

**St Andrew's Junior College****H1 Chemistry 2021****Lecture Notes 3: Chemical Bonding (TUTOR)****Assessment Objectives:**

- (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 (limited to s and p orbitals only), giving σ and π bonds (see also topic on Introduction to Organic Chemistry)
- (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
[quantitative treatment of electro-negativity is **not** required]
- (g) deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d));
- (h) describe the following forces of attraction (electrostatic in nature):
- (i) intermolecular forces, based on permanent and induced dipoles, as in liquid and gaseous $CHCl_3$, Br_2 and the noble gases
 - (ii) hydrogen bonding, using ammonia and water as examples of molecules containing $-NH$ and $-OH$ groups
- (i) outline the importance of intermolecular forces to the liquefaction of gases when subjected to high pressure and / or low temperature
- (j) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water
- (k) explain the terms *bond energy* and *bond length* for covalent bonds
- (l) compare the reactivities of covalent bonds in terms of bond energy, bond length and bond polarity

- (m) describe, in simple terms, the lattice structure of a crystalline solid which is:
- (i) ionic, as in sodium chloride, magnesium oxide
 - (ii) simple molecular, as in iodine
 - (iii) giant molecular, as in graphite; diamond
 - (iv) hydrogen-bonded, as in ice
 - (v) metallic, as in copper
- [the concept of the 'unit cell' is **not** required]
- (n) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances
- (o) suggest the type of structure and bonding present in a substance from given information

Introduction to Organic Chemistry:

- (f) (i) describe the shapes of the ethane, ethene and benzene molecules
- (ii) explain the shapes of, and bond angles, in the ethane, ethene and benzene molecules in relation to σ and π carbon-carbon bonds
- (iii) predict the shapes of, and bond angles in, molecules analogous to those specified in (f)(ii)

Content

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| 3 | Covalent bonding | 7 | Physical properties of Simple Covalent Molecules |
| 4 | Shapes of Molecules and Molecular Ions | 8 | Giant Molecular Structure |

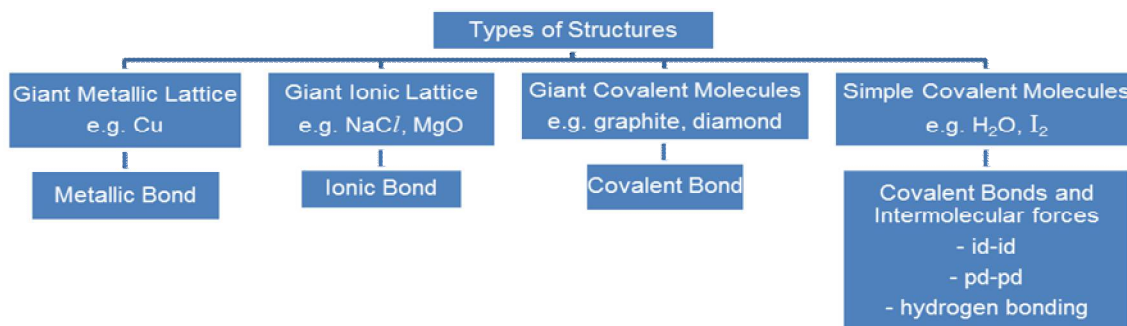
Recommended Materials:

- 1 Cann, Peter and Hughes, Peter, Chapter 3, Page 52, Chemical Bonding in simple molecules, Chemistry for advanced level, 2002
- 2 Covalent Bonding: <http://chemguide.co.uk/atoms/bonding/covalent.html>



Introduction

The reaction of two or more elements results in the formation of a chemical bond between atoms. The chemical bond formed between atoms results in the formation of different types of structures.



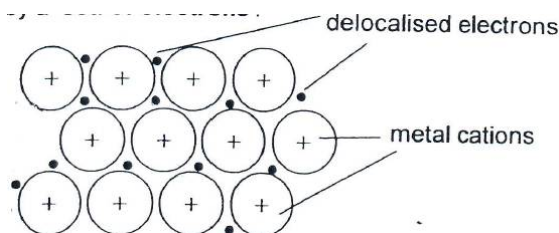
1 Metallic Bonding

- (a) show understanding that all chemical bonds are electrostatic in nature and describe:
- (iii) metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons
 - (m) describe, in simple terms, the lattice structure of a crystalline solid which is:
 - (v) metallic, as in copper

1.1 Formation of Metallic Bonds

Definition: Metallic bonding is the **electrostatic attraction between a lattice of positive ions** and **delocalised electrons**.

