

CHEMICAL BONDING

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 Al_2Cl_6 molecule
- (c) describe covalent bonding in terms of orbital overlap giving σ and π bonds.
- (d) explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (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)
- (f) explain and deduce bond polarity using the concept of electronegativity
- (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 $CHCl_3(l)$; $Br_2(l)$ 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
- (l) 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
- (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

- Cambridge International AS and A Level Chemistry by Peter Cann and Peter Hughes, published by Hodder Education
- A Level Chemistry (4th Edition) by E. N. Ramsden, published by Oxford University Press



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A. INTRODUCTION

All matter on earth are made of atomic particles bonded together to form molecules or compounds. These binding forces (chemical bonds) result in the substance achieving a lower energy arrangement. The re-distribution of the outer electrons (valence electrons) of the atoms is required for the formation of a bond. Chemical Bonding is at the heart of Chemistry.

Generally, there are two categories of chemical bonds --- **inter-atomic bonds** and **intermolecular forces**.

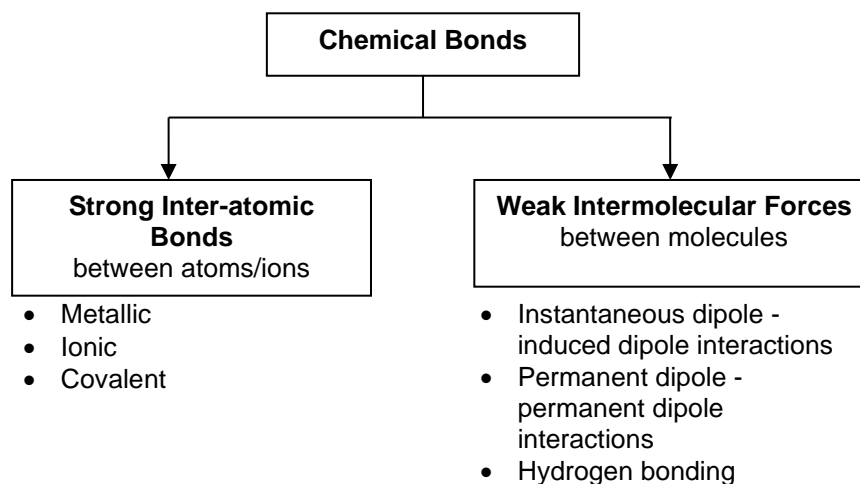


Table 1: Type of chemical bonds and their approximate strengths

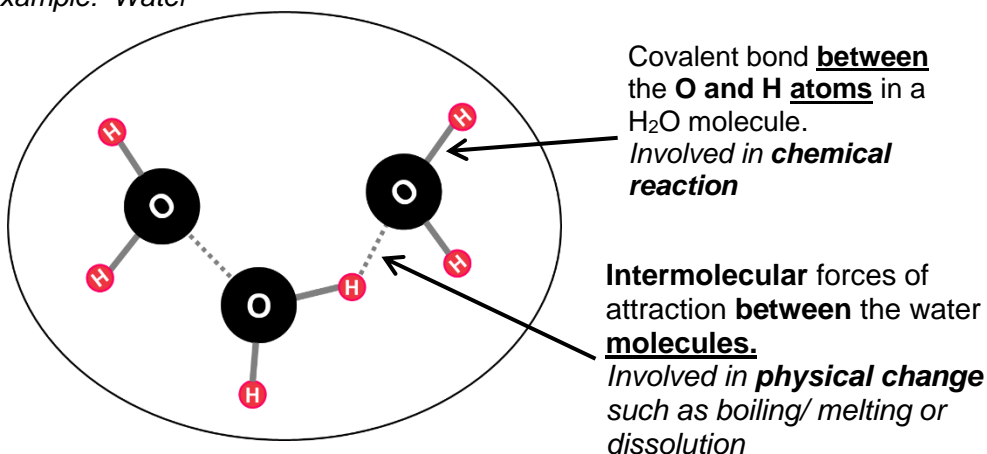
Type of bond	Strength of bond	Bond Energy/ kJ mol ⁻¹
Ionic bond	Strong	120 – 450
Covalent bond	Strong	120 – 550
Metallic bond	Strong	80 – 580

Type of Intermolecular Forces	Strength of IMF	Bond Energy/ kJ mol ⁻¹
Instantaneous dipole - induced dipole (id-id) interactions	Very weak	<4
Permanent dipole - permanent dipole (pd-pd) interactions	Weak	<13
Hydrogen bonds	Weak	20 – 100

Example: Water

Note:
Strong covalent bond between O and H atoms.

Weaker intermolecular forces between H₂O molecules.



Success criteria:

understand that all interatomic bonds and intermolecular forces of attraction are electrostatic in nature and energy is required to overcome them. Thus, the magnitude of the melting/boiling points reflects the strength of the different electrostatic forces of attraction.

	Name of Bond	Diagrammatic Representation	Electrostatic Forces of Attraction between	
Inter-atomic Bonding	Metallic Bond		(+) metal cations And sea of delocalised electrons	(-) sea of delocalised electrons
	Ionic Bond		(+) Cations And Anions	(-) Anions
	Covalent Bond		(+) Nucleus (proton) And Shared Electrons Pair	(-) Shared Electrons Pair
Intermolecular Bonding	Instantaneous dipole - induced dipole interactions		(+) Instantaneous dipole (δ^+) And Induced dipole (δ^-)	(-) Induced dipole (δ^-)
	Permanent dipole – Permanent dipole interactions		(+) Permanent dipole (δ^+) And Permanent dipole (δ^-)	(-) Permanent dipole (δ^-)
	Hydrogen bonds		(+) Protogenic H bonded to O, N or F And Lone pair electrons on O, N or F	(-) Lone pair electrons on O, N or F
Ion - Molecule	Ion – dipole interaction (mixture)		(+) Cations And Permanent Dipole (δ^-)	Permanent dipole (δ^+) And Anions

B. INTER-ATOMIC BONDS

Inter-Atomic Bonds

Success criteria:

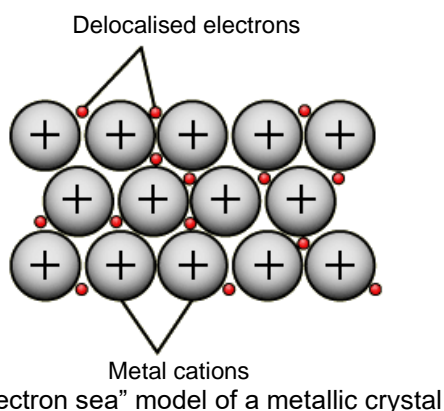
- describe metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons
- describe the metallic lattice structure of a crystalline solid as in copper (see checkpt 6 on pg 21)
- describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

1 METALLIC BONDS

The **metallic bond** is the electrostatic forces of attraction between **metal cations** and the **sea of delocalised electrons**.

1.1 Structure and Bonding of Metals

- Metals consist of crystalline structures of closely packed atoms with 8-12 atoms surrounding any given atom and at equal distance from it.
- The **metallic lattice** structure comprises metal cations immersed within a sea of delocalised electrons. This is due to each metal atom contributing its loosely bound valence electrons to form a sea of delocalised electrons. The metallic cations are attracted to the sea of delocalised electrons. The sea of delocalised electrons prevents the repulsion between the cations.
- The electrons are no longer bound to a particular metal cation but are free to move throughout the metal (delocalised electrons).



- The metallic bonding is **non-directional**.
i.e. no preferred attraction for delocalised electrons in any particular direction.

1.2 Factors affecting Strength of Metallic Bonds

Different no. of delocalised electrons per metal atom	➡	Metallic Bond strength \propto No. of delocalised electrons (cation of higher charge)
For same no. of delocalised electrons per Metal atom	➡	Metallic Bond strength $\propto \frac{1}{\text{ionic radius}}$

1.3 Physical Properties of Metals

❖ High melting and boiling points

- Large amount of energy is required to overcome the **strong** metallic bonds between cations and the sea of delocalised electrons in the **lattice structure** during a change in physical state.

❖ Hard

- Presence of strong and non-directional metallic bonds

❖ Good electrical conductors

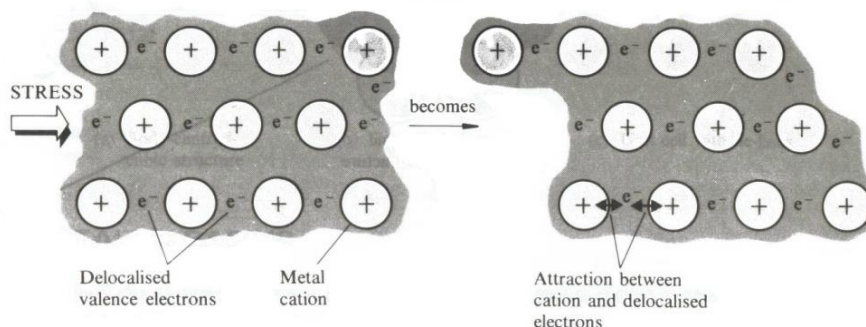
- Presence of mobile electrons which act as charge carriers
- When a potential difference is applied, the delocalised electrons flow through the lattice towards the positive potential.

❖ Thermal conductivity

- Conduction of heat occurs by vibration of the positive ions and the mobile electrons.

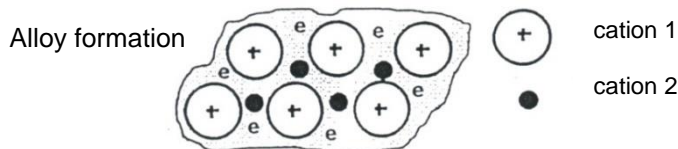
❖ Malleable (can be hammered into shapes) and ductile (can be drawn out into long wires)

- When shear stress is applied, the non-directional character of metallic bonding and the mobility of the sea of delocalised electrons allow the metal ions in the structure to slide past each other, readily **accommodate any distortion in the lattice without fracturing**.
- The metal lattice does not break because the sea of delocalised electrons prevents repulsions between the cations.



❖ Soluble in other metals (alloys)

- The mobile sea of delocalised electrons can accommodate a variety of cations



- Alloys are harder and stronger than pure metals. Brass (alloy of copper with zinc) is harder and stronger than copper because the zinc ions cause a less regular copper lattice, making it more difficult for the metallic ions to slide past each other.
- Alloys have increased electrical resistance and lower conductivity. The lattice of an alloy is less regular and thus affects mobility of the electrons.

Checkpoint 1



1. Explain the difference in the melting point between Li and Na.

Metal	Melting point / °C
Li	180
Na	98

Thinking process

- State the **structure** of the two substances
- State the **number of valence electrons** contributed per metal atom
- Compare the ionic radius of metal cation (**ONLY** for metals with **same** no. of delocalised electrons. Skip this comparison if different no. of delocalised electrons.)
- State which metal cation ion has greater attraction for the delocalised electrons.
- State which metal requires more energy to break the stronger metallic bonds to account for the melting point.

Explanation

Both Li and Na have _____ structures. Metallic bonds are overcome during melting. Thus need to compare metallic bond strength to account for the difference in m.pt.

Both Li and Na contribute _____ **valence electron per atom** to form the sea of delocalised electrons.

Li⁺ ion has a _____ ionic radius than Na⁺ ion.

Hence Li⁺ ions have _____ attraction for the delocalised electrons.

_____ energy is needed to break the _____ **bonds in Li**, thus Li has a higher melting point.

2. Explain the difference in the melting point between Na and Mg.

Metal	Melting point / °C
Na	98
Mg	650

Success criteria:

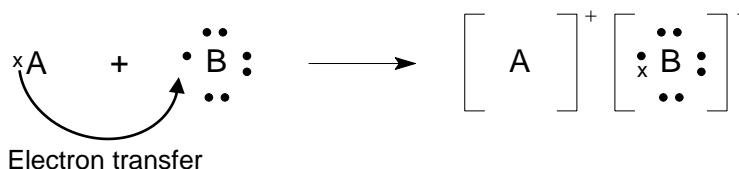
- describe ionic bond as the electrostatic attraction between oppositely charged ions
- use of 'dot-and-cross' diagrams to describe ionic bonding as in NaCl and MgO
- describe the ionic lattice structure of a crystalline solid as in NaCl and MgO. See Figures 2.2 under section 2.2.
- describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

2 IONIC (ELECTROVALENT) BONDS**Inter-Atomic Bonds**

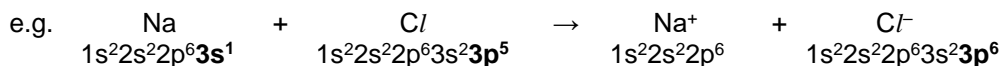
The **ionic bond** is the electrostatic forces of attraction between **oppositely charged ions** in an ionic compound.

An **ionic bond** is **usually** formed between a metallic element and a non-metallic element with great difference in electronegativity.

Its formation involves the **complete transfer** of valence electrons from one atom (*usually* a metal) to another atom (*usually* a non-metal) which results in the formation of cation and anion respectively.



The cations and anions formed usually have the electronic configuration of a noble gas, i.e. (octet) ns^2np^6 .



Some exceptions to the octet rule:

Atoms	Ions	Remarks
Transition metals		
Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	Fe²⁺ $1s^2 2s^2 2p^6 \underline{3s^2 3p^6 3d^6}$	Fe ²⁺ ion has 14 electrons in <u>outermost shell</u> .
Mn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	Mn²⁺ $1s^2 2s^2 2p^6 \underline{3s^2 3p^6 3d^5}$	Mn ²⁺ ion has 13 electrons in <u>outermost shell</u> .
Pb [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	Pb²⁺ [Xe] $4f^{14} 5d^{10} \underline{6s^2}$	Pb ²⁺ ion has 2 electrons in <u>outermost shell</u> .

2.1 Dot-and-cross diagrams of ionic compounds

Note:

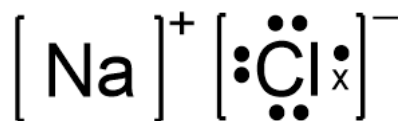
For A level dot-and-cross diagram:

1) electron shell (orbit) are **NOT** shown

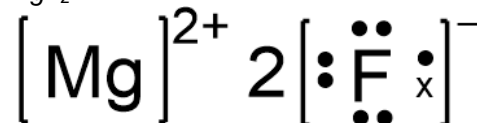
2) Only the outermost shell (valence) electrons are shown

Dot-and-cross diagrams are used to represent the **valence electrons of individual elements** in a compound.

NaCl



MgF₂

**Checkpoint 2**

Draw a dot and cross diagram for

(i) K₂O (K - Grp 1; O - Grp 16)

(ii) Al₂O₃ (Al - Grp 13; O - Grp 16)

2.2 Structure and Bonding of Ionic Compounds

In the solid state, the oppositely charged ions are held in fixed positions by strong ionic bonds, in an orderly manner, forming a regular 3-dimensional crystal lattice structure.

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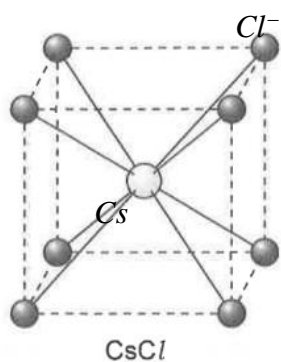
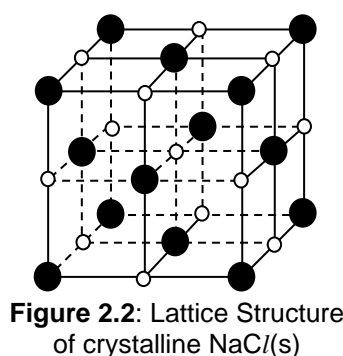
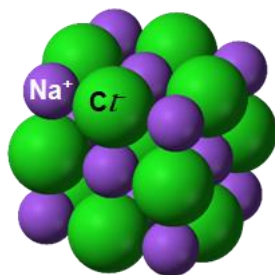


Figure 2.2: Lattice Structure of crystalline CsCl(s)

Size of Cs⁺ > Na⁺, in fact size of Cs⁺ > Cl⁻. Thus Cs⁺ is surrounded by 8 Cl⁻ ions while Na⁺ is surrounded by 6 Cl⁻ ions only.

Assessed in 2009/ 2021 A IM P2.



● chloride ion
○ sodium ion

Each Na⁺ ion is surrounded by 6 Cl⁻ ions

Each Cl⁻ ion is surrounded by 6 Na⁺ ions

- Ionic bond is **non-directional**. i.e. no preferred attraction in any particular direction.

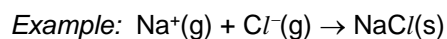
Each ion in the crystal lattice is attracted equally to several surrounding ions of opposite charge as ions are spherical with uniform electric fields around them.

- Ionic bonds are **strong forces of attraction**. A lot of energy is required to break such bonds.

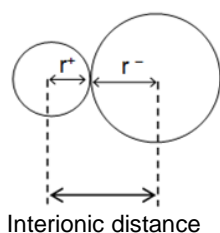
2.3 Factors affecting Strength of Ionic Bonds

Lattice energy is defined as the energy released when one mole of ionic solid is formed from its constituent gaseous ions. = amt of energy required to overcome the giant ionic lattice. (To be covered in **Chemical Energetics**)

The strength of ionic bonds in ionic solids with the same crystal structure is thus proportional to its **lattice energy (L.E.)** magnitude.



