region)
- This results in a less effective overlap and therefore weaker bond strength.

Can a π bond be formed without the presence of a σ bond between two atoms?

No. Between a σ bond and a π bond, the two atoms 'prefer' to form a σ bond as it is more stable and stronger than a π bond due to its more effective overlap of atomic orbitals.

Note: A single bond consists of $\underline{a} \sigma \underline{bond}$.

A double bond consists of <u>a σ bond and a π bond</u>. A triple bond consists of a σ bond and 2 π bonds.

Example:

0=0	There are a total of $\underline{\bf 1}$ σ and $\underline{\bf 1}$ $\underline{\pi}$ bonds in the molecule.
N≡N	There are a total of $\underline{1}$ σ and $\underline{2}$ $\underline{\pi}$ bonds in the molecule.
H—C≡C—H	There are a total of $\underline{3}$ σ and $\underline{2}$ $\underline{\pi}$ bonds in the molecule.

4.3 Co-ordinate Bond (Dative Covalent Bond)

 Co-ordinate bond is a <u>type of covalent bond</u> in which the shared electron pair comes from one atom.

A X B

A B

normal covalent bond

co-ordinate bond

It is formed when the donor atom donates a pair of electrons to the acceptor atom for sharing.

'donor' atom: has a **lone pair of electrons** available in the valence shell

'acceptor' atom: has an vacant low-lying orbital in its valence shell so that it can accept

the lone pair of electrons from the 'donor' atom

- Once the dative bond is formed, it is <u>indistinguishable from a normal covalent bond</u>. The dative bond has the same bond strength as a normal covalent bond.
- A dative bond can be represented by:

 - 2 electrons of the same type (: or :) in the dot-and-cross diagram

Examples of co-ordinate bonding

(a) In simple covalent molecules / molecular ions

H₃O⁺ (hydroxonium ion)

Dative bond formed between a proton (H⁺) and a lone pair of electrons on O atom of H₂O

$$H_2O^{\bullet \bullet} + H^+ \longrightarrow \begin{bmatrix} \bullet \\ H \end{bmatrix}$$

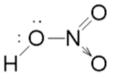
NH₄⁺ (ammonium ion)

➤ Dative bond formed between a proton (H⁺) and a lone pair of electrons on N atom of NH₃

CO (carbon monoxide molecule)

× C × C ← O:

HNO3 (nitric acid)

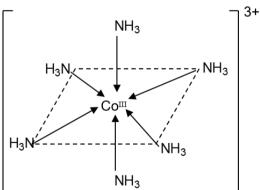


(b) In complex ions

[Co(NH₃)₆]³⁺ complex ion

➤ Each N atom in NH₃ uses its lone pair of electrons to form a dative bond to the central positive metal ion.

(You will learn more about complex ions in 'Transition Elements' in JC 2)



(c) In addition compounds

<u>Electron–deficient</u> molecules tend to react with other molecules or ions <u>so that the central atom</u> <u>can achieve an octet of electrons</u>.

Compounds formed in this way are called addition compounds.

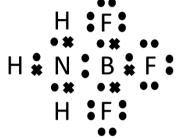
Eg: Reaction between ammonia and boron trifluoride

When these two gases are mixed, a vigorous reaction occurs producing a solid addition compound.

NH₃ + BF₃
$$\longrightarrow$$
 H₃N \longrightarrow BF₃ (can be written as NH₃.BF₃)

Notice that in the Lewis diagram above, an arrow is used to show the pair of electrons donated from N to B.

While in the dot and cross diagram on the right, both electrons shared between N and B are from N atom, and **the arrow is not drawn**.



(d) Dimerisation

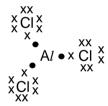
➤ Dimerisation is a reaction in which two same molecules (called monomers) react to form a single molecule called a **dimer**.

Electron-deficient molecules dimerise so that each central atom in the monomer achieves an octet of valence electrons.

E.g. dimerisation of aluminium chloride

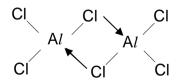
$$2AlCl_3 \longrightarrow Al_2Cl_6$$
 (dimer)

Structure of AlCl₃



No. of valence electrons around Al in AlCl₃: **6**

Structure of Al₂Cl₆ dimer



In forming the Al_2Cl_6 dimer, two $AlCl_3$ molecules are joined by **2 dative bonds**.

No. of valence electrons around each Al in A l_2 C l_6 : **8**

(e) Lewis Acid-Base Theory

- Gilbert N. Lewis in 1938 expanded the definition of acids and bases to the following.
- An acid—base reaction involves the transfer of an electron pair from a Lewis base to a Lewis acid, forming a covalent bond.

Lewis acid:	electron pair acceptor	contains an atom with vacant low-lying orbital to	
		accept a lone pair of electrons.	
Lewis base:	electron pair donor	contains an atom with a lone pair of electrons	
		that it can donate.	

■ The reaction between ammonia (NH₃) and boron trifluoride (BF₃) on page 13 is an example of **Lewis acid–base reaction**, in which NH₃ and BF₃ act as a Lewis base and a Lewis acid, respectively.

4.4 Electronegativity and Bond Polarity

Electronegativity

- The electronegativity of an atom is a <u>measure of its ability to attract the shared pair of electrons</u> in a covalent bond to itself.
- The diagram below shows the trends in the electronegativity of elements in the Periodic Table.

General Trend of Electronegativity

increases across the period, e.g. F is more electronegative than N



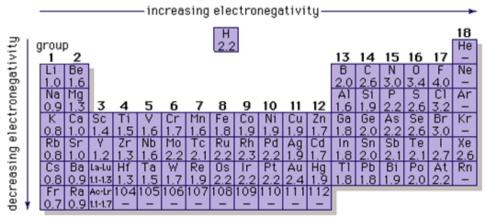
Recall: Atomic Structure Lecture

Across the period, nuclear charge increases. Since increase in shielding effect is negligible, valence electrons will be more strongly attracted towards the nucleus.

decreases down the group, e.g. Br is less electronegative than Cl



Down the group, as the no. of electron shells increases, valence electrons will be further away and more shielded form the nucleus. Hence, the valence electrons are less strongly attracted towards the nucleus.



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Bond Polarity

When 2 atoms form a covalent bond, the bonding electrons are shared between the 2 nuclei. When both atoms are of the same element, they have the same electronegativity. There is equal sharing of bonding electrons between the 2 nuclei. The covalent bond formed is said to be non-polar.

Examples of non-polar bonds:

$$H-H$$
 $O=O$ $Br-Br$ $*C-H$ $*P-H$ $*S-H$

However, when the bonding atoms are different, there exists a difference in the electronegativity. The bonding electrons are drawn towards the more electronegative atom. The more electronegative atom will acquire a partial negative charge while the other atom a partial positive charge. This permanent separation of charges in the bond is known as a dipole. The covalent bond formed is said to be polar.

Examples of polar bonds:

By convention, $+\rightarrow$ is used to represent a dipole, with the arrow pointing to the more electronegative atom.

• The greater the difference in electronegativity between the bonding atoms, the more polar the bond is.

4.5 Strength of a Covalent Bond

Bond energy and bond length are two **indicators** of the strength of a covalent bond.

Bond Energy

• Bond energy (BE) is the <u>amount of energy absorbed/required</u> to break <u>one mole of covalent bond</u> between 2 atoms in the <u>gaseous state</u>.

Example: Bond energy for Cl-Cl is +242 kJ mol⁻¹

$$Cl_2$$
 (g) \longrightarrow 2 Cl (g) Bond (dissociation) energy = + 242 kJ mol⁻¹

The stronger the covalent bond, the greater is its bond energy.

^{*} the difference in electronegativity is very small, hence the bond is normally taken to be non-polar

For covalent bonds present in polyatomic molecules, such as CH₄, the <u>average bond energy</u> is used.

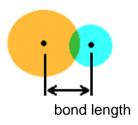
Example:

There are four C-H bonds in CH₄. The average bond energy for each C-H bond is 410 kJ mol⁻¹.

Covalent molecules with <u>higher bond energies generally have lower tendency to undergo</u> reaction.

Bond Length

Covalent bond length is defined as the distance between the nuclei of the two atoms in the bond.
 It is also the sum of the covalent radius of the two atoms.



A shorter bond length indicates the presence of a stronger covalent bond.

Note: Both bond length and bond energy is a result of bond strength, we **cannot** use bond length to explain the differences in bond energy.