- Metal atoms have low electronegativities and low ionisation energies.
- Hence, they lose electrons readily to form positive ions which are arranged in a lattice structure.
- The **valence** electrons lost form a mobile sea of electrons which are **free to move** throughout the three-dimensional structure. i.e. **delocalised**. They occupy the space between the metal cations.



Note: (+) cations should be **regularly arranged** and **should not touch**.

1.2 Strength of Metallic Bond

- (a) Metallic bond is strong.
- (b) The stronger the metallic bond, the higher its melting and boiling point. The strength of metallic bond is dependent on:
- (i) **Number of valence electrons contributed to the sea of delocalised electrons / Charge of the cation:** Generally, the more valence electrons the metal contributes (the higher the charge of the metal cation), the stronger the electrostatic forces of attraction between metal cation and sea of delocalised electrons. Hence, the metallic bonding will be stronger.
 - (ii) **Size of the cation:** Given the same type of packing, the smaller the size of the cations, the closer the delocalised electrons are to the positively charged nuclei. Hence, the metallic bonding will be stronger.

E.g. m.p. of $\text{Al} > \text{Mg} > \text{Na}$ due to increasing ionic size (i.e. $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$) and decreasing number of delocalised valence electrons.

E.g. Transition metals have very high m.p. ($> 1000\text{ }^{\circ}\text{C}$) due to their very small ionic size and large number of delocalised electrons (the d electrons and the s electrons in the valence shell can both delocalise).

Format of answering boiling/melting point questions:



| |
|--------------------------|
| <u>S</u> tructure |
| <u>I</u> nteraction |
| <u>A</u> mount of Energy |

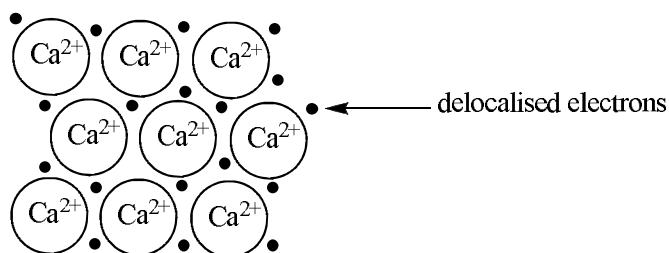
**Exercise 1** [Nov 2013 / II / 4b(i)]

- (a) Describe the structure and bonding in calcium with the aid of a labelled diagram.
 (b) Suggest why the melting point of calcium is higher than potassium.

Answer:**Thinking Process:**

- What structure does Ca (and K) have?
- What type of bond is broken during melting of Ca (and K)?
- What are the factors that affect the strength of this type of bond?

- (a) Calcium has a **giant metallic lattice structure** with **strong electrostatic forces of attraction** between the **lattice of Ca^{2+}** and the **delocalised electrons**.

**(b)**

| | Calcium | Potassium |
|---------------------------------|-------------------------|------------------------|
| <u>S</u> tructure | Giant Metallic lattice | Giant Metallic lattice |
| <u>I</u> nteraction | Stronger metallic bonds | Weaker metallic bonds |
| <u>A</u> mount of Energy | More energy | Less energy |

Both calcium and potassium have **giant metallic lattice structure** but calcium has a **greater number of delocalised valence electrons and a smaller cationic** size than potassium and **stronger electrostatic forces of attraction** between the cations and the valence electrons. Hence, **more energy** is required to overcome the metallic bonds in calcium and hence higher melting point.

1.3 Physical Properties

(n) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

(a) High melting and boiling point

- Metals have **giant metallic** lattice structures whereby metal atoms pack closely together in a regular structure.
- Hence, a lot of energy is required to break the strong metallic bonds resulting in them having high melting and boiling points.
- The **stronger** the metallic bond, the **higher** the melting and boiling points.