L.E. = -771 kJ mol^{-1}



$$|\text{L.E.}| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$$

where

q_+ is charge of cation

q_- is charge of anion

r_+ is radius of cation

r_- is radius of anion

Magnitude of lattice energy depends on:

1) Product of Charge of the ions:

the greater the charge of the ions, the larger the magnitude of lattice energy

2) Interionic distance:

the shorter the interionic distance, the larger the magnitude of lattice energy

Checkpoint 3



1. Explain the difference in ionic bond strength between NaCl and MgO.

❖ Compare the charge and size of the ions

	ionic charge	ionic size
Na^+		
Mg^{2+}		
Cl^-		
O^{2-}		

❖ Compare the product of charges of ions and interionic distance

The product of charges in MgO is _____ compared to that in NaCl

The interionic distance in MgO is _____ than that of NaCl.

❖ Compare the magnitude of lattice energy to determine the strength of the ionic bond

Given $|\text{L.E.}| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$,

Magnitude of lattice energy of MgO is _____ than that of NaCl.

Thus, ionic bond strength in MgO is _____ than that in NaCl.

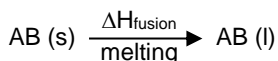
2. Explain the difference in ionic bond strength between NaCl and Na_2O .

2.4 Physical properties of ionic solids

Note:

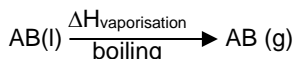
Enthalpy change of fusion is the energy required to melt one mole of a substance

Melting process involves the breakdown of **crystal lattice structure** and overcoming **some** of the **ionic bonds**



Enthalpy change of vaporisation is the energy required to vaporise one mole of a substance

Boiling involves overcoming **all ionic bonds**

**a) High melting point (ΔH_{fusion}) and boiling point ($\Delta H_{\text{vaporisation}}$)**

Large amount of energy is required to overcome **strong** ionic bonds between oppositely charged ions in the **lattice structure** during a change in physical state.

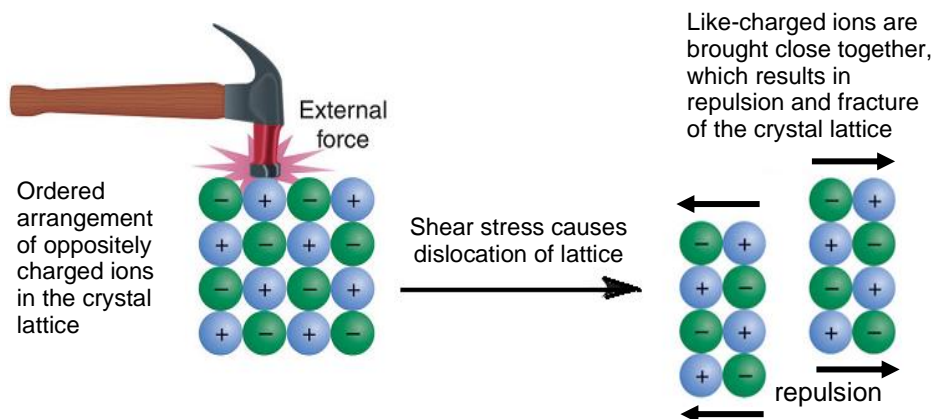
The energy needed to break down a lattice is reflected in its melting point.

Ionic Compound	Cationic Radius /nm	Anionic Radius /nm	Lattice Energy /kJ mol ⁻¹	Melting Point /°C
NaCl	0.095	0.181	-771	808
NaBr	0.095	0.195	-743	750
MgO	0.065	0.132	-3889	2852
CaO	0.099	0.132	-3513	2614

- The greater the magnitude of the lattice energy (L.E.), the stronger the ionic bond.
- More energy is needed to break the stronger ionic bond.
∴ Higher melting point

b) Hard and brittle

- Ions are held in specific positions throughout the crystal lattice by strong ionic bonds.
- Moving the ions out of position requires overcoming these strong forces of attraction, so the ionic solids resist denting.
- When a sheer stress is applied, the layers of ions will slide past each other, resulting in repulsion between like-charged ions, causing the ionic crystal to break apart. (Unlike metals)



An ionic lattice shatters when deformed

c) Different electrical conductivity in different physical states

- In solid state, the ions are held in **fixed positions** by strong ionic bonds, hence unable to conduct electricity due to absence of *mobile* charge carriers.
- In molten and aqueous states, the ionic crystal lattice is **broken down**. The ions, acting as **mobile charge carriers**, are free to move (mobile) to conduct electricity.

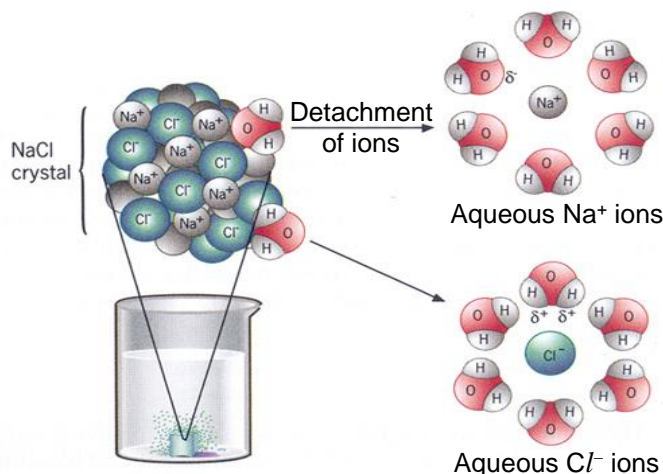
d) Soluble in water and polar solvents (usually)

Note:

To dissolve an ionic solid, large input of energy is required to break down the crystal lattice. (Endo)

This input of energy can be offset by the energy **released** caused by **hydration** of the ions with water (or **solvation** if solvent is another polar solvent). (Exo)

If the energy released is insufficient to overcome the strong attractive forces in the crystal lattice, the ionic solid will not dissolve.



The cations are surrounded by the partially negative 'δ-' oxygen-ends of the water molecules.

The anions are surrounded by the partially positive 'δ+' hydrogen-ends of the water molecules. /

- When an ionic solid is placed in water, each ion on the crystal's surface attracts oppositely charged poles of polar water molecules.
- Formation of extensive **ion-dipole interactions** results in release of sufficient energy to overcome the ionic bonds and break down the crystal lattice.
- Hence, solid dissolves.

Checkpoint 4

By quoting suitable data from the Data Booklet, explain why the melting point of NaCl is higher than that of NaBr.

(**Note:** The physical property of a compound (e.g. mp) is determined by its structure and bonding)

❖ State the structure of the two compounds

❖ State the relevant data from the Data Booklet

❖ Compare the strength of ionic bond between the two compounds

❖ State which compound requires more energy to break the stronger ionic bonds to account for the melting point.

Since the ionic bonds are broken during melting, m.pt magnitude reflects the strength of ionic bonds.

Recall ionic bond strength \propto lattice energy (L.E.) $\propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$,

Ionic Size

Na⁺: _____ (common between 2 species)

Cl⁻: _____ **Br⁻:** _____

The product of charges in NaCl and NaBr is the _____ since Na⁺, Cl⁻ and Br⁻ ions are all singly charged.

The interionic distance in NaCl is _____ than that of NaBr as Cl⁻ ion is _____ than Br⁻ ion.

Given $|L.E. \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$, magnitude of lattice energy of NaCl is _____ than NaBr.

More energy is needed to break the _____ ionic bonds in NaCl than that of NaBr.

Thus, NaCl has a _____ melting point than NaBr.

Success criteria:

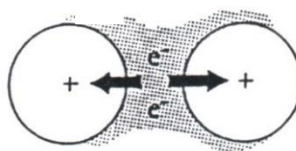
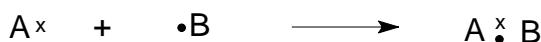
- describe covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei.

3 COVALENT BONDS**Inter-Atomic Bonds**

The **covalent bond** is the electrostatic forces of attraction of the **positively charged nuclei** of each bonding atom for the **shared pair of electrons**.

A covalent bond is the result of the sharing of a pair of electrons between two atoms with **similar electronegativity**.

(**Note:** Electronegativity is the relative ability of a bonded atom to attract shared electrons.)



Electron sharing in a covalent bond

3.1 Theories on Covalent Bond Formation

Early scientists used the limited information they had about the structure of matter and creatively came up with sound theories to explain the bonding present that resulted in these structures. With new discoveries and understanding, recent scientists modify the initial theories to improve on their accuracy leading to the scientific knowledge we have today.

a. Lewis Theory (1916)

In 1916, Gilbert N. Lewis, American chemist, stated that two atoms may achieve noble gas configuration, not only by transfer of electrons from one atom to another, but also by sharing one or more pairs of valence electrons. This idea was a compilation of knowledge on bonding that existed then.

To show how electrons in the valence shell of an atom are shared to complete the stable octet configuration of the noble gases, Lewis structure was introduced to represent atoms and molecules, where dots represent electrons and lines represent covalent bonds.

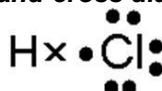
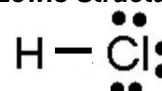
Note:

Within a HCl molecule, there are:

- 1 bond pair of electrons, i.e. the electron pair involved in forming the covalent bond and
- 3 lone pairs of electrons, i.e. the electron pairs which are not involved in bonding.

The 2 types of electron pair exhibited in the Lewis structure are:

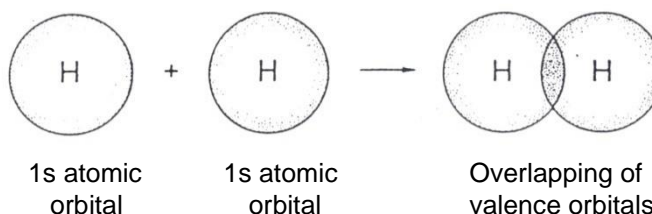
- Bond pair: A pair of electrons (2 electrons) in a **covalent bond**.
- Lone pair: A pair of electrons (2 electrons) in the valence shell **not involved in bonding**

Dot-and-cross diagram**Lewis Structure**

b. Valence Bond Theory: The Overlap of Atomic Orbitals (1927)

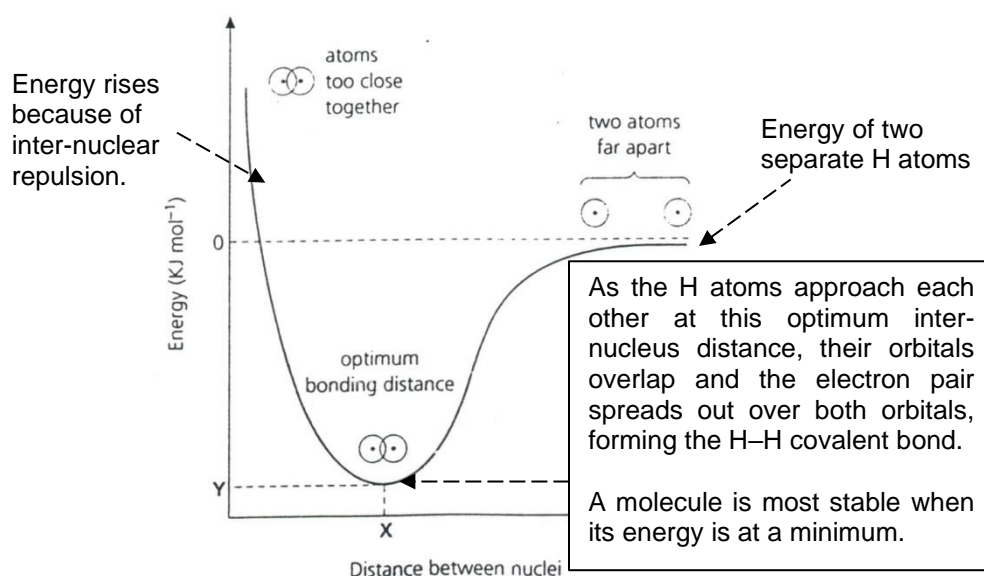
With the advent of quantum mechanics, Walter Heitler and Fritz London in 1927 devised the valence bond theory of bonding.

In valence bond theory, the covalent bond is formed as a result of an **overlap of valence atomic orbitals** containing one electron each. The resultant electron cloud is called a bonding orbital and the shared pair of electrons occupies the bonding orbital with opposite spins.



The orbitals involved must have maximum overlap so that the electron density is concentrated between the nuclei and this can hold the atoms against the mutual repulsion of the nuclei.

The electrostatic attraction between the electron density and the bonded nuclei constitutes the covalent bond.



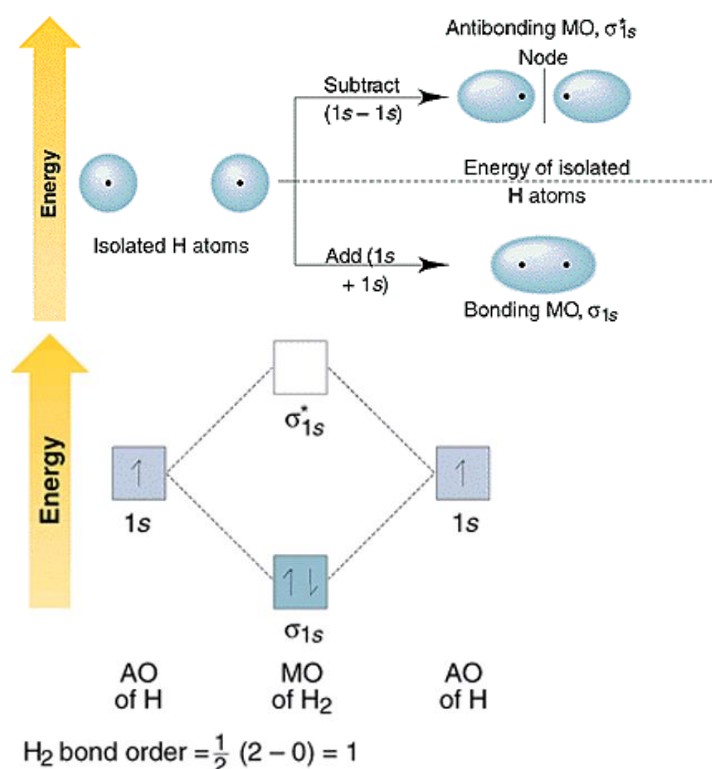
Potential energy vs distance between nuclei

- The driving force behind covalent bond formation is the lowering of the energy level of the isolated gaseous atoms when they undergo bonding.

c) Molecular Orbital Theory (1927) – Covered in H3 syllabus!

Molecular orbital theory was developed, in the years after valence bond theory had been established (1927), primarily through the efforts of Friedrich Hund, Robert Mulliken, John C. Slater, and John Lennard-Jones. According to German physicist and physical chemist Erich Hückel, the first quantitative use of molecular orbital theory was the 1929 paper of Lennard-Jones, which notably predicted a triplet ground state for the dioxygen molecule which explained its paramagnetism. The word *orbital* was introduced by Mulliken in 1932. By 1933, the molecular orbital theory had been accepted as a valid and useful theory.

Molecular orbital (MO) theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. The spatial and energetic properties of electrons within atoms are fixed by quantum mechanics to form orbitals that contain these electrons.



Success criteria:

- describe co-ordinate (dative covalent) bonding where both electrons in the covalent bond comes from only one of the bonding atoms. E.g. formation of the ammonium ion and Al_2Cl_6 molecule.

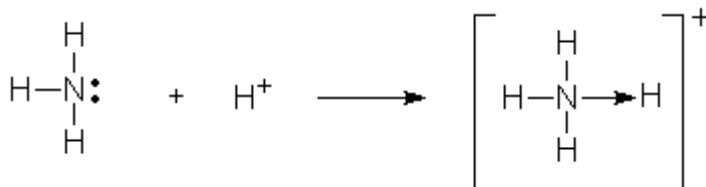
3.2 Co-ordinate Bond (Dative covalent bond)**Note:**

Dative bond has the same characteristics as an ordinary covalent bond.
i.e. it has the same bond strength and bond length.

- If **both electrons** in a covalent bond come from **only one of the atoms**, the bond is called a **co-ordinate bond /dative covalent bond**.
- Dative bond is formed when a filled valence orbital of an atom overlaps with a vacant valence orbital of another atom, i.e. an atom (donor) donates **a lone pair of electrons** to another atom (acceptor) which has **a empty low-lying orbital (energetically accessible orbital)** to **accommodate** the electrons.

E.g. Ammonium ion, NH_4^+

NH_3 has a lone pair on N which is donated to the empty low-lying orbital of the H^+ ion, forming a dative bond.

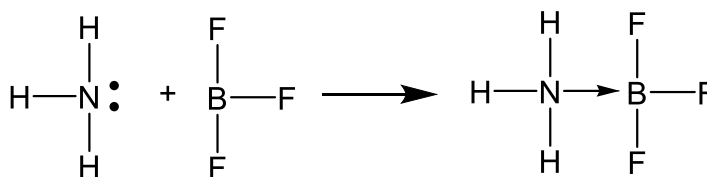


- The dative bond is denoted by an arrow \rightarrow . The direction of the arrow is drawn from the donor atom to the acceptor atom.
- The **bonding electron pair** comes from **only one** atom.