Factors affecting covalent bond strength

(a) Effectiveness of orbital overlap

<u>Example</u>: [Comparing atoms that belong to the same group]

Account for the trend of bond energies of chlorine to iodine:

 $BE(C_l-C_l) = 244 \text{ kJ mol}^{-1}, \quad BE(B_r-B_r) = 193 \text{ kJ mol}^{-1}, \quad BE(I-I) = 151 \text{ kJ mol}^{-1}$

- As atoms from Cl to Br to I become larger, the size of valence orbitals increases.
- These larger orbitals become <u>more diffused</u> and when they overlap, the accumulation of electron density within the inter–nuclei region is lower.
- Orbital overlap is <u>less effective</u>, resulting in weaker bond strength.

(b) Difference in electronegativity between bonding atoms (Bond Polarity)

<u>Example:</u> [Comparing bonds of similar number of bonding electrons but different polarity]

bond	electronegativity difference between atoms	bond energy / kJ mol ⁻¹
N–H	0.9	+390
O–H	1.4	+460
F–H	1.9	+562

- Since the electronegativity increases in the order N < O < F, <u>bond polarity increases</u> in the order N-H < O-H < F-H.
- In addition to the existing covalent bond, there is <u>increase in the electrostatic attraction</u> between the two partial charges ($\delta + / \delta -$). Therefore, an increase in bond strength.

(c) Number of bonding electrons

As the <u>number of bonding electrons increases</u> within the inter–nuclei region for multiple bonds, the <u>attractive forces for these electrons increase</u>. Thus, the covalent bond strength increases from single to double to triple.

Example: [Comparing bonds with same atoms but different multiplicity]

bond	bond energy / kJ mol ⁻¹	bond length / nm
$C\!-\!C$	350	0.154
c = c	610	0.134
c≡c	840	0.120

Why is BE (C=C) less than twice that of BE (C-C)?

Recall from page 10

 π bond is <u>weaker</u> than σ bond since side—on overlap of valence orbitals is less effective.

(d) *Hybridisation state of bonding atom

(You will learn more about hybridisation in 'Intro to Organic Chemistry')

4.6 Dot-and-Cross diagram and Lewis Structure

Drawing dot-and-cross diagrams of molecules / molecular ions

- Step 1: Identify the central atom Usually the atom that can form the most number of bonds or the least electronegative (except H atom)
- Step 2: For anions, as a rule-of-thumb, add electron(s) corresponding to the charge on the ion to the more electronegative atom(s). Draw a square bracket outside the molecule and place the charge as a superscript outside the bracket.

For cations, as a rule-of-thumb, subtract electron(s) corresponding to the charge on the ion from the less electronegative atom(s). Draw a square bracket outside the molecule and place the charge as a superscript outside the bracket.

For neutral molecules, you can ignore Step 2.

- Step 3: Complete valence shell of each atom by deciding on the type of bond (single / double / triple) each surrounding atom needs to form with the central atom to achieve octet configuration.
- Step 4: Check that for Period 2 elements should only have a maximum of 8 valence electrons.

Tip: Reduce the number of valence electrons (on the central atom) by shifting a pair of these electrons to one of the surrounding atoms.

Exceptions to the octet rule (see page 21)

- \Rightarrow electron deficient species (BeC I_2 , BF $_3$ and A ICI_3)
- \Rightarrow odd number of (or unpaired) electrons (C/O₂, NO, NO₂ \rightarrow radicals)

Example:

particles	dot-and-cross diagram	Lewis structure
CO ₃ ²⁻	*O * C * O *	

Lewis Structures

In Lewis structures, a bonding pair of electrons is represented by a line '—' and the lone pair of electrons (on both central **and surrounding atoms**) is represented as '••'.

Checkpoint 3

particles	dot–and–cross diagram	Lewis structure
F ₂ O		
NO ₂ +		

Exceptions to the Octet Rule

- Many atoms undergoing reactions often gain, lose or share electrons to achieve eight valence electrons (noble gas configuration).
- This rule is simple and useful in understanding the basic concepts of bonding. However, it does not apply in transition metal complexes and some covalent molecules.
- The following are examples of exceptions to the octet rule in covalent molecules.

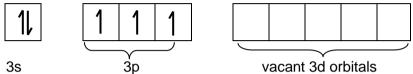
(a) Species in which the central atom has expanded octet

> Central atoms in these molecules are from Period 3 or higher.

	:Cl: :Cl·x * x · Cl: :Cl: :Cl:	:F: :F: :F.*S*.F: :F::F:	*** * O * O ***	:F. x xx x . F: :X Xe x . F: :F. x xx . F:
	<u>P</u> C <i>l</i> ₅	<u>S</u> F ₆	<u>S</u> O ₄ 2-	<u>Xe</u> F₄
No. of electrons in valence shell of central atom:	10	12	12	12

- The central atoms in these molecules have 'expanded' their octet configuration; i.e. have more than 8 valence electrons (including both bonding electrons and lone pairs) around the central atom.
- Elements of Period 2 have only one 2s and three 2p valence orbitals available for bonding. These orbitals together (2s²2p6) can hold a maximum of eight electrons only. Thus, a Period 2 element cannot expand its octet configuration.
- For non–metal elements from Period 3 and higher, in addition to the outer–shell s and p orbitals, there are vacant, low–lying d orbitals that can accommodate extra electrons.

Example: valence shell of phosphorus, P



- Size of the atom partly determines whether the atom can accommodate more than eight electrons. The larger the central atom, the larger the number of atoms that can surround it in a molecule.
- The size of the surrounding atoms is also important. Expanded valence shells occur most often
 when the central atom is bonded to small and highly electronegative atoms, such as F, Cl, and
 O.

Why NCl₅ does not exist?

N atom cannot expand its octet to accommodate all the bonding electrons as it does not have vacant, low–lying d orbitals. (Its next available vacant orbital is 3s, which is energetically unfavourable to utilise for bonding.)

(b) Species in which the central atom has less than an octet

(Also called <u>electron-deficient</u> molecules)

Often encountered in covalent compounds containing beryllium (Be), boron (B) and aluminium (AI) as central atoms.

(c) Species with an odd number of (or unpaired) electrons

- In most molecules, the total number of electrons is even, and complete pairing of valence electrons occurs.
- However, in some molecules the total number of electrons is an odd number. Hence complete pairing of the valence electrons is impossible.

Examples of molecules with odd number of electrons	ClO ₂	NO	NO ₂
Total number of valence electrons	19	11	17

Particles with unpaired or odd number of electrons (e.g. ClO₂, NO, NO₂) are called <u>radicals</u>. These particles are <u>very reactive</u>. They tend to react in such a way that pairing of electrons occur.

Example: 2NO₂ → N₂O₄

Checkpoint 4

Which of the following dot-and-cross diagram(s) best represent(s) the following molecules?

Nitrogen monoxide, NO	Nitrogen dioxide, NO ₂	Chlorine dioxide, ClO ₂
·Ņ·×Öxx	·Ö·×××Ö·	:Ö:ẍ́ Č́́́¿ž:Ö:
·Ñ:ŠŠ	:Ö:xĂx:Ö:	:ÖxĞlx:Ö:
·Ñ:ặČX	:Ö:xŇxÖ:	:ÖxŠıkÖ:

4.7 Determining shapes and bond angles of molecules using VSEPR theory

- VSEPR stands for Valence Shell Electron Pair Repulsion. This theory allows one to predict the shapes of molecules and their bond angles.
- Covalent bonds are directional. Covalently bonded atoms have a preferred specific orientation in space relative to one another.
- This gives rise to covalent molecules having definite geometrical shapes characterised by their bond angles.

Key principle 1

Electron pairs (bond pairs and lone pairs) around the <u>central atom</u> of a molecule arrange themselves as far apart as possible to **minimise inter–electronic repulsion**.

- All <u>electron pairs</u> around the <u>central atom</u> are taken into account when determining the molecular shape.
 Each double bond or triple bond is also counted as one region of electron density (or one bond).
 - Each double bond or triple bond is also counted as one region of electron density (or one bond pair)
- The table below shows the basic molecular shapes that occur when all the electron pairs around the central atom are bond pairs (no lone pairs). Bond angle refers to the angle between two bond pairs.

No. of electron pairs around central atom	spatial arrangement of electron pairs to minimise electron pair repulsion central atom bonded atom bonding electron pair	basic molecular shape	bond angle
2	• •	linear	180°
3		trigonal planar	120°
4		tetrahedral	109.5°
5		trigonal bipyramidal	120° x 3 90° x 6
6		octahedral	90°

Effect of lone pairs on the shapes of molecules

- In the experimental determination of shapes of molecules which contain lone pairs, only the relative positions of the nuclei of atoms can be detected. Lone pairs of electrons cannot be 'seen' although they are present and exerting repulsion on the bond pairs and on one another.
- Thus, the molecular shape is described by the positions of bond pairs, as fixed by the arrangement of all the electron pairs with minimum repulsion.

Key principle 2

A lone pair exerts a stronger repulsion than a bond pair as a lone pair is non-bonding and thus the electron density is closer to the nucleus of the atom.

Hence, the strength of electrostatic repulsion between electron pairs decreases in the order:

lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

• The difference in the strength of repulsions affects the <u>bond angles</u> in the molecules.

Example:

Molecule	No. of bond pairs	No. of lone pairs	Bond angle
CH ₄	4	0	109.5°
NH ₃	3	1	107°
H ₂ O	2	2	104.5°

• The difference in the strength of repulsions also affects the <u>position of lone pairs</u> in the molecules, and hence the molecular shape.

How to determine the shape of a molecule

You have to first memorise the 5 basic shapes of molecules (linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral) because all other shapes are derived from them.

Method 1 [Non oxygen–containing compound]

Step	Instructions	Eg 1: IC <i>l</i> ₄ ⁻	Eg 2: PCl ₄ ⁺
1	Identify the central atom and note the no. of valence efor this element.	I 7 valence e⁻	P 5 valence e⁻
2	Add the no. of bonding e ⁻ from surrounding atoms to it.	7 + 4(1) = 11	5 + 4(1) = 9
3	Add / subtract this no. by the charge.	11 + 1 = 12	9 – 1 = 8
4	Divide the no. by 2 (to determine no. of e ⁻ pairs).	12/2 = 6	8/2 = 4
5	Distinguish between bonding e ⁻ pair and lone e ⁻ pair (clue: use the no. of surrounding atoms to first determine the no. of bonding e ⁻ pair)	bp: 4 lp: 2	bp: 4 lp: 0
6	Based on the total no. of e ⁻ pairs (from Step 4), identify the basic shape from the 5 basic molecular shapes listed on Pg 21.	octahedral	tetrahedral
7	Locate the ideal position(s) for the lone e ⁻ pairs present (to minimise repulsion). Molecular shape decided.	square planar (lp must be 180° from each other to minimise repulsion)	tetrahedral (since no lp)

> Read page 44 for two other ways to determine the shape of molecules

Summary

No. of electron regions	Basic molecular shape	No. of bond pairs	No. of lone pairs	Sh	Shape	
2	linear —A—	2	0	linear	—A—	180°
3	trigonal planar	3	0	trigonal planar	A	120°
-	A	2	1	bent	Ä	<120°
	tetrahedral	4	0	tetrahedral	1111	109.5°
4	,,,,,,,	3	1	trigonal pyramidal	(i) Ä	107°
		2	2	bent	;Ä	104.5°
	trigonal bipyramidal	5	0	trigonal bipyramidal	A	120° (equatorial) 90°(axial)
5 (lone pair is ALWAYS* on equatorial		4	1	seesaw / distorted tetrahedral	A:	<120° (equatorial) <90°(axial)
position) *refer to page 45 for the explanation	A—	3	2	T-shaped	:A	<90°
		2	3	linear	:A:	180°
6 (lone pair is ALWAYS on axial position)	octahedral	6	0	octahedral	A A	90° (equatorial & axial)
		5	1	square pyramidal	A. A.	<90° (equatorial & axial)
		4	2	square planar	Ä	90°

<u>Note:</u> For molecules or molecular ions with a 3-dimensional shape, e.g. tetrahedral, trigonal bipyramidal, octahedral, etc. use for bond pointing towards you

for bond pointing away from you

An **exact numerical value** has to be quoted when stating the estimated bond angle; inequality symbols are not allowed.



<u>Actual shapes of molecules and their bond angles</u>
(https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes en.html)

Molecule	Dot-and-cross	Lewis structure	No. of electron regions	Electron pair arrangement	No. of bond pairs	No. of lone pairs	Molecular shape	Sketch the shape	Bond angle(s)
CO ₂	:Ö: <u>`</u> ,C.;:Ö:	:Ö=C=Ö:	2	linear	2	0	linear	O=C=O	180°
BF ₃	:Ë: :˷׊׷Ë:	:Ë: :Ë—B—Ë:	3	trigonal planar	3	0	trigonal planar	F B F	120°
SO ₂	:Ö:ێ ^{XX} X:Ö:	:Ö=S=Ö:							< 120°
CH₄	H H·×Č×·H × H	H-C-H	4	tetrahedral	4	0	tetrahedral	H C H	109.5°
NH₃	H×·N·×H × H	H-N-H H							107° (< 109.5°)
H₂O	Hו֕×Н	H-Ö-H	4	tetrahedral	2	2	bent	H, H	104.5° (<< 109.5°)

Molecule	Dot-and-cross	Lewis structure	No. of electron pairs	Electron pair arrangement	No. of bond pairs	No. of lone pairs	Molecular shape	Sketch the shape	Bond angle(s)
PCl ₅	:Cl: :Cl·x × x·Cl: :Cl: :Cl:	:Çl: :Cl → P — Cl: :Cl: :Cl:	5	trigonal bipyramidal	5	0	trigonal bipyramidal	Cl = Cl $Cl = Cl$ Cl Cl	120° 90°
SF ₄	: : : : : : : : : : : : : : : : : : :	: Ë— Ë : : E :	5	trigonal bipyramidal	4	1	see-saw	F 	< 120° < 90°
ICl ₃ (similar to ClF ₃)	:Cl: * i * :Cl: * * . Cl:	:Çl-:::: :Cl:	5						< 90°
XeF ₂	x F x · Xe · x F x	:Ë—Xe—Ë:	5	trigonal bipyramidal	2	3	linear	F—Xe−F	180°
SF ₆	:F: :F: :F·×s·F: :F::F:	:F: :F: :F: :F: :F: :F:	6						90°
BrF₅	:F. _x xx x.F: :F. ^x xx x.F: :F. x x x.F: :F:	:F: :F: :F :Br :F: :F:	6	octahedral	5	1	square pyramidal	F F F	< 90°
XeF ₄	:F. x xx x . F: :F. x Xe x . F: :F. x xx x . F:	:Ë	6	octahedral	4	2	square planar	F F	90°

Answer template

To predict or account for shapes of molecules / molecular ions or bond angles:

- 1. There are _____(no. of) bond pairs and _____(no. of) lone pairs around _____ (central atom)
- 2. To minimise repulsion and maximise stability, the _____ (total no. of bond + lone pairs) electron pairs are arranged as far apart as possible
- 3. _____ (molecule/molecular ion) has a _____ (state shape) shape with a bond angle of _____ (if required).

Shapes of molecules with more than one central atom

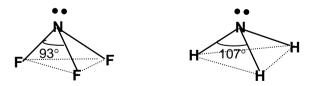
Molecule	Dot–and–cross diagram	Diagram showing shape of molecule	Shape and Bond angle
C ₂ H ₆ (CH ₃ CH ₃) ethane	HוC••C•×H	H 109.5° H C H H	Tetrahedral with respect to each C atom H–C–C bond angle: 109.5° H–C–H bond angle: 109.5°
C ₂ H ₄ (CH ₂ =CH ₂) ethene	H H	H 120° H 120° H	Trigonal planar with respect to each C atom H-C-C bond angle: 120° H-C-H bond angle: 120°
H ₂ O ₂ hydrogen peroxide	H × O × O × H	Ü Ö H	Bent with respect to each O atom H–O–O bond angle: 104.5°

Effect of electronegativity on bond angle

(a) Molecules with same shape and same central atom but different surrounding atoms

Example:

Both NF₃ and NH₃ have the same shape (trigonal pyramidal) but the bond angle of NF₃ (93°) is smaller than NH₃ (107°).



F is more electronegative than H. Hence,

- → bonding electrons in N–F bond are closer to the F atoms
- → less crowding of electron density around the N atom in NF₃
- → less inter–electronic repulsion between the electron pairs around the N atom
- → smaller bond angle than expected

(b) Molecules with same shape and same surrounding atoms but different central atom

Example

Bond angle of H₂O (105°) is larger than H₂S (92°).

O is more electronegative than S. Hence,

- → bonding electrons in O–H bond is drawn more towards the O atom
- → more crowding of electron density around O atom
- → more inter–electronic repulsion between the electron pairs around the O atom
- → larger bond angle in H₂O

4.8 Polarity of Molecules

Remember that due to the differences in electronegativity between atoms within some molecules, there would be uneven distribution of electrons within the molecules forming polar bonds. (refer back to page 15.)