Other examples:

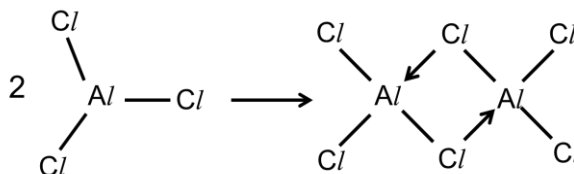
(i) $BF_3.NH_3$

(NH_3 has a lone pair on N which is donated to the empty low-lying orbital of B in BF_3)



(ii) Al_2Cl_6 (Al forms covalent bond with Cl. See section B 4.2)

($AlCl_3$ has a lone pair on Cl which is donated to the empty low-lying orbital of Al in **another** $AlCl_3$ molecule)



Success criteria:

- Describe, in words or diagrams, covalent bonding in terms of orbital overlap (use s and p orbitals only), giving σ and π bonds in **diatomic** molecules.
- Understand that the **pair of orbitals** taking part in covalent bonding must **either** have one unpaired electron each (see section 3.3) **or** one orbital with lone pair while the other orbital is without electrons (see section 3.2).
- Covalent bond strength increases with increase in shared electron density between 2 nuclei. See section 3.3 (sigma > pi) and 3.4. (i) bond order (ii) effectiveness of orbital overlap.

3.3 Types of Covalent Bondsa. Sigma (σ) Bond**Note:**

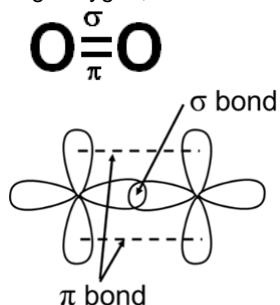
For a pair of H atoms, the unpaired electron is in the 1s atomic orbitals, thus 1s orbitals take part in covalent bonding.

For a pair of F atoms, the unpaired electron is in the 2p atomic orbitals, thus 2p orbitals take part in covalent bonding.

Note:

A **double bond** consists of a σ bond and a π bond.

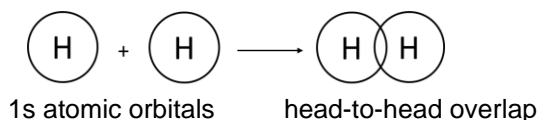
E.g. Oxygen, O_2 :



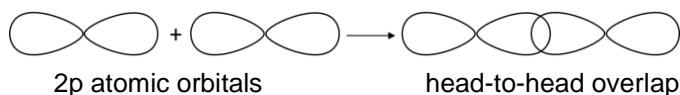
- σ bond is formed by **head-on (collinear) overlap** of two atomic orbitals.
- Shared electron density** is concentrated **along the inter-nuclei axis** of the bonding atoms.
- There can only be **ONE** sigma bond **between any two atoms** as it is **NOT possible for another head-on overlap** of the atomic orbitals to take place **between the same pair of atoms**.

Examples of sigma bond:

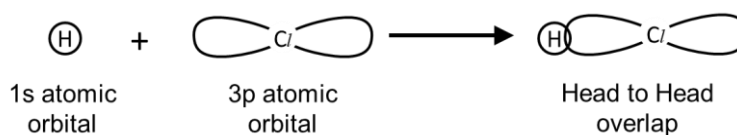
- s – s overlap (e.g. H_2)



- p–p overlap (e.g. F_2)

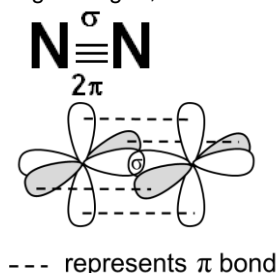


- s–p overlap (e.g. HCl)

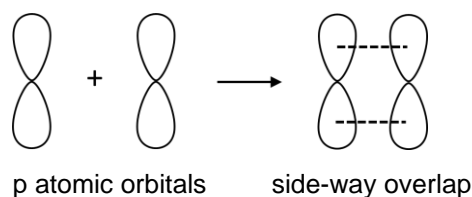
b. Pi (π) Bond

A **triple bond** consists of a σ bond and **two** π bonds.

E.g. Nitrogen, N_2



- π bond is formed by **side-way (collaterally) overlap** of **two p atomic orbitals**.
- Shared electron density** is concentrated **above and below the inter-nuclei axis** of the bonding atoms



Sigma (σ) versus Pi (π) bonds

- The strength of a covalent bond increases with a more effective orbital overlap. Head-on overlap of the orbitals is more effective than lateral overlap, thus **a sigma bond is stronger than a pi bond**.
- A pi bond is formed **only after** a sigma bond is first formed.
 - Therefore, π bonds are present only in multiple bonds (such as double bond or triple bond).

Success criteria:

- Define the terms '*Bond energy*' and '*Bond length*'.
- '*Bond energy*' and '*Bond length*' are numerical values that help us compare covalent bond strength.
- Compare covalent bond strength qualitatively by considering in decreasing order of priority (a) bond order (b) effectiveness of orbital overlap.

3.4 Covalent Bond Strength and Bond Length

Covalent bond is **localised** and **directional** as the bonding electron pair is confined between nuclei of two bonding atoms.

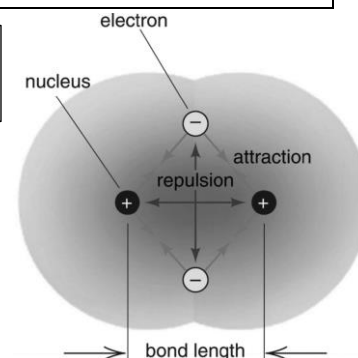
The strength of the covalent bond can be inferred from its **bond dissociation energy (bond energy)**.

Bond dissociation energy (bond energy) is the energy required to break **one mole** of covalent bonds between atoms in a **gaseous molecule**.

Bond length: The distance between the nuclei of the two atoms covalently bonded to each other.

Bond length is a result of 2 opposing forces:

- the maximum attraction between the nuclei for the shared electron density and
- the minimum repulsion between the two positive nuclei and between the electron clouds of each atom.



Generally, the **stronger** the covalent bond, the **shorter** is its bond length.

The strength of covalent bonds is affected by several factors:

- Bond Order
 - Effectiveness of Orbital Overlap
 - Decreases with larger **atomic** size
 - Increases with greater % s character in hybridised orbital of the central atom (see pg 37: application in organic chemistry context).
- a) Bond Order** – the number of covalent bonds formed between the 2 atoms
- Strength of triple bond > double bond > single bond
 - The **higher the bond order**, the **greater the no. of orbitals overlapped**, hence **increase in electron density** between the bonding atoms, **greater attraction** between the bonding nuclei and the shared electrons, and **stronger** covalent bond.

Note: covalent bond strength increases with shared electron density between two nuclei.




b) Effectiveness of Orbital Overlap

- In general, **more effective orbital overlap** results in a **stronger bond**
- Bigger atoms** undergo a **less effective orbital overlap** (lower percentage of electron density between the nuclei). Hence the **covalent bond is weaker**.

Note:

Why is bond energy of F–F bond (158 kJ mol^{-1}) less than that of Cl–Cl bond (244 kJ mol^{-1})?

The small atomic size of F atoms causes the **lone pairs of electrons on the fluorine atoms to repel** each other and **weakens** the **F–F bond**

Bond	Cl–Cl	Br–Br	I–I
Bond Energy (kJ mol^{-1})	244	193	151
Orbital overlap			
Relative Effectiveness of Orbital Overlap (% of electron cloud that overlap)	Highest		Lowest

Checkpoint 5



Answer the following questions by referring to the table below:

Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)
C–C	350	C–O	360
C=C	610	C=O	740
C≡C	840	C≡O	1080

(a) Suggest, in terms of orbital overlap, why

(i) Bond energy increases with the bond order for the same pair of bonding atoms

(ii) the bond energy of C=C is less than twice of C–C.

(iii) covalent bonds formed between C and O is stronger than between C and C for the same bond order

	Atomic radius/ nm
C	
O	

(b) Explain whether this statement is true: C≡O is very strong because it consists of one pi (π) bond and two sigma (σ) bonds.

Success criteria:

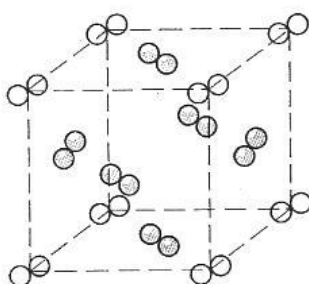
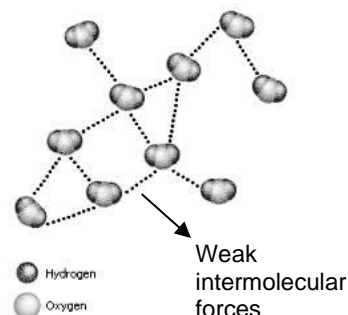
- describe the lattice structure of a crystalline solid of simple covalent molecule such as iodine and giant molecular lattice (giant covalent lattice) structure of a crystalline solid as in graphite and diamond (see figure 3.5b.1 and 3.5b.2.) see checkpt 6.
- use of 'dot-and-cross' diagrams to describe covalent bonding.
- Able to use the concept of the number of orbitals in the valence shell and electronegativity to explain why certain compounds can be formed with period 3 element but not period 2 element. See checkpt 7.

3.5 Physical Properties of Covalent substances

- A lattice consists of particles that are arranged in a regular three-dimensional pattern, in section 1 and 2, we described the metallic and ionic lattices respectively.
- The physical properties of covalent compounds are dependent on the structures of covalent substances:

a. Simple Molecular Structure**(e.g. H_2O , CO_2 , I_2 , Br_2 , Cl_2 , N_2 , O_2 , H_2SO_4 , S_8 , CH_4)**

- consist of simple discrete molecules held by comparatively weak intermolecular forces.
- Strong covalent bonds exist between the atoms.
- **Low melting point and boiling points** (exist as gases, liquids or low-melting solids)
 - Small amount of energy is needed to overcome the weak intermolecular forces between the molecules
 - Covalent bonds remain intact
- Usually **soluble in non-polar organic solvents** such as CCl_4
 - Polar covalent molecules have greater solubility in polar solvent such as H_2O
- Usually a non-electrical conductor due to absence of mobile charge carriers
 - Simple covalent molecules with acidic or basic properties releases H^+ or OH^- ions in water, resulting in electrical conductivity e.g. HCl (aq)

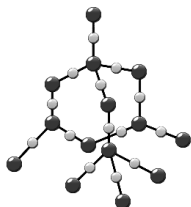
**Iodine in solid state****Water**

See pg 35-36 for the concept related to hybridisation.

Note:

Si solid has the same lattice structure as diamond.

SiO₂ has a structure that is similar to diamond



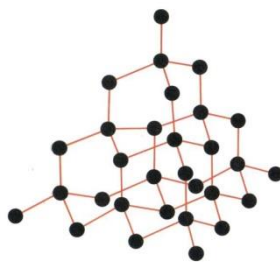
Each Si atom is bonded to four O atoms by strong covalent bonds in a tetrahedral arrangement while each O atom is covalently bonded to two Si atoms.

This gives a Si:O ratio of 1:2 and thus a formula of SiO₂.

b. Giant Molecular Lattice Structure (e.g. Diamond, graphite, Si, SiO₂)

- Atoms are held by strong covalent bonds throughout the lattice.

I. Diamond and its properties

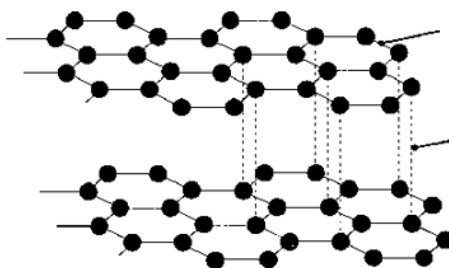


Each **sp³** hybridised carbon atom forms strong covalent bond with **4 carbon atoms** in **3-dimensional tetrahedral** arrangement throughout the lattice.

Figure 3.5 b.1

- Very high melting point** - Large amount of energy is required to break the strong covalent bonds throughout the lattice.
- Non- electrical conductor** - Absence of mobile charged carriers
- Hard** - Atoms are held rigidly by the strong covalent bonds throughout the covalent lattice.
- Insoluble in all solvents** - Solvent molecules are not able to form favourable interactions that releases the energy required for breaking down the giant covalent lattice.

II. Graphite and its properties



Each **sp²** hybridised carbon atom forms strong covalent bonds with **3 other carbon atoms** in a **2-dimensional layer of hexagonal carbon rings**.

Weak intermolecular forces between the graphene layers

Figure 3.5 b.2

The unhybridised p orbital of each sp² C atom is perpendicular to the plane of the hexagons.

The continuous lateral overlap of p orbital of every carbon atom results in:

- Electronic conductivity: highly mobile pi electrons** located above and below the graphene layers.
- High melting point: strengthening of the C–C covalent bonds** which required large amount of energy to overcome during the melting process.
- Slippery and lubricating properties** – **weak intermolecular forces** of attractions instead of strong covalent bonds **are formed between the graphene layers formed**. This enables the layers can slide over one another easily.
- Insoluble in all solvents** - Solvent molecules are not able to form favourable interactions that releases the energy required for breaking down the giant covalent lattice.

Checkpoint 6

2009 MCQ 32

Which statements concerning the lattice structures of graphite and diamond are correct?

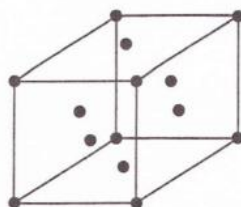
- 1 The C-C-C bond angle between the nearest neighbours is smaller in diamond than in graphite.
- 2 The shortest carbon-carbon bond occurs in diamond.
- 3 All covalent bonds in diamond are of the same strength but those in graphite are not.

A 1,2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

Learning point:

2008 MCQ 8

Copper and iodine are both shiny crystalline solids. The crystal structures of copper and iodine are both face-centred cubic. The diagram shows the arrangement of particles in this type of crystal lattice.



What are the particles present in each lattice?

	copper	iodine
A	atoms	anions
B	atoms	atoms
C	cations	atoms
D	cation	molecules

Learning point:

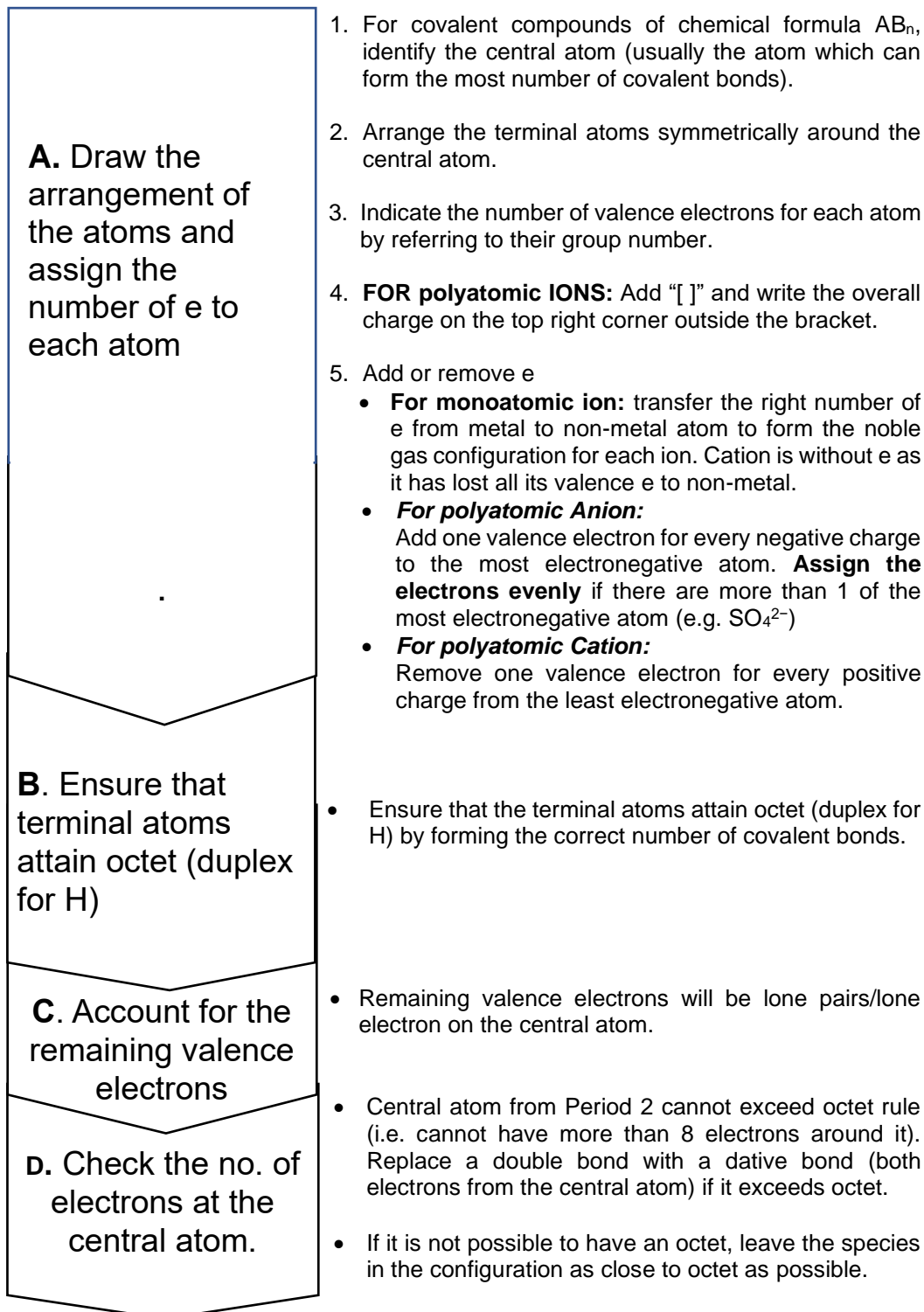
3.6 Dot-and-Cross Diagrams for covalent molecules and polyatomic ion

Note:

'Dots' and 'crosses' are the only symbols used to represent the electrons unless stated otherwise by the question.

To determine the geometry of a molecule/ polyatomic ion, we will first need to determine the number of electron regions around the central atom via the drawing of dot-and-cross diagram.

General guidelines for drawing dot-and-cross diagrams



Done!

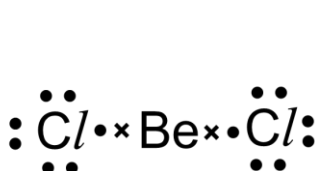
Exceptions to the octet rule

When atoms form bonds, they are very likely to achieve the octet configuration by sharing electron pairs. This provides stable electronic arrangements for the compound formed. There are, however, exceptions.

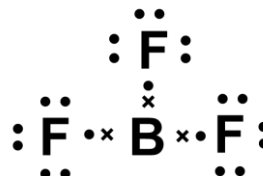
(I) Species with less than 8 electrons in the valence shell of an atom

Note: The terminal atoms are more electronegative than the central atom, thus their lone pairs will not be used to form pi bonds to help the central atom attain octet.

Beryllium, boron and aluminium may have incomplete octets when they form simple covalent molecules.



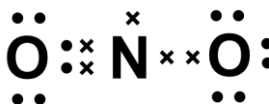
(4 electrons around Be after bonding)



(6 electrons around B after bonding)

(II) Species with Odd Number of Valence Electrons

This occurs most often when the central atom is nitrogen.



(7 electrons around N after bonding => 1 electron which is unpaired)

(III) Species with more than 8 electrons in the valence shell of an atom

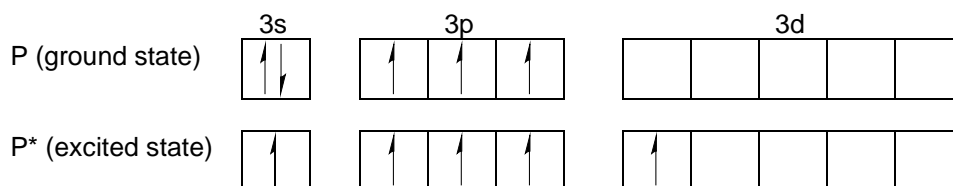
Elements from **Period 3 and beyond** can expand octet due to the availability of the energetically accessible d orbitals (vacant d orbitals in the same valence principal quantum shell) to accommodate additional electrons from the bonded atoms.

Note:

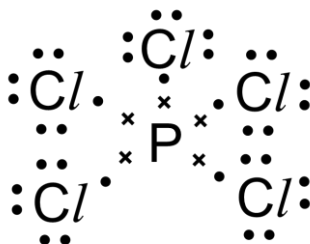
P (ground state) can form 3 covalent bonds but P* (excited state) can form 5 bonds.

Except for formation of co-ordinate bonds, number of unpaired e = number of covalent bonds.

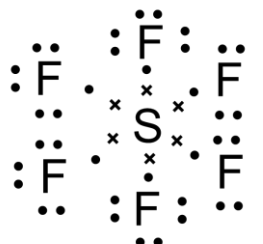
Thus, the valence principal quantum shell, $n \geq 3$ can accommodate more than 8 electrons.



Energy difference between the subshells within the same valence principal quantum shell is very small. Thus, **energy required to promote electrons** to a **higher subshell** can be **easily compensated** by energy release in bond formation.



(10 electrons around P after bonding)



(12 electrons around S after bonding)

Example: Methane CH₄

A Draw the arrangement of the atoms and assign the correct number of valence e to each atom.	<ol style="list-style-type: none"> 1. For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds). 2. Arrange the terminal atoms symmetrically around the central atom. 3. Indicate the number of valence e for each atom. 	
B Ensure that terminal atoms attain octet (duplex for H) by forming the correct number of covalent bonds.		
C Account for the remaining valence electrons	Remaining valence electrons will be lone pairs/lone electron on the central atom.	
D Check the no. of electrons at the central atom.	<ul style="list-style-type: none"> • Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it). 	

Example: Ammonia (NH₃)

A Draw the arrangement of the atoms and assign the correct number of valence e to each atom.	<ol style="list-style-type: none"> 1. For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds). 2. Arrange the terminal atoms symmetrically around the central atom. 3. Indicate the number of valence e for each atom. 	
B Ensure that terminal atoms attain octet (duplex for H) by forming the correct number of covalent bonds.		
C Account for the remaining valence electrons	<ul style="list-style-type: none"> • Fill in any remaining valence electrons as lone pairs on the central atom. 	
D Check the no. of electrons at the central atom.	<ul style="list-style-type: none"> • Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it). 	

Example: Ammonium ion (NH_4^+)

A Draw the arrangement of the atoms and assign the correct number of valence e to each atom.	<ol style="list-style-type: none"> For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds). Arrange the terminal atoms symmetrically around the central atom. Indicate the number of valence e for each atom. FOR IONS: Add “[]” and write the overall charge on the top right corner outside the bracket. Remove e from the least electronegative atom. 	
B Ensure that terminal atoms attain octet (duplex for H) by forming the correct number of covalent bonds.		
C Account for the remaining valence electrons.	<ul style="list-style-type: none"> Fill in any remaining valence electrons as lone pairs on the central atom. 	
D Check the no. of electrons at the central atom.	<ul style="list-style-type: none"> Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it). 	

Example: Nitrate ion (NO_3^-)

A Draw the arrangement of the atoms and assign the correct number of valence e to each atom.	<ol style="list-style-type: none"> 1. For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds). 2. Arrange the terminal atoms symmetrically around the central atom. 3. Indicate the number of valence e for each atom. 4. FOR IONS: Add “[]” and write the overall charge on the top right corner outside the bracket. 5. Add e to the most electronegative atom. 	
B Ensure that terminal atoms attain octet (duplex for H) by forming the correct number of covalent bonds.		
C Account for the remaining valence electrons.	<ul style="list-style-type: none"> • Fill in any remaining valence electrons as lone pairs on the central atom. 	
D Check the no. of electrons at the central atom.	<ul style="list-style-type: none"> • Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it). <p>Replace a double bond with a dative bond (both electrons from the central atom) if it exceeds octet.</p>	

Checkpoint 7

(a) Draw dot-and-cross diagrams of the following molecules or ions:

CCl_4	$\text{BH}_3(\text{g})$
NO_2	NO_2^+
AlCl_4^-	ICl_4^-
Na_2CO_3	

(b) The compound FO_2 does not exist but ClO_2 does.

By considering the different types of covalent bonds that can be formed in the two compounds suggest reasons for this difference. (Assume the halogen atom occupies the central position in each of these molecules.)

4 POLAR COVALENT BONDS AND IONIC BOND WITH COVALENT CHARACTER

Inter-Atomic Bonds

There are compounds that might be expected to be ionic but exhibit properties typical of covalent compounds and vice versa. For example,

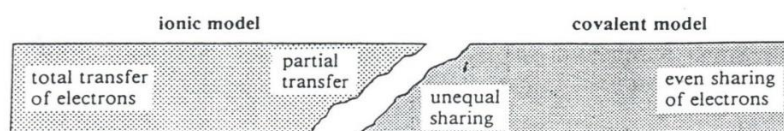
- some salts sublime at low temperatures, e.g., aluminium chloride, $AlCl_3$.
- there are simple covalent molecules that dissolve readily in water to produce aqueous ions, e.g. HCl gas and NH_3 , ammonia.

From the earlier sections, the formation of a compound can involve either covalent or ionic bonding.



However, there are few compounds with either purely ionic or covalent bonds. The bonds in most compounds, in reality, are often intermediates between these two extreme cases with one type predominating over the other. Thus, the two models are further classified into the four categories to show the **gradual transition** between ionic and covalent bonding.

4.1 Transition from transfer of electrons to unequal sharing



Model 1	Model 2	Model 3	Model 4
<p>Pure ionic bond</p>	<p>Polarised ionic bond</p>	<p>Polar covalent bond</p>	<p>Pure (Non-polar) covalent bond</p>
Ions exist as discrete, point charges with NO electron density between them.	<p>The cation attracts and distorts the electron cloud of the anion. This is called polarisation.</p> <p>The electron density is drawn into the region between the two nuclei, resulting in partial sharing of electrons.</p>	<p>Electron density is NOT symmetrically distributed in a bond between different atoms.</p> <p>The more electronegative atom has a greater share of the shared electron density.</p>	Electron density is symmetrically distributed in a bond between identical atoms.
This DOES NOT occur, in reality, for any ionic compound.	Ionic compounds with cation (1+, 2+ charge) and an anion with a distorted electron cloud. E.g. $MgCl_2$, $NaBr$,	Polar covalent bond is formed as there is a permanent separation of partial charges . E.g. HF , H_2O	Non-polar covalent bonds are formed E.g. Br_2 , C
Predominant inter-atomic bond: ionic . Structure: Giant ionic lattice		Predominant inter-atomic bond: covalent . Structure: simple covalent molecular/ giant covalent	

Note:

Whether a compound has a giant ionic lattice or simple covalent molecular/ giant covalent structure depends on the predominant interatomic bond.

Note: A compound consisting of metal and non-metal may have a predominant covalent bond.

Extensive distortion of the anion electron cloud may result in significant electron density being shared between the metal and non-metal nuclei.
The predominant interatomic bond becomes covalent instead of ionic.

Only physical properties such as **melting and boiling points** and solubility in polar or non-polar solvents can help us identify whether a (metal + non-metal) compound *have become a simple molecular structure or still a giant ionic lattice.*

4.2 Polarisation of Ionic Bond

The extent of distortion of the anion's electron cloud by the cation is influenced by:

(a) Charge to Size ratio of Cation

- Polarising power of cation
 - The ability of the cation to distort the electron cloud of anion
 - **Increases** with **increasing charge to size ratio** of cation.
- Cations carrying **high positive charge** and **small ionic size** have **strong polarising power**.

(b) Size of the Anion

- Polarisability of anion
 - The ease of distortion of the anion electron cloud.
 - An **anion of larger electron cloud** (from period 3,4 and above) is **more easily polarised**.
 - The electron cloud is more distant from its nucleus, easier to be attracted and distorted by the cation.

The **greater** the polarisation, the **greater** the **covalent character** in the ionic bond

Success criteria:

- deduce the type of structure and bonding present in a substance from given physical properties.

Note:

$AlCl_3$ and $BeCl_2$ are the common examples of simple covalent molecules formed by metals and non-metals.

Their melting/ boiling points are significantly lower than other ionic compounds.

To compare the m.pt of two giant ionic lattice,

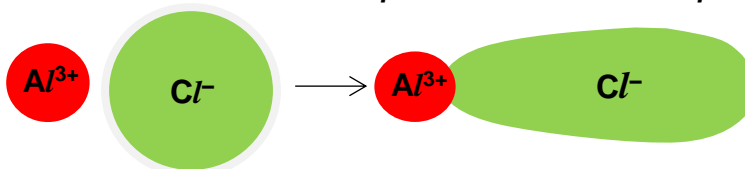
compare $|L.E.| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$

NOT % covalent character

Melting points of several aluminium compounds suggests that $AlCl_3$ have a different structure and bonding as compared to other aluminium compounds.

compound	$AlCl_3$	Al_2O_3	AlF_3
melting point / °C	192	2072	1290
structure	Simple molecular	Ionic lattice	Ionic lattice

Why does $AlCl_3$ exist as covalent compound and not ionic compound?



The much lower melting point of $AlCl_3$ reflects a simple molecular structure while Al_2O_3 and AlF_3 are giant ionic lattices. Hence, the predominant inter-atomic bond in $AlCl_3$ is covalent bond while that of Al_2O_3 and AlF_3 are still ionic.

Al^{3+} ion has a high polarising power due to its high charge to size ratio. Electron cloud of anions from period 3, 4 and above are more easily distorted. Thus, there is a significantly greater shared electron density in $AlCl_3$ than in Al_2O_3 and AlF_3 .

C. INTERMOLECULAR FORCES OF ATTRACTION

There are three types of intermolecular forces.

- **Instantaneous dipole-induced dipole (id-id) interactions**
- **Permanent dipole-permanent dipole (pd-pd) interactions**
- **Hydrogen bonds (H-bonds)**

As the term 'intermolecular' suggests these interactions are present between molecules (species whose atoms are bonded by covalent bonds).

They are electrostatic in nature (attraction between temporary and/or permanent dipoles). They become significant when the particles are close to each other.

The weak attractive forces between molecules are important in explaining physical properties such as melting and boiling points, and solubility.

The type of intermolecular forces present between the molecules depends on its polarity.

In order to determine the polarity of molecules, we must first determine the geometry of molecules.

Success criteria:

- Able to use dot-and-cross diagram and Valence Shell Electron Pair Repulsion theory to identify the different electron geometry of atoms covalently bonded to each other.
- Able to deduce and compare with reasoning, the shape (molecular geometry) and the bond angle by considering (i) the number of bonding and non-bonding pairs in the electron geometry and (ii) repulsive forces which increase with electron density of the electron pair nearer to the central atom.

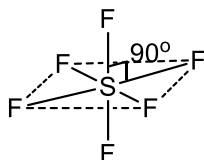
1 MOLECULAR GEOMETRY AND POLARITY

1.1 Determining Geometry of Molecules

In simple discrete molecules, formation of covalent bonds involves a maximum overlap of orbitals and has a preferred direction (i.e. covalent bonds are directional).

Hence **simple discrete molecules** have **definite shape** unlike ionic compounds and metallic elements that have no definite shape.

e.g. SF_6



Bond angle = 90°

Shape = Octahedral

These shapes can be observed from spectroscopic analysis such as single crystal X-Ray Diffraction (XRD). Understanding the shapes of molecules and polyatomic ions can help to explain many of their physical properties.

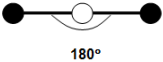
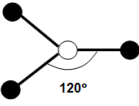
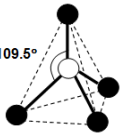
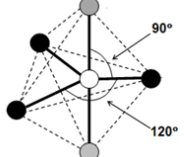
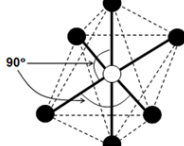
We can predict the geometry of the molecules based on **Valence Shell Electron Pair Repulsion (VSEPR) theory**.

a. General principle of VSEPR

1. Determine the **number of electron regions** around the central atom from the **dot-and-cross diagram**.
2. **Electron regions** (bond pairs and lone pairs) around the central atom **arrange themselves** to be as far apart as possible to **minimise mutual repulsion**. This arrangement is known as the **electron geometry**.

Note:

Each double bond or triple bond is counted as one **bond pair/ electron region**.

Number of electron regions derived from dot-and-cross diagrams				
2 e ⁻ regions	3 e ⁻ regions	4 e ⁻ regions	5 e ⁻ regions	6 e ⁻ regions
				
Linear	trigonal planar	Tetrahedral	trigonal bipyramidal	Octahedral
Electron geometry				

b. Determining the Shapes and bond angles**Shapes of Molecules/Polyatomic ions**

1. Draw the **dot-and-cross diagram** of the molecule or polyatomic ion.
2. Count the **total number of electron regions** around the central atom.

lone pair e ⁻ / lone e ⁻	}	Each counts as 1 electron region
single bond/ double bond/ triple bond		
3. Derive the **electron geometry** from the positions of **bond pairs** (bp) and **lone pairs** (lp) around the central atom using VSEPR.
4. The **positions of the terminal atoms** in the electron geometry determine the **shape/molecular geometry** around the central atom.

Bond angle refer to angle between bond pairs

Bond angle may differ from what is predicted by the electron geometry due to

(a)			lone pair- lone pair repulsion	>	lone pair- bond pair repulsion	>	bond pair- bond pair repulsion
-----	--	--	--------------------------------	---	--------------------------------	---	--------------------------------

See tables on pg 32 to 33

- (b) difference in electronegativity in the bonding atoms when **the two molecules being compared has either the same central atom or same terminal atoms**.

Shifting of **electron density in a bond pair towards the central atom increases the bond pair – bond pair repulsion** while shifting of electron density in a bond pair away from central atom decreases the bond pair – bond pair repulsion.

See section C on pg 34.

Note: Electron pairs with **higher electron density nearer** to the **central atom exerts greater repulsive forces**.

Lone pair of electrons are closer to the nucleus. They take up more space around the central atom and thus exerts greater repulsion.

Calculation of electronegativity in NOT required in A level assessment.

Just need to remember the increasing electronegativity trend across period and decreasing trend down the group.

Note:

Each double bond or triple bond is counted as one **bond pair**.

Note:

Presence of each lone pair electrons causes the bond angle to decrease by approximately 2.5° from the theoretical bond angle in the electron pair geometry.

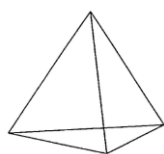
E.g.