Such polar bonds are said to have a dipole moment, may result in the overall molecule to be considered as a **polar molecule** (having a **net dipole moment**).

However, molecules with polar bonds can also be considered **non-polar**, when the individual dipole moments cancel out, resulting in **no net dipole moment**.

To determine if a molecule are polar, we need to determine if there is a NET dipole moment of the molecule. This can be done in 3 main steps:

- 1. Determine if there is any polar bonds in the molecule. This creates individual bond dipole moments.
- 2. Determine the actual shape of the molecule.
- 3. Determine whether there is a **net** dipole moment by resolving the individual dipole moments (based on how they are orientated in the 3D structures).
 - a. net dipole moment → Polar molecule
 - b. no net dipole moment → Non-Polar molecule

Examples:

Dipole			H H	H" A H
Overall dipole	None	None	+	<u></u>

Exercise

Determine the polarity of the following molecules. (*Note: A, B, C and D are atoms with different electronegativity*)

This exercise is meant for you to quickly identify if a molecule is polar, so there is no need to draw the dipole moments.

	T		Г	1	
linear	В—А—В	B-A-D	B •A • B		
	polar / non-polar	polar / non-polar	polar / non-polar		
	• A•	• A•		•	
bent	ВВВ	B D			
	polar / non-polar	polar / non-polar			
	В	В			
trigonal planar	ВВВ	B A D			
	polar / non-polar	polar / non-polar		1	
	B	B 	B 		
tetrahedral	B A B	B A C	B A C		
	polar / non-polar	polar / non-polar	polar / non-polar		
trigonal pyramidal	B A B	B A B			
	polar / non-polar	polar / non-polar			
trigonal bipyramidal	BA-B BA-B	CA-CB	B—A—B B	C A C B	
	polar / non-polar	polar / non-polar	polar / non-polar	polar / non-polar	
	A A A A A A A A A A A A A A A A A A A	C A. A	C A D B	D A A B	C A ₁ , D B
octahedral	AAA	A C	D C	AAA	A C
	polar / non-polar	polar / non-polar	polar / non-polar	polar / non-polar	polar / non-polar
see-saw	B A B				
	polar / non-polar			1	
	B ₁, •• , ₁ B	B, o	B , •• , D A		
square planar	B · B	C ✓ B	B · B		
	polar / non-polar	polar / non-polar	polar / non-polar		

Checkpoint 5

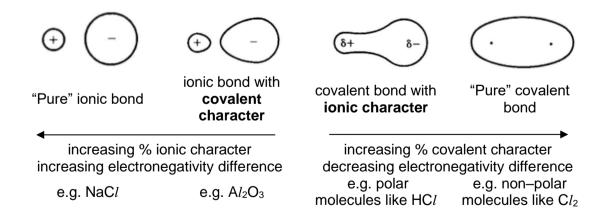
Fill in the blanks and show dipoles for polar bonds in the following molecules. Determine its overall polarity.

Molecule	Diagram showing dipoles and overall polarity of molecule	Is the molecule polar?
BF ₃		
CH ₂ C <i>l</i> ₂		
H₂O		
XeF ₄		

5. INTERMEDIATE BOND TYPES

Many covalent and ionic bonds have intermediate bond character:

- some covalent bonds have ionic character
- some ionic bonds have covalent character



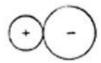
Experimental data shows that even for some supposedly ionic substances, there is <u>some degree of electron sharing</u> between oppositely charged ions.

For example, we may expect aluminium chloride to be ionic. However, the extent of sharing of electrons is so great that aluminium chloride exhibits characteristics of a covalent compound.

This indicates that the notion 'metals and non-metals combine to form ionic compounds' is **not completely true in all instances**.

5.1 Ionic bonds with covalent character

When there is a distortion / polarisation of electron cloud of the anion by the positively charged cation, electron density is drawn into the region between the 2 nuclei, resulting in <u>partial sharing of electrons</u>. Such an ionic bond exhibits <u>some covalent character</u>.





no polarisation

electron cloud of anion is polarised by the cation

The greater the polarisation of electron cloud, the higher the degree of covalency.

5.2 Factors affecting the extent of polarisation

Polarising power of the cation

Polarising power of the cation is dependent on its <u>charge density</u>. Charge density is directly proportional to q^+/r^+ , where q^+ is the charge size and r^+ is the cationic radius.

The higher the charge density, the greater the polarising power in distorting the electron cloud of the anion, the greater the degree of covalency.

Example:

Why is AlCl3 covalent while NaCl is ionic?

(**IF** we consider $AlCl_3$ to be ionic, then....)

Al³⁺ has a high charge size of +3 as compared to Na⁺ with a charge of +1.

At³⁺ also has a smaller ionic radius compared to Na⁺, giving rise to higher charge density and hence higher polarising power.

 Al^{3+} distorts the electron cloud of Cl^- anion to a great extent. The extent of sharing of electrons between the two nuclei is so great that $AlCl_3$ exhibits covalent character (and it is not an ionic compound).

Polarisability of the anion

Polarisability of the anion is largely dependent on the size of the anion.

The greater the electron cloud size of anion, the less strongly the valence electrons are attracted to the nucleus, the greater the ease of electron cloud being distorted by the cation, the higher the degree of covalency.

Example:

Why is AlF_3 ionic while $AlCl_3$ is covalent?

(**IF** we consider AlCl₃ to be ionic, then....)

 Cl^- has a larger ionic radius than F^- , resulting in a greater extent in the distortion of the electron cloud of Cl^- anion by Al^{3+} , leading to greater sharing of electrons between the two nuclei. $AlCl_3$ is therefore covalent (and not ionic) while AlF_3 is ionic.

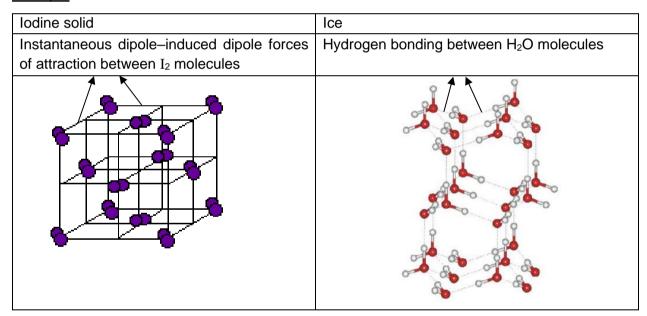
6. PHYSICAL PROPERTIES OF SIMPLE MOLECULAR STRUCTURES

Solids that have simple molecular structures tend to have low melting points because <u>little energy</u> is required to overcome the <u>weak</u> intermolecular forces of attraction **between** the molecules in order for the crystal lattice to be broken down into discrete **molecules** (or atoms for the noble gases).

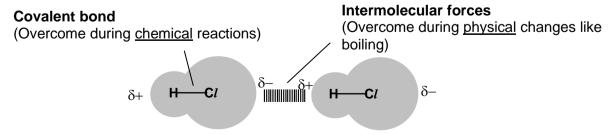
6.1 Intermolecular forces of attraction (Only for simple discrete molecules)

- Simple molecular structures consist of molecules held together by <u>intermolecular forces of</u> attractions (within molecules, atoms are joined by intramolecular covalent bonds).
- In a simple molecular structure, the lattice positions are occupied by discrete molecules (or by atoms (monoatomic molecules) in the case of noble gases).
- Three types of intermolecular attraction exist between molecules:
 - ➤ Instantaneous dipole—induced dipole attraction
 - > Permanent dipole—permanent dipole attraction
 - Hydrogen bonding

Example:



The <u>physical properties</u> of a simple molecular substance such as <u>melting point</u>, <u>boiling point</u> and <u>solubility depend on the type and strength of the intermolecular forces</u>, not on the strength of the covalent bond.



These forces involve electrostatic attraction between <u>partial charges</u> (δ+, δ-) to varying degrees. Since the attraction here only involves partial charges, intermolecular forces of attraction are <u>much weaker</u> compared to ionic / covalent / metallic bonds.

6.1.1 Instantaneous dipole-induced dipole (id-id) attractions

(a) What is id-id attraction?

- id-id attractions occur in all simple molecules and monoatomic noble gases.
- For <u>non-polar</u> molecules, id-id attraction is the **only type** of intermolecular force present. Examples of non-polar molecules: H₂, Cl₂, O₂, CO₂, CH₄, CCl₄, Ar, Ne
- Constant movement of electron density (of all the electrons) in a molecule can cause a temporary polarisation or distortion of the electron cloud in the molecule. This results in an instantaneous dipole formed in the molecule.