$3 e^-$ regions $\rightarrow 120^\circ$

$2b.p. + 1l.p. \rightarrow 117.5^\circ$

Note:

Tetrahedral is derived from the term tetrahedron, a polyhedron composed of four triangular faces



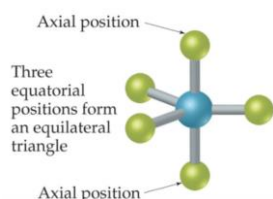
No. of electron regions	Electron Pair Geometry	No. of bond pairs	No. of lone pairs	Molecular Geometry / Shape	Example
2	$ \begin{array}{c} 180^\circ \\ \text{B} \text{---} \text{A} \text{---} \text{B} \end{array} $ Linear	2	0	$ \begin{array}{c} 180^\circ \\ \text{B} \text{---} \text{A} \text{---} \text{B} \end{array} $ Linear	$ \begin{array}{c} 180^\circ \\ \text{Cl} \text{---} \text{Be} \text{---} \text{Cl} \\ \text{BeCl}_2 \end{array} $
3	$ \begin{array}{c} \text{B} \\ \\ \text{B} \text{---} \text{A} \text{---} \text{B} \\ 120^\circ \end{array} $ Trigonal planar	3	0	$ \begin{array}{c} \text{B} \\ \\ \text{B} \text{---} \text{A} \text{---} \text{B} \\ 120^\circ \end{array} $ Trigonal planar	$ \begin{array}{c} \text{O} \\ \\ \text{H} \text{---} \text{C} \text{---} \text{H} \\ 120^\circ \\ \text{HCHO} \end{array} $
		2	1	$ \begin{array}{c} \text{B} \quad \ddot{\text{A}} \quad \text{B} \\ \quad \quad < 120^\circ \end{array} $ Bent	$ \begin{array}{c} \ddot{\text{S}} \\ // \quad \backslash \\ \text{O} \quad \text{O} \\ 117.5^\circ \\ \text{SO}_2 \end{array} $
4	$ \begin{array}{c} \text{B} \\ \\ \text{B} \text{---} \text{A} \text{---} \text{B} \\ \\ \text{B} \\ 109.5^\circ \end{array} $ Tetrahedral	4	0	$ \begin{array}{c} \text{B} \\ \\ \text{B} \text{---} \text{A} \text{---} \text{B} \\ \\ \text{B} \\ 109.5^\circ \end{array} $ Tetrahedral	$ \begin{array}{c} \text{H} \\ \\ \text{H} \text{---} \text{C} \text{---} \text{H} \\ \\ \text{H} \\ 109.5^\circ \\ \text{CH}_4 \end{array} $
		3	1	$ \begin{array}{c} \text{B} \quad \ddot{\text{A}} \quad \text{B} \\ \quad \quad \backslash \\ \quad \quad \text{B} \\ 107^\circ \end{array} $ Trigonal pyramidal	$ \begin{array}{c} \text{H} \quad \ddot{\text{N}} \quad \text{H} \\ \quad \quad \backslash \\ \quad \quad \text{H} \\ 107^\circ \\ \text{NH}_3 \end{array} $
		2	2	$ \begin{array}{c} \text{B} \quad \ddot{\text{A}} \quad \text{B} \\ \quad \quad \backslash \\ \quad \quad \text{B} \\ 105^\circ \end{array} $ Bent	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \quad \text{H} \\ \quad \quad \backslash \\ \quad \quad \text{H} \\ 105^\circ \\ \text{H}_2\text{O} \end{array} $

Table: Shapes of molecules or polyatomic ions based on different number of electron pairs (bond pairs (bp) and lone pairs (lp))

Note:

For species with 3, 4 and 6 e regions around the central atom, there is only one uniform bond angle when the terminal atoms 'B' are the same.

In contrast, for trigonal bipyramidal e⁻ pair geometry where there are 5 e regions around the central atom, there are 2 types of positions for the terminal atoms 'B'.

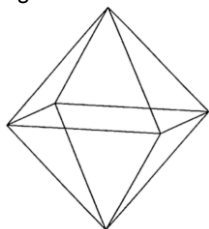


eq-eq bond angle = 120°
ax-eq bond angle = 90°

As lp-lp repulsion > lp-bp repulsion > bp-bp repulsion lone pair, lp preferentially occupy the **equatorial position** as 90° to 2 other e⁻ regions in the axial position)
[If the lp is in axial position, it is 90° to 3 other e⁻ regions]

Note:

Octahedral is derived from the term octahedron, a polyhedron composed of eight triangular faces



No. of electron regions	Electron Pair Geometry	No. of bond pairs	No. of lone pairs	Molecular Geometry/ Shape	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	 PCl ₅
		4	1	 Unsymmetrical tetrahedron (seesaw)	 SF ₄
		3	2	 T-shaped	 IF ₃
		2	3	 Linear	 IF ₂ ⁻
6	 Octahedral	6	0	 Octahedral	 SF ₆
		5	1	 Square pyramidal	 BrF ₅
		4	2	 Square planar	 XeF ₄

Table: Shapes of molecules or polyatomic ions based on different number of electron pairs (bond pairs (bp) and lone pairs (lp))

c. Deviation of Bond Angle Predicted by VSEPR **[For Your Information]****Note:**

These explanations are valid ONLY IF the central atom (in case 1) and terminal atom (in case 2) are different. All other atoms and molecular geometry must be the same before these reasonings are considered.

There are situations when molecules share the same electron geometry but their bond angles are different from what is predicted by VSEPR.

These could be due to the following reasons:

1. Different Electronegativity of **Central** Atoms (despite same terminal atoms)
2. Different Electronegativity of **Terminal** Atoms (despite same central atoms)

Example 1 – Different electronegativity of CENTRAL atom

Using VSEPR theory, explain the following observation:

Bond angle of $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

Molecule	NH_3	PH_3	AsH_3
Lewis structure			
No. of electron pairs around central atom	4	4	4
No. of lone pair	1	1	1
No. of bond pairs	3	3	3
Shape of molecule	trigonal pyramidal		

- *[Same Molecular Geometry]*
Each molecule has 3 bond pairs and 1 lone pair, hence trigonal pyramidal shape.
- *[Different electronegativity of CENTRAL atom]*
As electronegativity of the central atom increases from $\text{As} < \text{P} < \text{N}$, electron density in the bond pairs is drawn closer towards the central atom.
- Increased electron density around the central atom results in increasing bond pair-bond pair repulsion.
- *[Conclusion]* Therefore, bond angle increases from AsH_3 to NH_3 .

Example 2 – Different electronegativity of TERMINAL atom

Explain why the bond angle in NF_3 is smaller than that in NH_3 .

- *[Same Molecular Geometry]*
Both NH_3 and NF_3 have 3 bond pairs and 1 lone pair, hence trigonal pyramidal shape.
- *[Different electronegativity of TERMINAL atom]*
As the electronegativity decreases from $\text{F} > \text{N} > \text{H}$, the electron density of the bond pairs in NF_3 is lower at the central N atom than in NH_3 .
- lesser bond pair-bond pair repulsion in NF_3 .
- *[Conclusion]* Therefore, bond angle in NF_3 is smaller than that in NH_3 .

Atomic orbitals vs Molecular Orbitals [For Your Information]

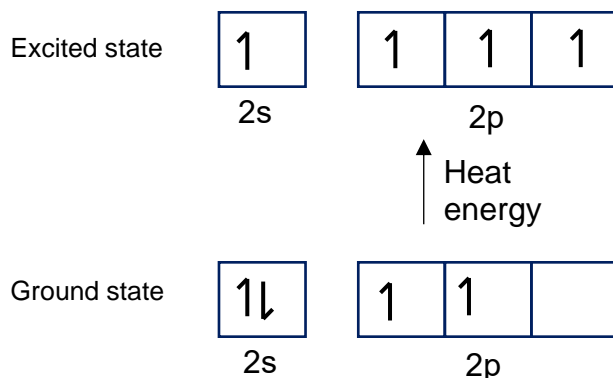
The shapes predicted by VSEPR cannot be accounted for if the original atomic orbitals are involved.

Let's consider the case of methane.

From VSEPR theory, methane is tetrahedral in geometry.

The central C atom has an electron structure of $1s^2 2s^2 2p^2$.

Arrangement of electrons in the valence shell of C at ground state and excited state are as shown:



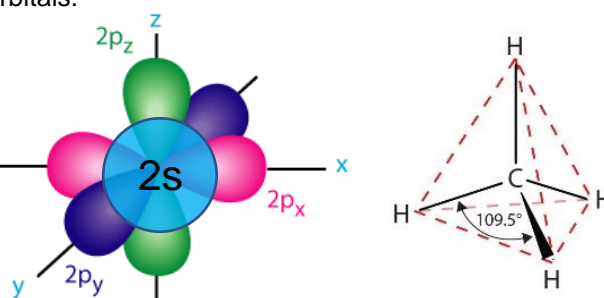
Why does C have to excite one of its electron from the s subshell to the p subshell (excited state)?

This creates 4 unpaired e in the valence shell which enable four covalent bonds to be formed.

The orientation of the s and p orbitals:

By considering the orientation of the s and p orbitals, can a molecule of tetrahedral shape be formed?

The terminal atoms will have to approach the carbon atom along the x, y and z axis. This results in a bond angle of 90° instead of the optimum bond angle of 109.5° .



The orientations of the s and p orbital do not account for a tetrahedral geometry! Hence, the only way a tetrahedral geometry can be accounted for is in considering a different set of orbitals overlapping to form the sigma bond.

We hence consider **orbital hybridisation** where orbitals 'mix' and reform into **degenerate orbitals** that **obeys VSEPR**. Hybridisation theory is proposed to show more consistency with the experimental data.

Note: hybridisation theory combines the valence bond theory (overlap of atomic orbitals) and VSEPR theory to explain the electron geometry of a molecule (consist of **at least 3 atoms**). A **diatomic** molecule does not have a geometry therefore **hybridisation** theory is **not relevant**.

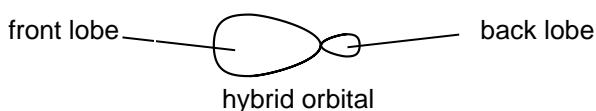
For A level syllabus, you are only required to deduce **type of hybridisation of central atom from three types of electron geometry**.

Note: except for coordinate bonds, only orbitals with unpaired e in the valence shell take part in covalent bonding.

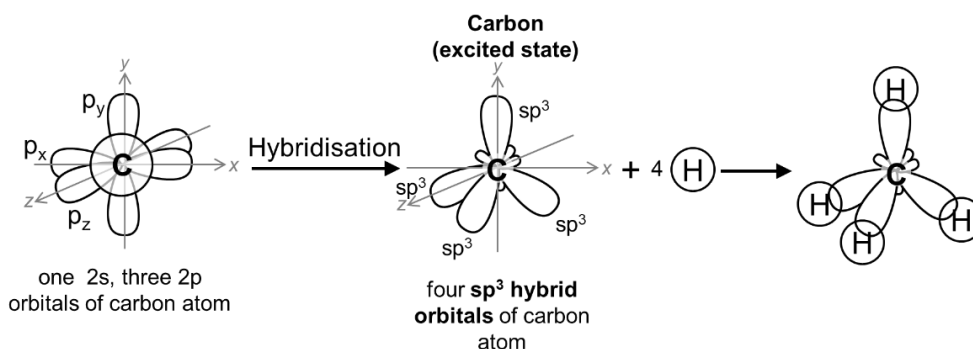
HYBRIDISATION AND HYBRID ORBITALS**[To be covered in Chemical Bonding for Organic Chemistry]**

- Hybridisation is a model used to explain the **observed shapes** and the **equivalence of bonds** of molecules about the central atom.
- Hybridisation model shows **mixing of pure atomic orbitals** in an atom to generate a **set of degenerate hybrid orbitals**.
- No. of atomic orbitals mixed = No. of hybrid orbitals formed**
Hybrid orbitals either take part in sigma (σ) bond formation or to contain a lone pair.
Unhybridised p orbitals take part in pi (π) bonds formation.

In the formation of covalent bonds, only the front lobe is used to overlap with an orbital of another atom as it is bigger and results in a more effective overlap.

*Overview and geometry of some hybrid orbitals*

No. of e ⁻ regions	Hybridisation of central atom	Formation of hybrid orbitals and arrangement of hybrid orbitals <u>around the central atom</u>	Example
4	sp^3	<p>one s three p four sp^3 hybrid orbitals in tetrahedral arrangement</p>	ethane $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} - & \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$
3	sp^2	<p>one s two p three sp^2 hybrid orbitals in trigonal planar arrangement</p> <p>Note: one unhybridised p orbital for π bonding</p>	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = & \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ ethene
2	sp	<p>one s one p two sp hybrid orbitals in linear arrangement</p> <p>Note: two unhybridised p orbitals for π bonding</p>	ethyne $\text{H} - \text{C} \equiv \text{C} - \text{H}$

(A) sp^3 hybridisation

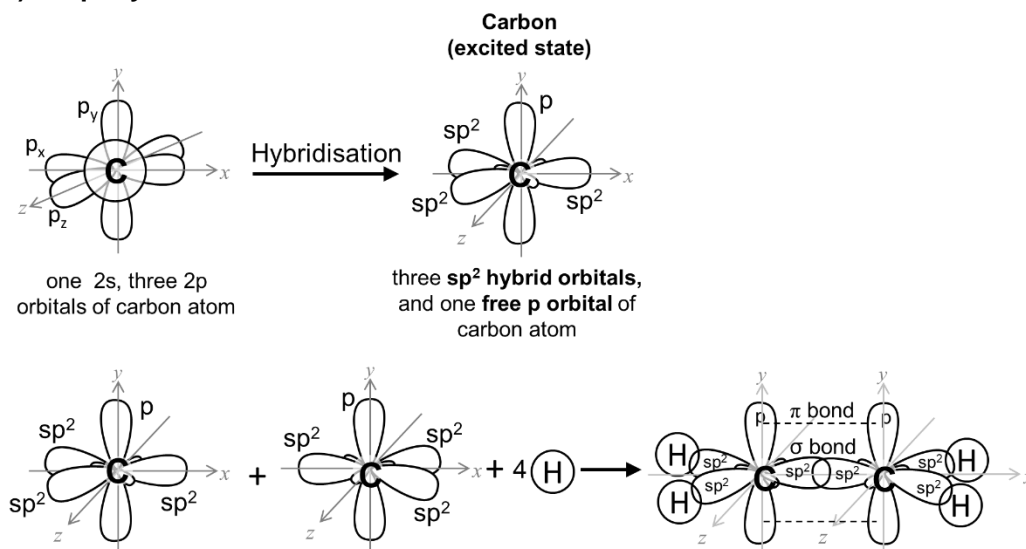
- The four **sp^3 hybrid orbitals are equivalent in energy** and arranged as far apart as possible in **tetrahedral geometry** to minimize repulsion. Bond angle = 109.5°
- Each sp^3 hybrid orbital **overlaps head-on** with the 1s orbital of H to form a σ bond.

Important note:

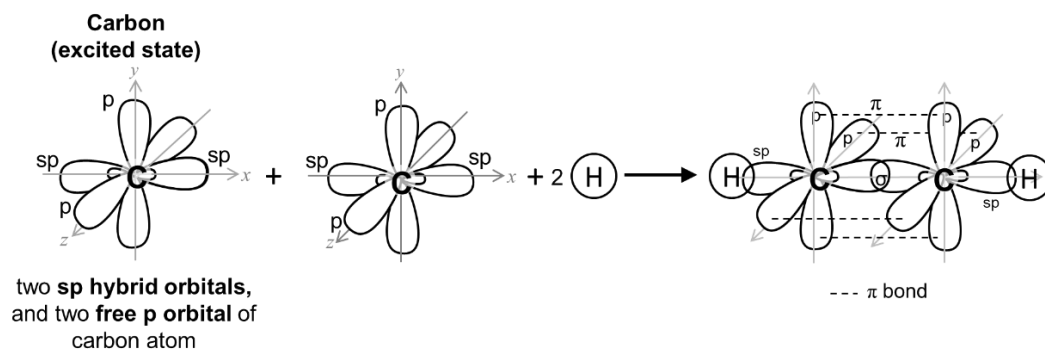
- (a) Identify the type of hybridisation based on the electron pair geometry.
- (b) The following table shows the percentage of "s" character in the three types of hybrid orbitals

Type of hybrid orbitals	% of "s" in hybrid orbitals
sp^3	25
sp^2	33.3
sp	50

Hybrid orbitals with higher % of "s" character overlap to form a stronger bond.

(B) sp^2 hybridisation

- The three **sp^2 hybrid orbitals are equivalent in energy** and arranged as far apart as possible in **trigonal planar** geometry to minimize repulsion. Bond angle = 120°
- Each of the two sp^2 hybrid orbitals of each C atom overlap head-on with one 1s orbital of two H atoms, forming two C-H σ bonds. The remaining sp^2 orbital of each C atom overlaps head-on with each other, forming a C-C σ bond.
- The **unhybridised p orbital** of the two C atoms **overlaps side-way** with each other, **forming a C-C π bond**. The C=C bond in ethene consists of 1 σ bond and 1 π bond.