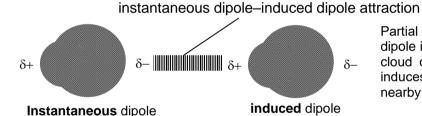


movement of electrons in a molecule causes fluctuations in electron density, thus causing <u>distortion</u> in the electron cloud



instantaneous dipole formed due to uneven distribution of electrons in the molecule

This instantaneous dipole will induce new dipoles in molecules that surround it. This forms weak attractions between the molecules, known as id-id attractions.



Partial negative end, δ –, of temporary dipole in one molecule <u>repels</u> the electron cloud of another nearby molecule, thus induces a δ + end and a δ – end on the nearby molecule as shown in the figure.

(b) Factors affecting the strength of id-id attractions

Factor 1: No. of electrons (Electron cloud size)

- of molecules results in greater <u>ease of distortion</u> of electron cloud / <u>more polarisable</u> electron cloud and thus <u>stronger id-id attractions between molecules</u>.
- Stronger id—id attractions between molecules result in higher boiling point. In other words, boiling point increases with increase in electron cloud size of molecule.

Compound	Structural formula	* <i>M</i> _r	Boiling point / °C
fluorine	F–F	38.0	-188
chlorine	C <i>l</i> –C <i>l</i>	70.0	-34
bromine	Br–Br	159.8	59

*A higher M_r indicates that there are more electrons. **HOWEVER**, **we should NOT use** larger Mr as the reason for stronger id-id.

Factor 2: Surface Area of Contact

Used when comparing molecules with similar no. of electrons but different extent of branching

(You will learn more about branching in 'Intro to Organic Chemistry')

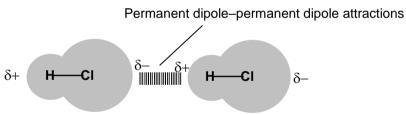
- Attraction between elongated molecules is stronger than attraction between spherical molecules.
- Molecules that are elongated provide a <u>surface area of contact</u> (extensiveness of id–id interactions) which allows for stronger id–id attractions between molecules.

Compound	mpound Structural formula		Boiling point / °C
pentane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	72.0	36
2,2-dimethylpropane	CH ₃ CH ₃ —C—CH ₃ CH ₃	72.0	10

6.1.2 Permanent dipole-permanent dipole (pd-pd) attractions

(a) What is pd-pd attraction?

- Permanent dipole—permanent dipole attraction occurs only between polar molecules. This attraction is in addition to the id—id forces present in the polar molecule.
 Examples of polar molecules: H₂O, HCl, NH₃, CHCl₃, CH₃COCH₃
- Due to the <u>difference in electronegativity</u> between 2 atoms in a polar bond, the bonding electrons will be drawn towards the more electronegative element, resulting in a permanent uneven distribution of electronic charges within the bond.
- The <u>partial positive end</u> of one polar molecule will <u>attract</u> the <u>partial negative end</u> of a nearby polar molecule. This weak electrostatic attraction between the polar molecules is known as <u>pd-pd attractions</u>.



(b) Factor affecting the strength of pd-pd attractions

Magnitude of dipole moment

Compound	Formula	M _r	Polarity of molecule	Boiling point/ °C
pentanal	CH₃CH₂CH₂CHO	86.1	more polar	103
1-chlorobutane	CH ₃ CH ₂ CH ₂ CH ₂ C <i>l</i>	92.5	less polar	78

(c) Relative contributions of id-id versus pd-pd attractions

For molecules with similar M_r , attractions between non-polar molecules (id-id) is <u>weaker</u> than attractions between polar molecules (id-id and pd-pd).

Example

Compound	Formula	M _r	Polarity of molecule	Boiling point/ °C
propene	$CH_3CH = CH_2$	42	non-polar	-48
ethanal	CH₃CHO	44	polar	20

Propene is <u>non-polar</u> and ethanal is <u>polar</u>. Instantaneous dipole-induced dipole attractions between propene molecules are than permanent dipole-permanent dipole attractions between ethanal molecules. <u>Less energy</u> is required to overcome the attraction, therefore, propene has a lower boiling point.

• For molecules with <u>different M_r </u>, id–id **may be the more significant** type of intermolecular forces of attraction as compared to pd–pd attractions. Therefore, substances with <u>large non–polar molecules</u> may have <u>higher boiling point</u> than substances with <u>small polar molecules</u>.

Example

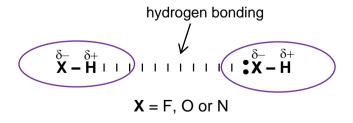
Compound	Formula	M _r	Polarity of molecule	Boiling point/ °C
chloromethane	CH₃C <i>l</i>	50.5	more polar	-24
bromomethane	CH₃Br	94.9	less polar	4

Since bromomethane has a <u>much larger electron cloud size</u>, this leads to greater polarisability / <u>ease of distortion</u> of the electron cloud. This results in <u>stronger id-id attractions between molecules</u>, <u>greater amount of energy</u> is required to <u>overcome the attraction</u> and therefore higher boiling point.

6.1.3 Hydrogen bonding

(a) What is hydrogen bonding?

It is a special type of dipole–dipole attraction between a <u>hydrogen</u> covalently bonded to a small, highly electronegative atom i.e. F, O or N and <u>a lone pair</u> on F, O and N of a <u>neighbouring</u> molecule.



- The bonding electrons between hydrogen and the F, O or N atom are <u>pulled closer towards the</u> more electronegative F, O or N atom. Thus, the hydrogen atom in the molecule is almost a bare proton of the hydrogen nucleus.
- This **strong partial positive charge on the hydrogen atom** is strongly attracted to the negative charge of a lone pair of electrons in F, O or N atom of a nearby molecule or ion.

Note: To illustrate the hydrogen bonding in a diagram, these 3 features must be shown clearly.

- (i) Lone pair on F, O or N atom
- (ii) **2 pairs** of dipoles (δ + and δ –)
- (iii) Label and name the hydrogen bond

Why only F, O and N?

- F, O and N atoms are highly electronegative atoms which will polarise the bond to such a great extent that the H atom has a high partial positive charge.
- The lone pair residing in the smaller 2p orbital of F, O or N also results in higher electron density and therefore stronger attraction with the partial positive charged hydrogen of the neighbouring molecule.

Exercise

Which of the following substances contain hydrogen bonding? (put a tick in the checkbox)

 \square CH₃F \square HCl \square CH₃NH₂ \square H₂S \square CH₃OH \square CH₃COOH \square NH₄⁺

(b) Factors affecting the strength of hydrogen bonding

<u>Factor 1: Average number of hydrogen bonds</u> that can be formed by per molecule of the substance (This is a measure of the extent of hydrogen bonding present)

This number in turn depends on:

- > the number of H atom bonded to F, O or N atom
- > the <u>number of lone pair</u> present in F, O or N atom that is available for hydrogen bonding

Whichever is the <u>smaller</u> number is the average number of hydrogen bond per molecule.

Example

Molecule	H ₂ O	HF	NH₃
Number of H atom per molecule	2	<u>1</u>	3
Number of lone pair per molecule	2	3	<u>1</u>
Average number of hydrogen bond per molecule	2	1	1

The <u>larger the number of hydrogen bond</u> that can be formed per molecule, the <u>greater the amount of energy</u> needed to break the hydrogen bonds between molecules.

Considering this factor, hydrogen bonding between water molecules is <u>more extensive</u> than between HF molecules or between NH₃ molecules, thus <u>greater the amount of energy</u> is needed to break the larger number of hydrogen bonds between molecules.

Factor 2: Electronegativity difference between H and the atom bonded to H in the molecule

Electronegativity difference between the atoms increases in the order: N-H < O-H < F-H

Thus, the hydrogen bonding between lone pair of F atom in a molecule and H of another molecule is stronger than that between O and H, which is in turn stronger than between N and H.

Example:

The observed boiling points for H₂O, HF and NH₃ are 100, 20, -33 °C respectively.

> Based on the extensiveness of H-bonding, boiling point is predicted to be in the order:

➤ Based on the <u>electronegativity difference with H</u>, boiling point is predicted to be in the order:

$$HF > H_2O > NH_3$$

> Extensiveness of hydrogen bonding precedes electronegativity difference with H, therefore boiling point is in the order:

$$H_2O > HF > NH_3$$

(c) Effects of hydrogen bonding on physical properties

(i) Abnormally high melting points and boiling points

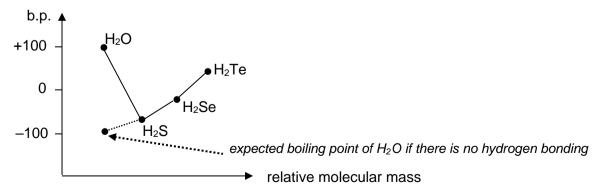
For molecules with **similar molecular size** (or **similar number of electrons**), the strength of the intermolecular forces depend on the type of forces:

Molecules with similar number of electrons held together by hydrogen bonds have higher melting points and boiling points than molecules held by pd–pd or id–id attractions only.

Example:

Melting points and boiling points of HF, H_2O and NH_3 are higher than expected in the corresponding groups as illustrated in the following figures.

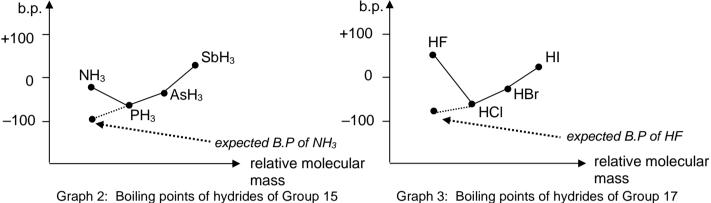
Graph 1: Boiling points of hydrides of Group 16



Explanation for trend in Graph 1

- The number of electrons in the molecule increases from H₂O to H₂Te.
- This results in increasing strength of id-id attractions between molecules.
- Based on this trend, boiling point of H₂O is expected to be lowest; but H₂O actually has the highest boiling point as shown.
- The anomaly is due to the presence of hydrogen bonding between H₂O molecules, which is stronger; thus requiring more energy to overcome, than pd-pd and id-id attractions between the other hydrides molecules.

Similar explanation can be used for trends observed in Graphs 2 and 3.



Graph 3: Boiling points of hydrides of Group 17

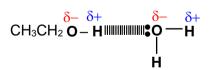
Why is iodine a solid at room temperature and water is a liquid at room temperature?

lodine is non-polar with intermolecular instantaneous dipole - induced dipole intreactions, and water is polar with intermolecular hydrogen bonding. For molecules with different M_r, id-id may be the more **significant** type of intermolecular forces of attraction. (refer to page 34)

(ii) Solubility of some substances

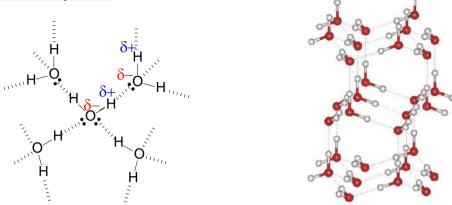
Some molecular substances (e.g. HF, NH₃, ethanol, ethanoic acid) are miscible in water by forming hydrogen bonds with water molecules.

Example Ethanol in water



The formation of hydrogen bonds between ethanol and water molecules releases energy to separate the ethanol molecules and the water molecules, so that ethanol and water molecules can mix.

(iii) Anomalous density of ice



Each O atom in water forms 2 covalent bonds with H atoms. The two lone pairs on the same O atom are bonded to the hydrogen atoms of 2 neighbouring molecules by hydrogen bonds. Hence, each water molecule is surrounded by 4 neighbouring molecules in a <u>tetrahedral manner</u>.

The <u>open structure</u> i.e. lots of empty space between molecules explains why the <u>density of ice is</u> <u>lower than that of water</u>. When ice melts, some of the hydrogen bonds are weakened and the volume contracts due to closer packing of the molecules.

(iv) Anomalous relative molecular mass, Mr

Example

Ethanoic acid, CH_3COOH , dissolved in non-aqueous solvents such as benzene, has an apparent M_r of 120 instead of the expected value of 60.

This is due to the hydrogen bonds between two CH₃COOH molecules forming dimers.

<u>Note:</u> In aqueous form, ethanoic acid will form H–bonds with the water molecules because water is in large excess.

Example

Hydrogen fluoride forms acid salt (e.g. KHF₂) containing the anion, HF₂⁻.

(d) Intramolecular hydrogen bonding

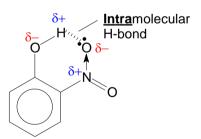
- <u>Intramolecular</u> hydrogen bonding occurs when the H atom in a molecule is in close proximity to the electronegative atom of the same molecule.
- The difference in boiling points of some compounds can be explained by the presence of intramolecular hydrogen bonding.

Example

Observe the structures of 2–nitrophenol and its isomer 4–nitrophenol below. They have the same molecular formula but have different boiling points.

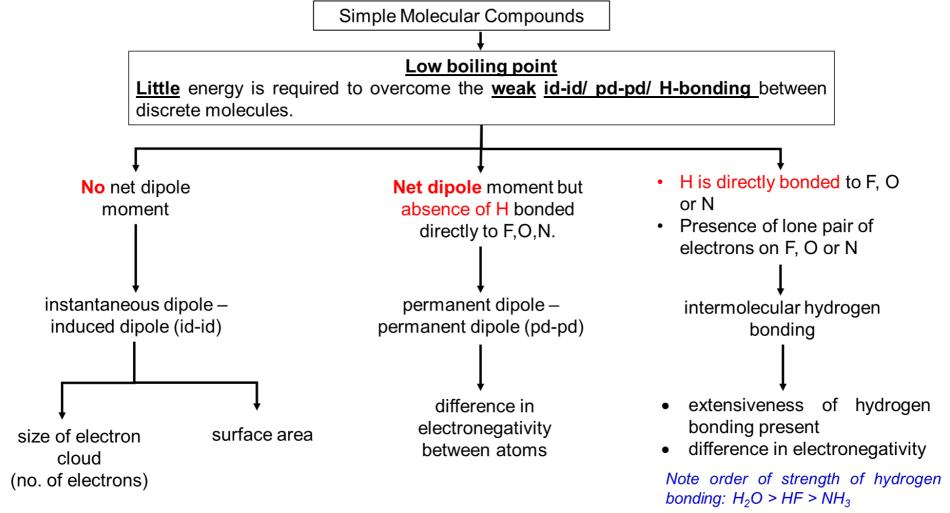
➤ 4—nitrophenol can only form intermolecular hydrogen bonding:

> 2-nitrophenol can form both <u>intermolecular</u> H-bonding, as well as <u>intramolecular</u> H-bonding due to close proximity of the 2 substituent groups.



- Presence of intramolecular H-bonding in 2-nitrophenol <u>reduces</u> the number of sites available for <u>intermolecular hydrogen bonding</u>.
- Less energy is needed to overcome the <u>less extensive intermolecular hydrogen bonding</u> during boiling. Boiling point of 2–nitrophenol is therefore lower than 4–nitrophenol.

Summary

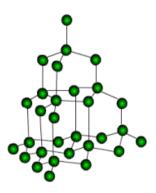


7. GIANT MOLECULAR LATTICE

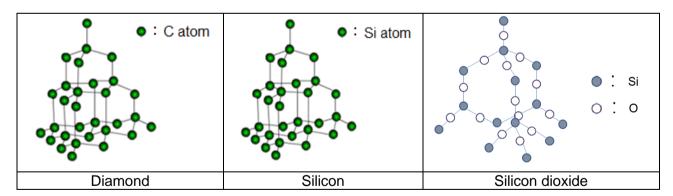
Many atoms can link up to form a giant covalent structure or lattice. The atoms are usually non-metals. This gives them significantly different properties from the small simple covalent molecules.

E.g. Diamond, graphite, silicon dioxide, silicon, boron nitride

7.1 Diamond



- Each carbon is joined by **strong covalent bonds** to four other carbon atoms, in a tetrahedral arrangement. This results in a tightly, interlocking rigid structure which accounts for the great hardness of diamond and its consequent use as an abrasive.
- Because the carbons are held extensively by strong covalent bonds, diamond has a very <u>high</u> melting point (about 4000 °C).
- Diamond <u>does not conduct electricity</u> because no mobile ions or delocalised electrons exist in the structure.
- Diamond <u>does not dissolve in water</u> because the water molecules cannot break the strong covalent bonds.
- Diamond, silicon and silicon dioxide have similar structures.

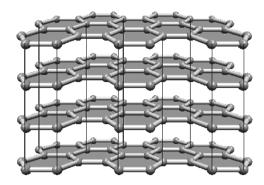


Question:

Account for the higher melting point of diamond (3350 °C) compared to silicon (1410 °C).