(C) sp hybridisation

- The **two sp hybrid orbitals are equivalent in energy** and arranged as far apart as possible in **linear geometry** to minimise repulsion. Bond angle = 180°
- One sp hybrid orbital of each C atom overlaps head-on with the 1s orbital of H atom to form one C-H σ bond each. The remaining sp orbital of each C atom overlaps head-on with each other, forming a C-C σ bond.
- Two unhybridised p orbitals** of the two C atoms **overlap sideways** with each other, **forming 2 C-C π bonds**. The C \equiv C bond in ethyne consists of 1 σ bond and 2 π bonds.

Success criteria:

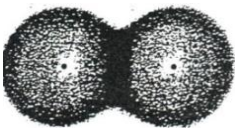
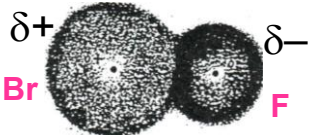
- explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is **not** required]
- deduce the polarity of a molecule using bond polarity and its molecular shape

1.2 Polarity of Molecules

To understand intermolecular forces, we need to first learn about the polarity of molecules.

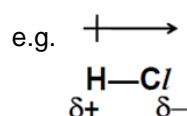
(a) What makes a Covalent Bond Polar?

Polarity is the state of having poles, or in this context, separation of charges (positive and negative pole). This polarity of a covalent bond is determined by the electronegativity difference between the bonding atoms.

NON-POLAR Bonds	POLAR Bonds
No Difference in Electronegativity	Difference in Electronegativity
<p>Atoms of Same Element</p> <p>E.g. Cl_2</p>  <p>Electron density is symmetrically distributed between two chlorine atoms in the bond.</p> <p>Note: The difference in electronegativity between C and H is negligible. So, a C–H bond is considered as non-polar.</p>	<p>Atoms of Different Element</p> <p>E.g. Polar covalent bond in Br–F</p>  <p>Fluorine, being more electronegative than bromine, attracts the bonding electrons more strongly and hence has a greater share of the shared pair of electron, acquiring a partial negative charge (δ^-). The less electronegative atom then acquires a partial positive charge (δ^+). The permanent separation of a pair of charges in a polar covalent bond is known as a dipole.</p>

Take Note:

- The partial charges, δ^+ and δ^- , do not imply the existence of ions in the molecule. A polar molecule is **electrically neutral**.
- The **greater** the difference in electronegativity, the **greater** the **ionic character** in the covalent bond.
- The degree of polarity of a bond is measured by its **dipole moment**. Dipole moment is a vector quantity and has both magnitude and direction. It is shown by the symbol " $\text{+} \longrightarrow$ " where the arrow points towards the more electronegative atom,

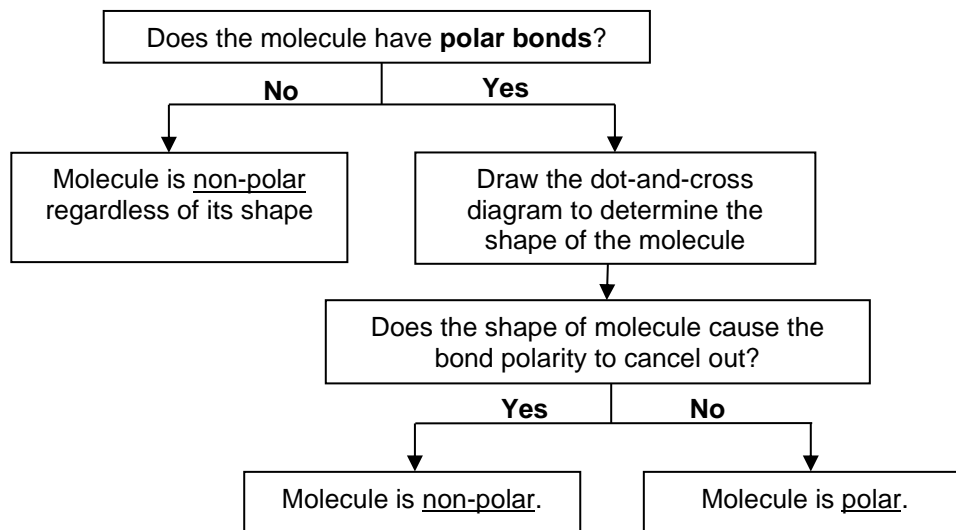


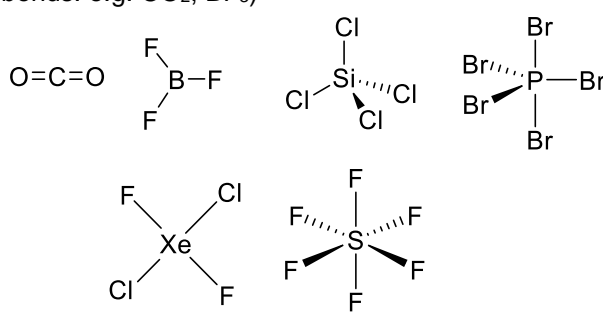
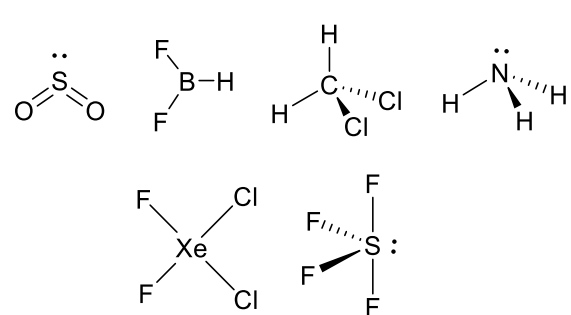
(b) How Do I Know if a Molecule is Polar?**Note:**

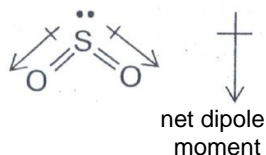
C-H bond is non-polar!

To determine whether a molecule is polar or non-polar, consider the

- 1) **bond polarity** of all the bonds in the molecule and
- 2) **shape** of the molecule.

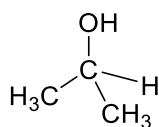
**Examples of Polar and Non-Polar Molecules**

NON-POLAR Molecules	<p>(1) it contains no polar bonds (e.g. Br₂, CH₄) or</p> <p>(2) individual bond dipoles cancel each other completely with zero net dipole moment (For molecule with polar bonds. e.g. CO₂, BF₃)</p> <div style="text-align: center;">  </div> <p><i>[Note: Highly symmetrical molecules with same terminal atoms are usually non-polar.]</i></p>
POLAR molecules	<p>(1) it contains <u>polar bond(s)</u> AND</p> <p>(2) the individual dipole moments do not cancel out each other, giving rise to a net dipole moment</p> <div style="text-align: center;">  </div>

Note:SO₂ has a net dipole moment as shown

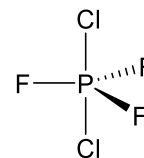
Checkpoint 8

1. Which molecules are polar?



Hexane (C_6H_{14})

Ammonia (NH_3)



2. State the molecular geometry of each of the following compounds. State if this molecule is polar.

(i) PBr_3

Molecular Geometry :

Polarity :

(ii) CF_4

Molecular Geometry :

Polarity :

(iii) CHBr_3

Molecular Geometry :

Polarity :

(iv) AlCl_3

Molecular Geometry :

Polarity :

Success criteria:

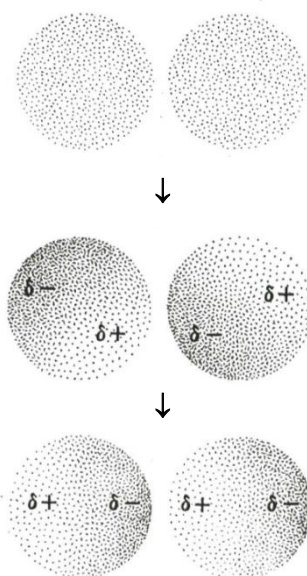
- Describe in words or using suitable diagrams to illustrate the formation of the following intermolecular forces (IMF)
 - instantaneous dipole-induced dipole interactions. (id-id)
 - permanent dipole-permanent dipole (pd-pd) interactions between polar molecules.
 - hydrogen bonding between molecules with protonic hydrogen (H directly bonded to N, O and F).
- For simple covalent molecules, only IMF are overcome during a physical change while interatomic covalent bonds are broken during a chemical change.
- Strength of Hydrogen bonding > pd-pd > id-id when molecules of similar M_r are being compared.

2 INSTANTANEOUS DIPOLE-INDUCED DIPOLE INTERACTIONS

Intermolecular Forces

This is the dominant interaction between **non-polar molecules** and **noble gases**. Intermolecular forces can be between molecules and between discrete atoms.

How is instantaneous dipole-induced dipole interaction formed?



Consider a collection of He atoms.

Average distribution of electron charge about each nucleus is spherically symmetrical.

As electrons are in constant motion, at some instant, there is a temporary shift of electron to one side of the atom and results in **an instantaneous dipole**.

The instantaneous dipole **induces** a similar dipole on an adjacent atom
 \Rightarrow an **induced dipole** is formed.

The "cycle" repeats.

The dipoles are instantaneous (dipole magnitude and direction is always changing) but the **net attraction** which they produce is **permanent**.

Note:

The attraction between non-polar molecules can be explained similarly

Factors affecting strength of instantaneous dipole-induced dipole (id-id) interactions

Note:

M_r of covalent molecules is a good indicator of the electron cloud size.

A covalent molecule with a larger M_r would have a larger electron cloud.

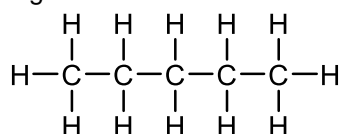
(1) **Size of the electron cloud** (ease of distortion)

In general, if a molecule has a larger M_r ,

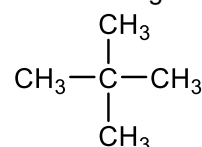
- larger electron cloud
- dipoles are **more** easily induced
- more energy** is required to overcome **stronger** id-id interactions
- boiling/melting point is higher

(2) **Surface area of contact between molecules**

- straight chain molecules vs branched chain isomers of organic molecules.



pentane (b.p. 36 °C)



2,2-dimethylpropane (b.p. 10 °C)

- Straight chain molecules have a **larger surface area of contact** between adjacent molecules than their branched chain isomers.
- Dipoles are **more** easily induced
- **More energy** is required to overcome **stronger** id-id interactions
- Straight chain molecule has a higher boiling point.

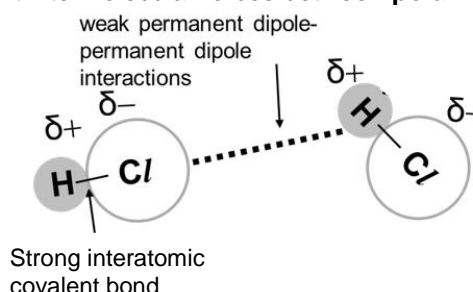
Checkpoint 9

Rank the following molecules in the order of increasing strength of instantaneous dipole – induced dipole interaction. iodine, CH_3CH_3 and BF_3

3 PERMANENT DIPOLE-PERMANENT DIPOLE INTERACTIONS

Intermolecular Forces

This is the predominant intermolecular forces between **polar molecules**.



Permanent dipole-permanent dipole (pd-pd) interactions are **stronger** than instantaneous dipole-induced dipole (id-id) for molecules of similar M_r .

4 HYDROGEN BONDING

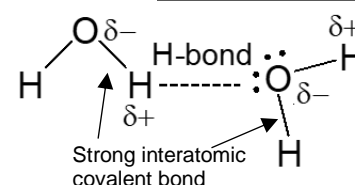
Intermolecular Forces

Note:

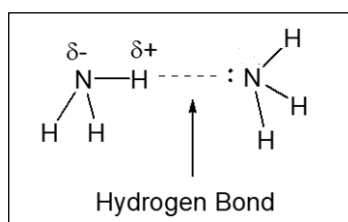
In a diagram showing hydrogen bonding between molecules, you must indicate

- partial charges: (δ^+) on protonic H, and (δ^-) on F, O or N that the protonic H is bonded to.
- a lone pair on F, O or N on a neighbouring molecule.
- a dotted line labelled as hydrogen bond.

- Hydrogen bond is a special type of permanent dipole-permanent dipole interaction.
- When H is bonded to N, O or F, the highly electronegative N, O or F attracts bonding electrons towards its side, leaving the hydrogen atom with a very small share of the electron pair.
- H then acquires a **large partial positive charge (δ^+)** and behaves almost like a **bare proton (H^+)**.
- Hydrogen bond is the electrostatic force of attraction between the **protonic H** atom in H-F , H-O , or H-N bond and a **lone pair** on an electronegative atom (**N, O or F in a neighbouring molecule**).



Conditions required for Hydrogen Bonding:



- (1) Protonic H in F-H , N-H and O-H covalent bonds
- (2) Lone pairs on a highly electronegative atom (N, O, F) in a neighbouring molecule.

Checkpoint 10

(a) Identify which of the following can form hydrogen bonding with another identical molecule.

			$\text{CH}_3\text{CH}_2\text{SH}$

(b) Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ undergoes hydrogen bonding with each other.

Use a labelled diagram to illustrate hydrogen bonding between the ethanol molecules.

Factors that affect strength of Hydrogen bonding**(1) Extensiveness of Hydrogen bonding (H-bonds)**

Different molecules can form different number of H-bonds.

The greater average number of H-bonds formed per molecule

- the more extensive the H-bonds present in the compound
- the greater the energy required to break the larger number of H-bonds
- the higher the boiling point

Steps to determine average number of Hydrogen bonds formed per molecule:

1. Count the total no. of protonic H per molecule
2. Count the total no. of lone pairs on F, O or N.
3. The lower of the two numbers is the average number of H-bonds formed per molecule.

Example:

	HF	H ₂ O	NH ₃
No. of protonic H	1	2	3
No. of lone pairs	3	2	1
Average no. of H-bonds per molecule	1	2	1

(2) Polarity of H–Y bond (Y = F, O or N)**More polar H–Y bond ⇒ Stronger H-bond formed**

Electronegativity decreases from F > O > N

⇒ Polarity of H–Y bond decreases from $\delta^+\text{H}-\text{F}^{\delta-} > \delta^+\text{H}-\text{O}^{\delta-} > \delta^+\text{H}-\text{N}^{\delta-}$

⇒ Strength of hydrogen bonding should decrease from **H–F > H–O > H–N**.

Worked Example 1

Account for the observed boiling points of the following compounds.

compound	HF	H ₂ O	NH ₃
M_r	20.0	18.0	17.0
boiling point / °C	20	100	–33

All three compounds are polar covalent molecules with intermolecular forces of hydrogen bonding. Their electron cloud sizes are comparable.

H₂O can form more extensive intermolecular hydrogen bonding (average 2 H-bonds per molecule) than NH₃ and HF (average 1 H-bonds per molecule).

More energy is required to overcome the more extensive hydrogen bonding between the H₂O molecules.

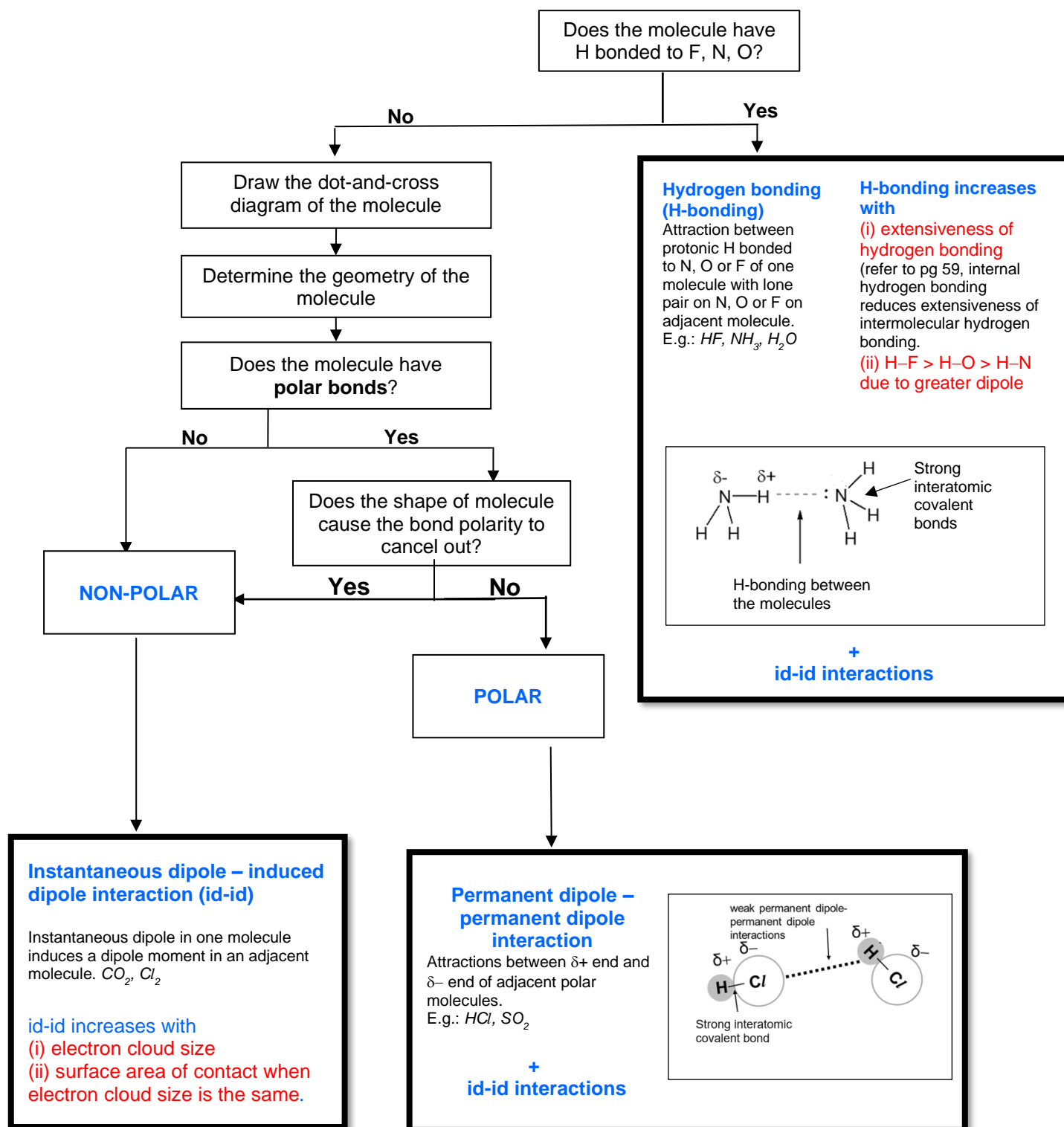
Hence H₂O has the highest boiling points.

Both HF and NH₃ forms equally extensive intermolecular hydrogen bonding. H–F bond is more polar than H–N bond, thus the hydrogen bonding between HF molecules are stronger than those between NH₃ molecules.

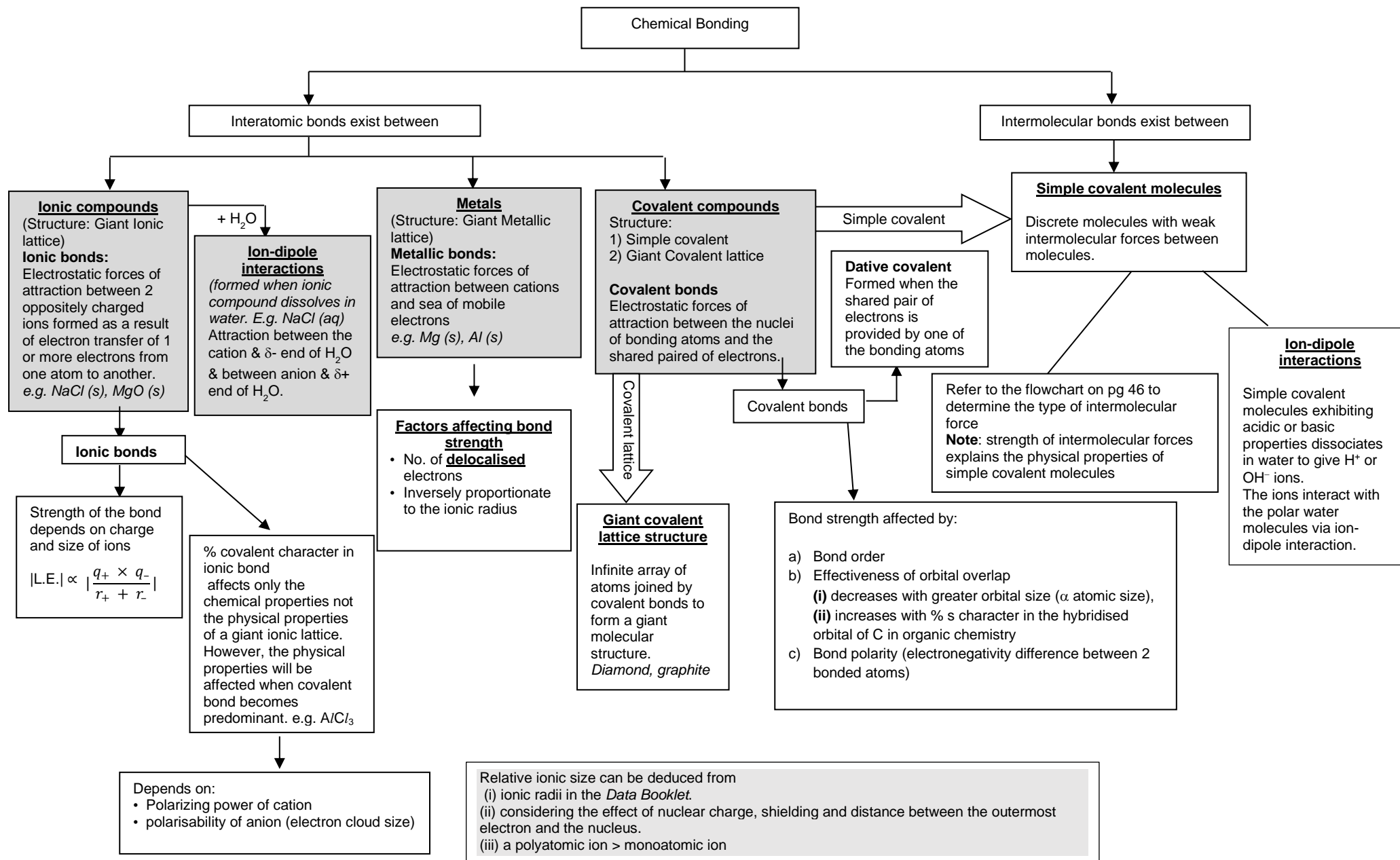
Hence, HF has a higher boiling point than NH₃.

5 STEPS TO DETERMINE THE TYPE OF INTERMOLECULAR FORCES

The type of **intermolecular forces** affects the **physical properties** of **simple covalent molecules**. Below details the steps to identifying the type of intermolecular forces.



The strong inter-atomic covalent bonds in simple covalent molecules are only broken during a chemical reaction while the intermolecular forces are broken during a physical change such as boiling and melting.



Success criteria:

- suggest the type of structure and bonding present in a substance from given physical properties.

D. APPLICATION: BOILING/MELTING POINT AND SOLUBILITY

In the previous sections, we learnt about the different types of chemical bonds which give rise to different types of structures.

However, how do we tell the structure and the type of chemical bonds that existed between two particles when the electrostatic forces are invisible?

We can only infer the type of structures and chemical bonds from the physical properties exhibited by these substances.

1 BOILING/ MELTING POINT (BP/MP)

Physical properties such as boiling/melting points, electrical conductivity, density and solubility are measurable traits of a substance.

Magnitudes of boiling and melting points reflect the strength of the attractive forces that are overcome during the physical change.

Higher BP/MP → More energy needed to break the bond → Stronger bond

Most of the time the BP/MP trends fit the factors which are used to compare the bond strength of different substances of the same structures and between substances of different structure. However, if the trend deviates from what we expect, inferences must be made from the given data.

Expected Trend 1: Compare substances of the same Giant lattice structure
thus need to consider factors affect the different types of Inter-atomic bonding

<i>Giant metallic lattice (Metallic Bonding)</i>	<u>Sodium</u> vs <u>Aluminium</u>
	<ul style="list-style-type: none"> • 1 valence e⁻ for delocalisation • 3 valence e⁻ for delocalisation
Expected BP/MP Trend	

<i>Giant ionic lattice (Ionic Bonding)</i>	<u>NaCl</u> vs <u>NaBr</u>
	<ul style="list-style-type: none"> • Same charge product • Br⁻ _____ ionic radius • _____ lattice energy magnitude
Expected BP/MP Trend	

<i>Giant covalent lattice (Covalent Bonding)</i>	<u>SiO₂</u> vs <u>GeO₂</u> (same structure as SiO ₂)
	<ul style="list-style-type: none"> • Ge _____ atomic radius • _____ orbital overlap
Expected BP/MP Trend	

Expected Trend 2: Giant lattice structure vs simple covalent molecules

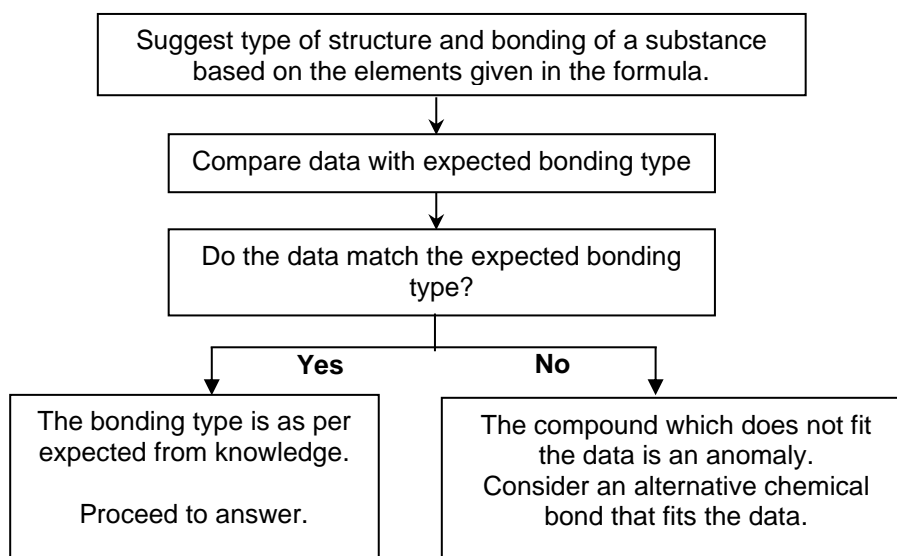
	Giant lattice structure	vs	simple covalent molecules
	<i>Bonds being Broken</i> Inter-atomic bond (e.g. ionic/ covalent bonding)	vs	<i>Bonds being Broken</i> Intermolecular forces (e.g. id-id)
Expected BP/MP Trend			

Note: When a molecule **A** that does not undergo hydrogen bonding has larger b.pt/ m.pt than a molecule **B** that undergoes hydrogen bonding, this implies that the M_r of **A** is significantly larger thus id-id becomes stronger than the intermolecular hydrogen bonding in **B**.

Expected Trend 3: Different Simple covalent molecules

	<i>Bonds being Broken</i> Instantaneous dipole – induced dipole	vs	<i>Bonds being Broken</i> Permanent dipole – permanent dipole	vs	<i>Bonds being Broken</i> Hydrogen Bonding
Intermolecular forces					
Expected BP/MP Trend					

****This is especially true if all 3 species we are comparing has similar electron cloud size.**

General Approach to thinking through BP/MP trend questions

Organisation of your answer to Boiling/Melting point question:

- | | |
|-------|--|
| (i) | State Structure |
| (ii) | IMF or inter-atomic bonds broken during melting/boiling |
| (iii) | Compare bond strength; more energy for stronger bonds |
| (iv) | Conclude with melting/boiling point. |

Note:

AlCl_3 and BeCl_2 are the common examples of simple covalent molecules formed by metals and non-metals. (pg 29)

Worked Example 1

Explain the trend in the melting points of NaCl (801°C) and AlCl_3 (193°C).

State structure

NaCl have giant ionic lattice structure, while AlCl_3 has simple molecular structure.

IMF or inter-atomic bonds broken during melting/boiling

NaCl : strong ionic bonds between the ions.
 AlCl_3 : instantaneous dipole – induced dipole interaction between the molecules.

- Do the data fit the expected trend?

Compare the strength of the bonds and link to energy required

More energy required to overcome the strong ionic bond in NaCl than the weak instantaneous dipole – induced dipole interaction between AlCl_3 molecules.

Conclude with melting/boiling point.

Therefore, NaCl has the higher melting point than AlCl_3 .

Worked Example 2

Explain the trend in the boiling points of the following halogens:

Boiling point of Cl_2 (-35°C) < Br_2 (59°C) < I_2 (184°C)

State structure

All 3 have simple molecular structures and are non-polar.

IMF or inter-atomic bonds broken during melting/boiling

instantaneous dipole – induced dipole interaction (id-id)

- Do the data fit the expected trend?

Electrons cloud size: $\text{I}_2 > \text{Br}_2 > \text{Cl}_2$

Compare the strength of the bonds and link to energy required

Electron cloud size in I_2 is the largest, so dipoles are most easily induced in I_2 , followed by Br_2 , then Cl_2 .

Hence, the instantaneous dipole – induced dipole interaction (id-id) between I_2 molecules are the strongest, followed by Br_2 , then Cl_2 .

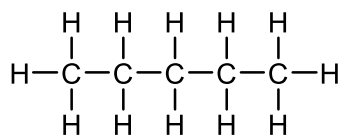
Conclude with melting/boiling point.

Most energy is required to overcome the strongest id-id in I_2 .

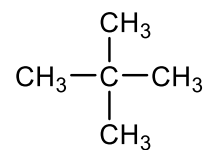
Therefore, I_2 have the highest boiling point and Cl_2 have the lowest boiling point.

Worked Example 3

Explain the difference in boiling points of the isomers of C_5H_{12} .



Pentane (b.p. = 36 °C)



2,2-dimethylpropane
(b.p. = 10 °C)

State **structure**

IMF or inter-atomic bonds broken during melting/boiling

- Do the data fit the expected trend?

Compare the strength of the bonds and link to energy required

Conclude with melting/boiling point.

Both covalent compounds have simple molecular structures and are non-polar.

instantaneous dipole – induced dipole interaction (id-id)
Similar electrons cloud size

Due to a greater surface area of contact between straight chain pentane molecules than between its branched isomer, dipoles are more easily induced in pentane molecules.

Hence, a stronger instantaneous dipole – induced dipole interaction (id-id) between pentane molecules than 2,2-dimethylpropane molecules.

More energy is required to overcome the stronger id-id in pentane than 2,2-dimethylpropane.

Hence, pentane has a higher boiling point than 2,2-dimethylpropane.

Worked Example 4

Explain the difference in boiling points between ethanol, ethanal and propane.

Compound	Structure	M_r	Boiling point / °C
Ethanol	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	46	78
Ethanal	$ \begin{array}{c} \text{H} \quad \text{O} \\ \quad // \\ \text{H}-\text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	44	21
Propane	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	44	-42

State structure

All 3 compounds have simple molecular structure.

However, ethanol and ethanal are polar while propane is non-polar.

IMF or inter-atomic bonds broken during melting/boiling

3 compounds have similar M_r / electron cloud size.

- Do the data fit the expected trend?

Ethanol: Hydrogen Bonding (H-Bond)

Ethanal: Permanent dipole – permanent dipole (pd-pd)

Propane: instantaneous dipole – induced dipole (id-id)

Compare the strength of the bonds and link to energy required

Hydrogen bonding between ethanol molecules are strongest among the 3 intermolecular forces.

The permanent dipole-permanent dipole interaction (pd-pd) between ethanal molecules is stronger than instantaneous dipole-induced dipole interaction (id-id) between propane molecules.

Most energy is required to overcome the strongest hydrogen bonding in ethanol, while the least is required for overcoming the id-id in propane.

Conclude with melting/boiling point.

Therefore, ethanol has the highest and propane has the lowest boiling point.

Worked Example 5

Iodine is solid at room temperature but water is liquid. Explain, in terms of structure and bonding the difference in physical states of the two compounds.

Note:

Hydrogen bonding is a stronger intermolecular force than id-id when the molecules being compared have similar electron cloud size.

When the electron cloud size or M_r of the molecules are significantly different, id-id can become stronger than hydrogen bonding, this can be inferred from the b.pt/m.pt data.

State structure

-

IMF or inter-atomic bonds broken during melting/boiling

- Do the data fit the expected trend?

Compare the strength of the bonds and link to energy required

Conclude with melting/boiling point.

Both covalent compounds have simple molecular structures. I_2 is non-polar while H_2O is polar.

The intermolecular forces in I_2 and H_2O are instantaneous dipole – induced dipole interaction (id-id) and hydrogen bonding respectively.

I_2 has a significantly larger electron cloud than H_2O , dipoles are much more easily induced.

The instantaneous dipole–induced dipole interaction (id-id) between I_2 molecules is stronger than the hydrogen bonding between H_2O molecules.

There is sufficient energy at room temperature to overcome the H-bonds in H_2O but not the id-id in I_2 .

Hence, H_2O is liquid but I_2 is a solid at room temperature.

Worked Example 6

Explain the difference in boiling point of HCl ($-85^\circ C$), HBr ($-67^\circ C$) and HI ($-35^\circ C$).

Note:

Individually the predominant forces for each molecule is pd-pd. But discussing pd-pd does not explain the trend. Hence we look at id-id.
(M_r of molecules is significantly different)

State structure**IMF or inter-atomic bonds** broken during melting/boiling

- Do the data fit the expected trend?

Compare the strength of the bonds and link to energy required

Conclude with melting/boiling point.

All 3 have simple molecular structures and are polar.

All 3 have instantaneous dipole–induced dipole interaction (id-id) and permanent dipole–permanent dipole interactions (pd-pd).

The electron cloud size of the 3 molecules is significantly different. HI has the largest electron cloud and hence dipole is most easily induced followed by HBr , then HCl .

The instantaneous dipole–induced dipole interaction (id-id) between HI molecules is strongest followed by HBr , then HCl .

Most energy is required to overcome the strongest id-id in HI , while the least is required for HCl .

Hence, HI has the highest boiling point and HCl the lowest.

2 SOLUBILITY OF COMPOUNDS IN SOLVENTS

Success criteria:

- Dissolution of a solute is **energetically favourable (exothermic)** if:

$$\text{energy released in the formation of solute-solvent interactions} \geq \text{energy taken in to break the solute-solute and solvent-solvent interactions}$$
- Able to illustrate ion dipole interaction with **one** water molecule using a labelled diagram.