The orbitals used for overlapping for diamond (2sp³) are smaller and less diffused than those used for forming Si–Si covalent bonds (3sp³). There is thus more effective overlap of orbitals of carbon and this accounts for the stronger C–C bond, which requires more energy to break.

7.2 Graphite



 Each carbon is bonded to 3 other carbon atoms in the same plane giving rise to layers of carbon atoms in a hexagonal arrangement.

Note: The unhybridised p orbital in each carbon overlap side—on to form a huge delocalised π electron cloud extending over and under each whole layer – to be explained in 'Organic Chemistry')

- \triangleright Graphite is a **good electrical conductor along the layers** because the <u>delocalised</u> π <u>electrons</u> can move along the layers under the influence of an electric field.
- > Graphite is a **poor conductor at right angles to the layers** because the delocalised electrons cannot move between the layers.
- The C–C bond length between C atoms within the same layer in graphite is <u>shorter</u> than the C–C bond length in diamond. This shows that C–C bonds in graphite are <u>stronger</u>.
- Since large amount of energy is required to break these strong and extensive covalent bonds, graphite has a very <u>high melting point</u> and is <u>insoluble in water</u>.
- The C–C bonds <u>between the layers</u> in graphite are <u>longer</u> than the C–C bond length inside the layer. The forces of attraction holding these layers together are not covalent bonds. This shows that the attractions between the layers are <u>very weak</u>. These attractions are instantaneous dipole—induced dipole forces.
- The presence of weak id-id attractions between the layers enables the layers to glide over one another. Hence, the graphite is soft and slippery which makes it a good lubricant.

Question:

Why are the C–C bonds in graphite stronger than those in diamond?

(To be explained in 'Intro to Organic Chemistry'. Refer to the factors affecting bond strength)

C–C bond in <u>graphite</u> results from overlapping of **sp**²**–sp**² hybrid orbitals whereas C–C bond in diamond results from overlapping of **sp**³**–sp**³ hybrid orbitals.

Overlapping of sp² hybrid orbitals is <u>more effective</u> since there is a greater s character (33%) and the bonding electrons are <u>closer to the nuclei</u> of two sp² carbon.

8. FURTHER READINGS

8.1 Coordination number in an ionic compound

- Oppositely charged ions attract each other but ions of the same charge repel each other, therefore we do not find two cations, or two anions adjacent to each other.
- The number of nearest ions that surround another of the opposite charge in an ionic lattice is called the coordination number of that central ion.
- The coordination number of the ion depends on two factors:
 - relative size of oppositely charged ions characterised by the ratio of anion radius cation radius
 - o If an ion is <u>very small</u>, there will not be room for many oppositely charged ions around it. In this case, the maximum coordination number is usually four.
 - o If the cations and anions are <u>nearly equal in size</u>, each ion can be surrounded by <u>eight</u> others.
 - The intermediate case of <u>six</u> surrounding ions occurs when one ion is <u>bigger</u> than the other, but <u>not by very much</u>. (In such a case, you have to use information given in the question to infer.)

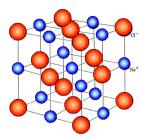
relative charges of oppositely charged ions

To gain electrical neutrality, a cation of charge of 2+ needs twice as many anions of charge 1– as does a cation of charge 1+. We therefore find that Ca^{2+} ion in calcium chloride is surrounded by twice as many Cl^- ions as the Li⁺ ion in lithium chloride.

These 2 factors are illustrated in the table below.

Compound	cation radius / nm	anion radius / nm	anion radius cation radius	coordination number of the cation	coordination number of the anion
NaC <i>l</i>	0.10	0.18	1.8	6	6
MgO	0.07	0.14	2.0	6	6
CsCl	0.17	0.18	1.1	8	8
CaF ₂	0.10	0.13	1.3	8	4
ZnS	0.08	0.19	2.4	4	4

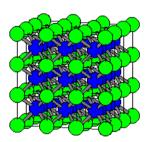
Example: Model of the lattice of NaCl



In a unit cell of NaCl, each Na⁺ is surrounded by 6 Cl⁻ ions and each Cl⁻ surrounded by 6 Na⁺ ions. The coordination number of both Na⁺ and Cl⁻ is 6.

lonic bonds are **non-directional**. Each Na⁺ ion is equally attracted to the neighbouring Cl^- ions without preference for any Cl^- ion in particular.

Example: Model of the lattice of CsCl



In a unit cell of CsCl where there is more room for Cl⁻ to surround the larger Cs⁺ ion, each Cs⁺ ion is surrounded by 8 Cl⁻ ions and each Cl⁻ is surrounded by 8 Cs⁺ ions. The coordination number of both Cs⁺ and Cl⁻ is 8.

8.2 Other methods to determine the shape of a molecule

Method 2 [Oxygen-containing compound]

Type of bonds O commonly forms =O		—O ⁻	→0	-0-	
Examples	CO ₂ , SO ₂	CO ₃ ²⁻ , SO ₄ ²⁻	NO_2	H ₂ O, H ₂ O ₂	

- Always try with the =O bond first. Only when the central atom (e.g. from Period 2) cannot allow for the formation of =O, then you'll replace it with →O.
- For oxoanions, the charge of the anion will tell you how many of this bond (-O⁻) is present.
- For compounds where O is not the surrounding atom, then it is most likely to form 2 single bonds, acting like a 'bridge' linking its adjacent atoms.

Method 3 [Substitution]

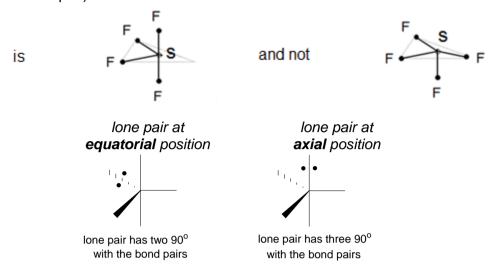
Simplify the formula by substituting less familiar element with one of the same **covalency** ¹ to form compound commonly seen, especially for compounds with more than 1 central atom.

CHCl ₃	H ₂ S	F ₂ O	CH₃CH₃	NH ₂ NH ₂	BH₄ ⁻	CH ₃ ⁺
tetrahedral [CH ₄]	bent [H ₂ O]	bent [H ₂ O]	tetrahedral w.r.t C [CH ₄]	trigonal pyramidal w.r.t N [NH ₃]	tetrahedral [CH ₄]	trigonal planar [BC/ ₃]
Cl same covalency as H	S same covalency as O	F same covalency as H	–CH₃ same covalency as H	–NH₂ same covalency as H	B ⁻ same covalency as C	C ⁺ same covalency as B

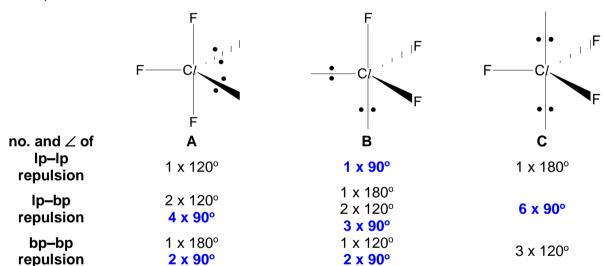
¹ covalency: the number of bonds formed by an element

8.3 Arrangement of electron pairs in trigonal bipyramidal shape

In a <u>trigonal bipyramidal shape</u>, there will be <u>less repulsion</u> between the <u>lone pairs</u> if we place them all at the <u>equatorial position</u> rather than at the axial position. Thus sulfur tetrafluoride, SF₄ (with 4 bond pairs and 1 lone pair)



Similarly, ClF_3 (with 3 bond pairs and 2 lone pairs). There are 3 possible arrangements of the electron pairs around the the central I atom.