2.1 Solubility of SIMPLE COVALENT Compounds

The 3 types of interactions involved in determining solubility of a solute in a solvent are:

- solute-solute interaction
- solvent-solvent interaction
- solute-solvent interaction

(A) To predict/ compare solubility, consider the following:

Answering format for questions involving comparison of solubility:

- Structure
- Solute-Solute/Solvent-Solvent interactions to be broken
- Solute-Solvent interactions to be formed
- Compare energy released in (C) vs energy used in (B),
 if $(c) \geq (B)$ solute will dissolve.
 If $(c) < (B)$ dissolution process is energetically NOT favourable i.e. solute cannot dissolve.

(B) To explain why a solute is insoluble in a particular solvent:

The solute **cannot form strong interactions** with the solvent molecules causing the **dissolution process to be energetically unfavourable**.

As a general rule, polar solute will dissolve in polar solvent, likewise non-polar solute in non-polar solvent.

Worked Example 7

Predict the solubility of ethanal, $\text{H}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$ in

- (a) CHCl_3 (b) water

Thinking process:

ethanal- CHCl_3 : pd-pd
 ethanal-ethanal: pd-pd
 CHCl_3 - CHCl_3 : pd-pd

ethanal- H_2O : H-bonding
 ethanal-ethanal: pd-pd
 H_2O - H_2O : H-bonding

- (a)** Solvent and solute are simple molecular structure.
 Energy released in the formation permanent dipole-permanent dipole interaction between ethanal and CHCl_3 is sufficient to overcome the permanent dipole-permanent dipole interaction between ethanal molecules and between CHCl_3 molecules.
 Therefore, ethanal is soluble in CHCl_3 .
- (b)** Energy released in the formation of hydrogen bonding between ethanal and water is sufficient to overcome the permanent dipole-permanent dipole interaction between ethanal molecules and hydrogen bonding between H_2O molecules.
 Therefore, ethanal is soluble in water.

Checkpoint 11

Explain whether or not iodine can dissolve in the following solvents: **(a)** hexane **(b)** water

(a) Solvent: Hexane

Thinking process

Structure	
Solute-Solute/Solvent-Solvent interaction to be broken	
Solute-Solvent interactions to be formed	
Compare the energy needed in the dissolution process	

Write the full answer below, using the information from the table.

(b) Solvent: Water

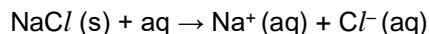
Structure	
Solute-Solute/Solvent-Solvent interaction to be broken	
Solute-Solvent interactions to be formed	
Compare the energy needed in the dissolution process	

Write the full answer below, using the information from the table.

2.2 Solubility of ionic compounds

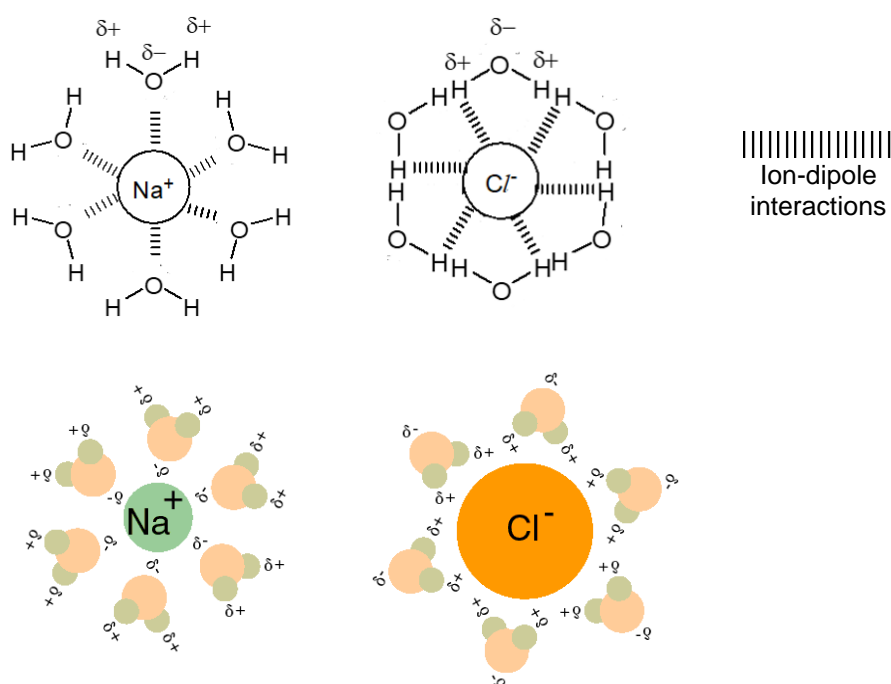
When ionic compounds dissolve in a polar solvent, it will form **ion-dipole interactions**.

Example: NaCl dissolving in water



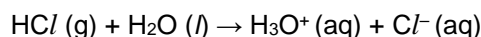
When NaCl (s) dissolves in water, Na^+ and Cl^- ions can form strong ion-dipole interactions with water. The large amount of energy released in the formation of ion-dipole interactions is sufficient to overcome the strong ionic bonds in NaCl (s) lattice structure and the hydrogen-bonds between water molecules.

The diagram below shows ion-dipole interactions between water and Na^+ & Cl^- ions. E.g. Na^+ interacts with δ^- on O of H_2O and Cl^- interacts with δ^+ on H of H_2O .



Molecular acid undergoing dissociation in water

Simple covalent molecules which exhibits acidic properties dissociate in water to form ions.



The dissociated ions formed from the reaction of HCl with water form ion-dipole interactions with water molecules.

Energy released in the formation of ion-dipole interactions between H^+ and Cl^- ions and water molecules is sufficient to overcome the hydrogen bond between water molecules and covalent bond between H and Cl atoms, hence HCl is soluble in water.

E OTHER APPLICATIONS

Learning Objective:

- outline the importance of hydrogen bonding to the physical properties of substances, including ice and water

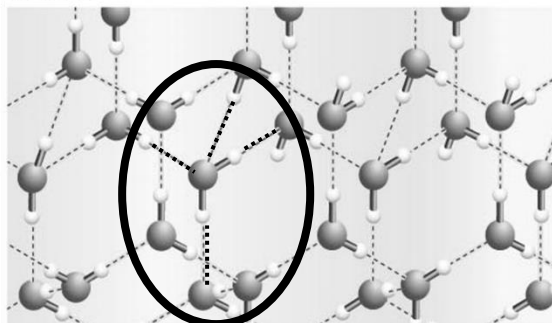
1 The Structure & Properties of Ice

Trend: When a substance changes from liquid to solid state, density should increase due to increase in attractive force which holds the particles closer together in fixed positions.

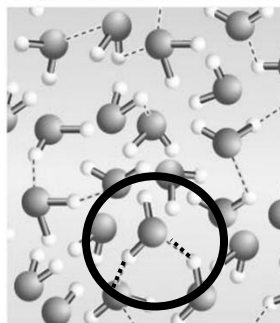
Anomaly: Ice (solid state of water) floats on water! This implies that ice have lower density than liquid water.

Using the picture below, explain this phenomenon.

(a) In ice, water molecules form a crystal lattice.



(b) In water, no crystal lattice forms.



- i) Comment on the arrangement of molecules, and
- ii) Compare the extensiveness of hydrogen bonding present in ice and water.

Formation of 4 intermolecular hydrogen bonding per H_2O molecule (max possible hydrogen bonding) hold the H_2O molecules in fixed positions resulting in solid state while

the less extensive hydrogen bonding between H_2O molecules allows random arrangement of H_2O molecules resulting in liquid state.

- Compare the distance between the molecules in ice and water.

H_2O molecules in ice are thus further apart (open structure), whereas H_2O molecules in water are closer to each other.

- Relate the distance of molecules in ice and water to density

H_2O molecules in ice occupies a larger volume compared to the same mass of water. Hence, Ice is less dense than water.

2 Dimerisation of ethanoic acid, CH_3COOH (via Hydrogen bonding)

Note:

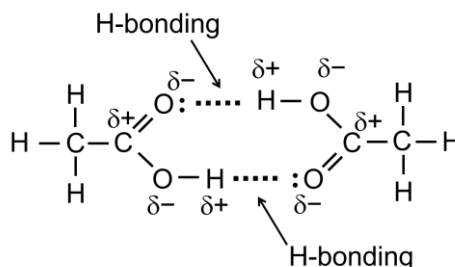
A dimer is formed when two identical molecules (monomer) are joined together.

Only consider dimerization when it is implied by the question. i.e. M_r is 2x of the original molecule.

M_r of CH_3COOH doubles (i.e. 120) in a non-aqueous solvent and in vapour state.

- Why does the molar mass of CH_3COOH double its actual value?

Its molecules have formed dimer due to the formation of hydrogen bonds between two molecules.



- Why not in aqueous state?
 - CH_3COOH is capable of forming hydrogen bond with water.
 - CH_3COOH dissociates partially in water to form CH_3COO^- and H_3O^+ .

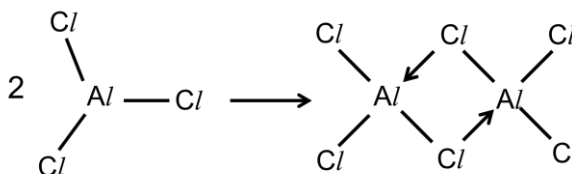
Hence, in both cases, dimerization does not occur.

3 Dimerisation of AlCl_3 (via dative bonding)

Molecules of AlCl_3 can dimerise to give Al_2Cl_6 .

In each molecule of AlCl_3 ,

- the Al atom only has 6 electrons in its valance shell after bonding. It has an empty low-lying 3p orbital that is able to accept 2 additional electrons.
- the Cl atom has lone pair electrons that can be donated.

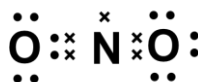


4 Dimerisation of NO_2 (via covalent bond)

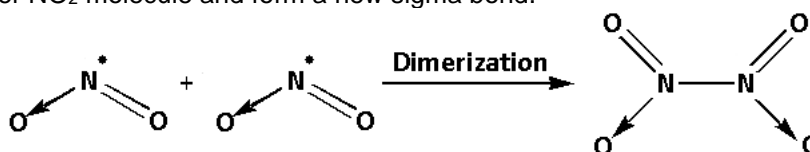
Molecules of NO_2 can dimerise to give N_2O_4 .

In each molecule of NO_2 ,

- the N atom only has 7 electrons in its valance shell after bonding.

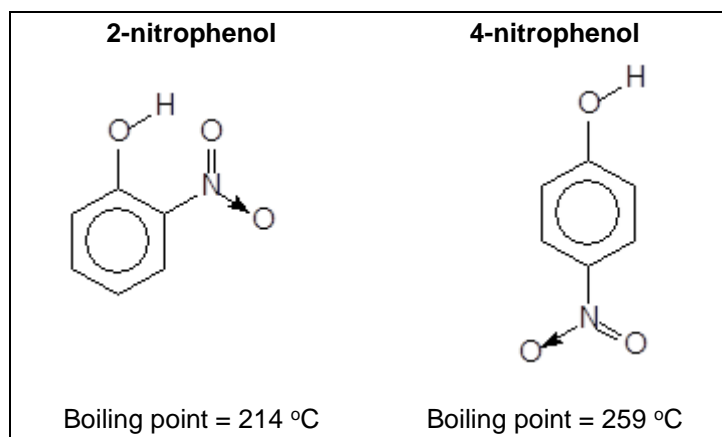


The NO_2 molecule can share the single electron on the N atom with the N atom of another NO_2 molecule and form a new sigma bond.



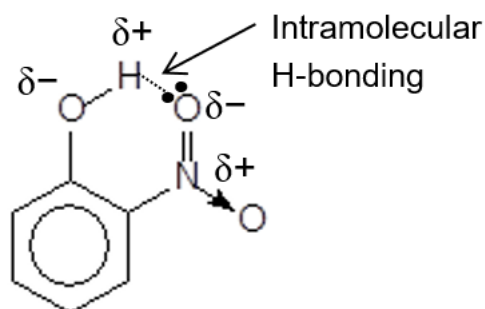
5 Intramolecular Hydrogen Bonding

Even though 2-nitrophenol and 4-nitrophenol are isomers (similar electron cloud size), their boiling points are significantly different.



The lower boiling point of 2-nitrophenol is due to intramolecular hydrogen bonding that occurs in 2-nitrophenol but not in 4-nitrophenol.

Due to the close proximity of the NO_2 and OH groups, 2-nitrophenol forms intramolecular hydrogen bonding, however 4-nitrophenol forms only intermolecular hydrogen bonding.



Less sites on 2-nitrophenol are available for intermolecular hydrogen bonding. More energy is required to overcome the intermolecular hydrogen bonding in 4-nitrophenol, resulting in it having a higher boiling point.

Success criteria:	Relevant Tutorial question	What do you still struggle with? Write your queries here.
<p>1. understand that all interatomic bonds and intermolecular forces of attraction are electrostatic in nature and energy is required to overcome them. Thus, the magnitude of the melting/boiling points reflects the strength of the different electrostatic forces of attraction.</p> <ul style="list-style-type: none"> describe metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons describe the metallic lattice structure of a crystalline solid as in copper (see checkpt 5 on pg 18) describe ionic bond as the electrostatic attraction between oppositely charged ions describe the ionic lattice structure of a crystalline solid as in NaCl and MgO. See Figures 2.2 under section 2.2 on pg 8. describe covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei 	Q1, Q2	
2. describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances.		
Refer to pg 12 - 18 of lecture notes		
3. describe co-ordinate (dative covalent) bonding where both electrons in the covalent bond comes from only one of the bonding atoms.	Q3a/ Q9d	
<p>4. describe covalent bonding in terms of orbital overlap (use s and p orbitals only), giving σ and π bonds in diatomic molecules.</p> <p>5. Understand that the pair of orbitals taking part in covalent bonding must either have one unpaired electron each (see section 3.3 on pg 16) or one orbital with lone pair while the other orbital is without electrons (see section 3.2).</p> <p>6. Covalent bond strength increases with increase in shared electron density between 2 nuclei. See section 3.3 (sigma > pi) and 3.4. (a) bond order (b) effectiveness of orbital overlap. See checkpt 5.</p>	Q3b Assess in chemical energetics/ organic chemistry	
<p>7. Define the terms '<i>Bond energy</i>' and '<i>Bond length</i>'.</p> <p>8. '<i>Bond energy</i>' and '<i>Bond length</i>' are numerical values that help us compare covalent bond strength.</p> <p>9. Compare covalent bond strength qualitatively by considering in decreasing order of priority (i) bond order (ii) effectiveness of orbital overlap. See checkpt 5.</p>	Q 4 (iii)	

Refer to pg 19 - 21 of lecture notes		
10. describe the lattice structure of a crystalline solid of simple covalent molecule such as iodine and giant molecular lattice (giant covalent lattice) structure of a crystalline solid as in graphite and diamond (see figure 3.5b.1 and 3.5b.2.) see checkpt 6.	Q1	
11. Able to use the concept of the number orbitals in the valence shell and electronegativity to explain why certain compounds can be formed with period 3 element but not period 2 element. See checkpt 7	Q6	
Refer to pg 22 - 23 of lecture notes for thinking process		
12. use of 'dot-and-cross' diagrams to describe covalent and ionic bonding	Q5 (1 st column)	
Refer to pg 32 - 35, 39 - 40 of lecture notes for thinking process		
13. Able to use dot-and-cross diagram and Valence Shell Electron Pair Repulsion theory to identify the different electron geometry of atoms covalently bonded to each other.	Q5 (2 nd column), Q7, Q8/ Q9	
14. Able to deduce and compare with reasoning, the shape (molecular geometry) and the bond angle by considering (i) the number of bonding and non-bonding pairs in the electron geometry and (ii) repulsive forces which increase with electron density of the electron pair nearer to the central atom.		
15. explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is not required]	Q 10	
16. deduce the polarity of a molecule using bond polarity and its molecular shape		
Refer to pg 46 thinking processes		
17. Describe in words or using suitable diagrams to illustrate the formation of the following intermolecular forces (IMF) i. instantaneous dipole-induced dipole interactions. ii. permanent dipole-permanent dipole interactions between polar molecules. iii. hydrogen bonding between molecules with protonic hydrogen (H directly bonded to N,O and F).	Q 5 (3 rd column) Q 11/ Q12/ Q 14/ Q16	
18. For simple covalent molecules, only IMF are overcome during a physical change while interatomic covalent bonds are broken during a chemical change.		
19. Strength of Hydrogen bonding > permanent dipole-permanent dipole > instantaneous dipole-induced dipole when molecules of similar M _r are being compared.		

Refer to pg 46 - 49 of lecture notes for the thinking process		
20. suggest the type of structure and bonding present in a substance from given information	Q4/ Q 13 Q18/ Q19	
Refer to pg 54 - 56 of lecture notes for thinking process		
21. Dissolution of a solute is energetically favourable if: <div> <div>energy released in the formation of solute-solvent interactions</div> <div>≥</div> <div>energy taken in to break solute and solvent interactions</div> </div>	Q15	
22. Able to illustrate ion dipole interaction with one water molecule using a labelled diagram.	Q16	
Refer to pg 57		
23. outline the importance of hydrogen bonding to the physical properties of substances, including ice and water	Q 17	