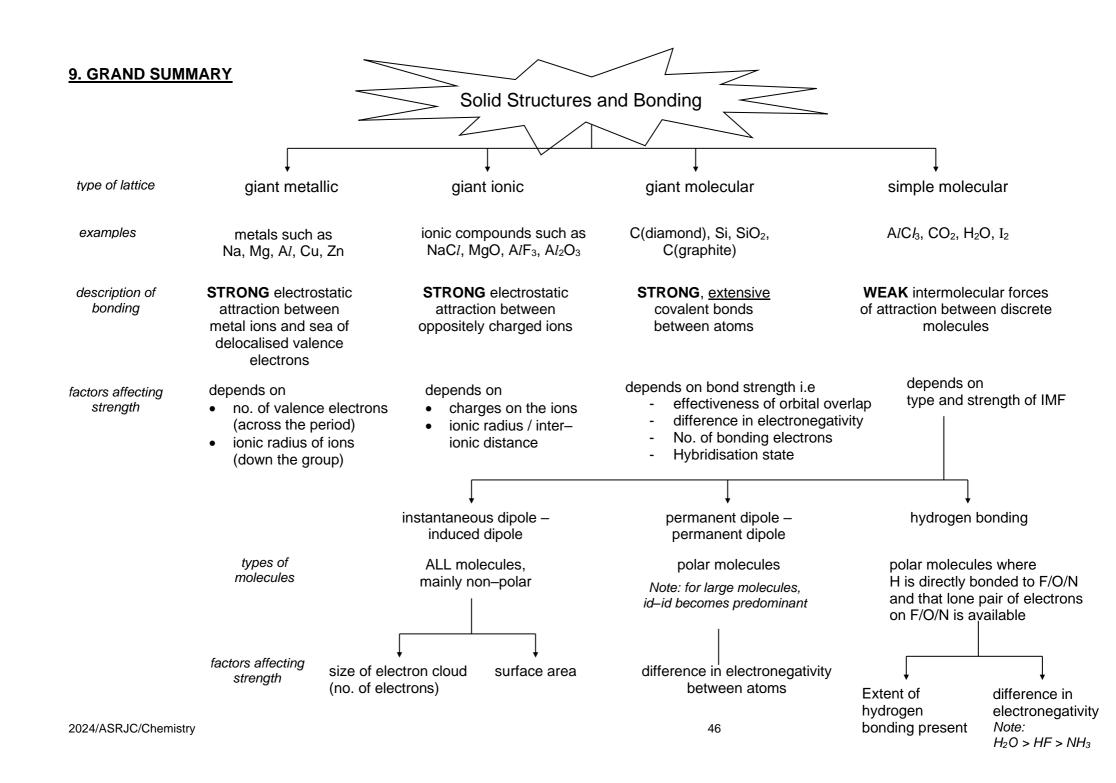
According to the VSEPR theory, <u>electron pairs</u> (both bond pairs and lone pairs) around an atom of molecule arrange themselves <u>as far apart as possible</u> in space to <u>minimise inter-electronic repulsion</u>, allowing the molecule to be low in energy and hence stable.

The strength of repulsion between electron pairs decreases in the order: lp-lp > lp-bp > bp-bp

As illustrated in the table previously, all 3 arrangements have 6 pairs of 90° repulsion but the strength of the 90° repulsion between the different types of electron pairs is the least for arrangement **A**, followed by **C** and then **B**. Hence arrangement **A** will be the most stable while arrangement **B** will be the least stable.

Note:

In an **octahedral arrangement of 4 bond pairs and two lone pairs**, repulsion is minimised when lone pairs are on opposite sides of central atom.



Physical Property: Melting / Boiling point

Big Idea: Energy required to overcome the attractive forces between the particles.

		Covalent Bonds						
Giant Metallic	Giant Ionic Structure	Giant Molecular Structure		Simple Molecular Structure (instantaneous dipole–induced dipole				
Structure		Graphite/ BN	Diamond	attractions / permanent dipole- permanent dipole attractions)	Simple Molecular Structure (hydrogen bonding)			
High	High	High		Low	High*			
Reason:	Reason:	Reason:		Reason:	Reason:			
Large amount	Large amount	Large amount of	energy is	Smaller amount of energy is needed to	Larger amount of energy is needed to			
of energy is	of energy is	needed to overcome the		overcome the weaker instantaneous	overcome the stronger intermolecular			
needed to	needed to	strong extensive covalent		dipole-induced dipole attractions /	hydrogen bonds (as compared to			
overcome the	overcome the	bonds between atoms in		permanent dipole-permanent dipole	simple molecular structures with weak			
strong	strong ionic	the giant molecular		attractions between molecules.	intermolecular instantaneous dipole-			
metallic bonds	<u>bonds</u>	structure			induced dipole attractions / permanent			
					dipole-permanent dipole attractions)			
					Note:			
					*melting / boiling points are still			
					considered low when compared to			
					giant ionic/metallic/molecular structures			

Answer structure to explain difference in boiling/melting point of 2 substances:

- ZZ has a giant ionic/giant metallic/giant molecular/simple molecular structure but YY has a....
- More energy is required to overcome the <u>stronger electrostatic forces of attraction/id-id/pd-pd/H-bonding</u> between the <u>oppositely charged ions/ cations and sea of delocalised electrons/ atoms/ molecules (type of particles)</u> of <u>ZZ</u> as compared to the <u>weaker electrostatic forces</u> of attraction/id-id/pd-pd/H-bonding between <u>Particles(state the type)</u> of <u>YY</u>.

Physical Property: Electrical Conductivity

Big Idea: Presence of mobile charged carriers i.e delocalised electrons or mobile ions

		Giant Molecular Structure		Simple Molecular Structure	Simple
Giant Ionic Structure	Giant Metallic Structure	Graphite/ BN	Diamond Diamon		Molecular Structure (hydrogen bonding)
Non-conductor in solid state but good conductor in molten / aqueous state	Good conductor in solid & molten state	Good conductor when parallel to layers but non-conductor when perpendicular to layers	Non-conductor		
Reason: - Solid: ions can only vibrate about fixed positions hence there are no free mobile ions to conduct electricity - Molten / aqueous: presence of ions as mobile charge carriers to conduct electricity. Electrical conductivity increases with increasing concentration of the ions in the solution.	Reason: Presence of delocalised electrons as mobile charge carriers to conduct electricity	Reason: E.g. graphite - parallel to layers: presence of delocalised electrons as mobile charge carriers to conduct electricity - perpendicular to layers: Electrons are localised in covalent bonds and not mobile to conduct electricity Note: BN is a non— conductor	Reason: Electrons are localised in covalent bonds and not mob conduct electricity		and <u>not mobile</u> to

Physical Property: Solubility

Big Idea: Energy released during formation of solute–solvent interaction > Energy taken in to overcome solute–solute and solvent–solvent interaction.

		Giant Molecular Structure			Simple Molecular Structure (hydrogen bonding)
Giant Ionic Structure	Giant Metallic Structure Graphite BN		Diamond	Simple Molecular Structure (instantaneous dipole–induced dipole attractions / permanent dipole–permanent dipole attractions)	
Generally <u>soluble in</u> <u>water</u>	Generally soluble in water due to chemical reaction	Insoluble in both polar and non-polar solvents		Insoluble in water but soluble in non-polar solvents	Soluble in water but insoluble in non-polar solvents

Answer Structure:

- Energy released during the formation of <u>ion-dipole interactions / hydrogen bonding / pd-pd/ id-id</u> attractions between solute and solvent is able/unable to compensate for the energy taken in to break the <u>strong ionic bonds/ strong extensive covalent bonds/ hydrogen bonding/ pd-pd/ id-id</u> during hydration.
- Hence, **soluble/ insoluble** in solvent.

Other special physical properties:

Cient Ionia Structura	Giant Metallic	Giant Molec	ular Structure	Simple Molecular Structure (instantaneous dipole–induced dipole	Simple Molecular	
Giant Ionic Structure	Structure	Graphite/ BN	Diamond	attractions / permanent dipole-permanent dipole attractions)	Structure (hydrogen bonding)	
Hard and brittle	Malleable & ductile	Soft and slippery	Extremely hard	Soft	Soft	
Reason: Hard: strong electrostatic forces of attraction between oppositely charged ions in giant ionic lattice structure Brittle: stress applied on the ionic lattice with regular pattern causes sliding of layers of ions, resulting in ions of similar charges coming together & resultant repulsion shatters the ionic structure Uses: Refractory material	Reason: Stress applied causes sliding of layers of cations over one another without causing the metallic structure to break down as the 'sea' of delocalised electrons are holding the cations together to prevent repulsion between the metal ions Uses: Alloy formation (due to different cations) Opaque and lustrous surface (sea of delocalised electrons absorb and re—emit light over a wide range of wavelengths)	Reason: Adjacent layers are held together by weak instantaneous dipole—induced dipole attractions. Hence, layers can easily slide over each other Uses: As machinery lubricant	Reason: Atoms are held together by strong covalent bonds in the giant molecular structure Uses: Cutting tool	Reason: Small amount of energy is needed to overcome the weak intermolecular instantaneous dipole—induced dipole attractions / permanent dipole—permanent dipole attractions	Reason: Small amount of energy is needed to overcome the weak intermolecular instantaneous dipole—induced dipole attractions / permanent dipole—permanent dipole attractions	