(b) High electrical conductivity even in the solid state

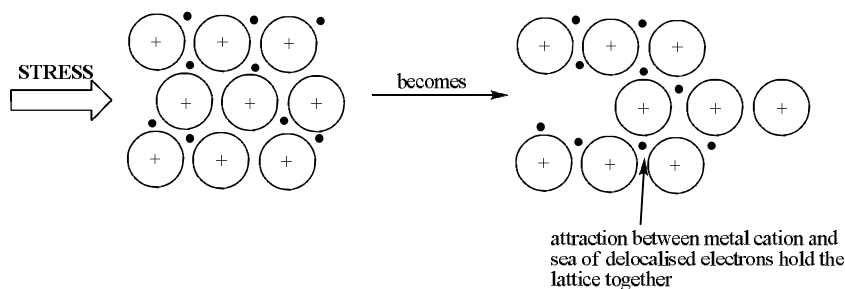
- Metals are good conductors of electricity due to the presence of **delocalised electrons**.
- These delocalised electrons (**charge carriers**) are free to move throughout the 3-dimensional structure when a potential difference is applied.

(c) Good thermal conductivity

- Metals are good conductors of heat.
- Due to delocalised electrons, when metal is heated at one end, the electrons pick up the thermal energy and vibrate faster. They then **collide** with the other electrons, passing on the energy to them.

(d) Malleable and ductile

- Metals can be beaten into shape (malleable) or drawn into wires (ductile).
- When a force is applied, the cations are able to move over one another without the breaking of metallic bonds.



Video: Metallic bonding: <https://www.youtube.com/watch?v=vOuFTuvf4qk>

2. Ionic Bonding

- (a) show understanding that all chemical bonds are electrostatic in nature and describe:
- (i) ionic bond as the electrostatic attraction between oppositely charged ions;

2.1 Formation of Ionic Bonds

Definition: Ionic bonds are the electrostatic attraction between oppositely charged ions.

- They are usually formed between **metals** (e.g. Group 1, 2) and **non-metals** (e.g. Group 16, 17).
- Metals have low ionisation energies hence metal atoms lose electrons to form cations.
- Non-metals have high electron affinities hence non-metal atoms gain electrons to form anions.

2.2 Structure

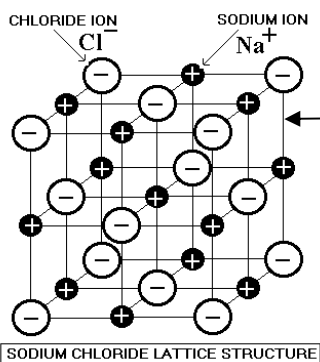
- (m) describe, in simple terms, the lattice structure of a crystalline solid which is:
- (i) ionic, as in sodium chloride, magnesium oxide

- Ionic solids have giant ionic lattice structure, consisting of regular three-dimensional arrangement of positive and negative ions forming a giant network. Each ion in the crystal lattice is attracted equally to several surrounding ions of opposite charge.

2.2.1 Coordination Number

- The **coordination number** for a crystal lattice is defined as the number of ions that surround another ion of opposite charge.
- The arrangement of the ions depends on the **radii** of the **cations and anions** and the **ratio of cations to anions**. The ions are arranged so as to maximise attractive forces between ions of opposite charge and minimise repulsion between ions of like charges, hence achieving the most stable arrangement.

Example: sodium chloride, NaCl



Strong electrostatic forces hold the ions together in an orderly manner.

- **Magnesium oxide** also has the same arrangement as sodium chloride.
- In both compounds, one cation is surrounded by six anions while one anion is surrounded by six cations. Hence the **coordination number** is 6.

**Exercise 2** [Nov 2009 / II / 1d(ii)]

In the crystal lattice of sodium and potassium chlorides, the co-ordination number of each ion is 6. In the crystal lattice of caesium chloride, CsCl , the co-ordination number has a different value. Suggest an explanation for the co-ordination number in CsCl lattice being different from those in NaCl and KCl .

Thinking Process:

- What is co-ordination number?
- What affects co-ordination number?
- What is the difference between NaCl and CsCl ?

Answer:

Cs^+ has a larger ionic radius than Na^+ and K^+ . More Cl^- can surround the cation hence higher coordination number.

2.3 Octet Rule

- When studying chemical bonding, we are usually interested in the valence electrons of the atoms that interact.
- Atoms often react with each other to reach a state in which their valence shells are filled to achieve the configuration of the noble gas closest to them in the Periodic Table. This is usually done by either **gaining or losing electrons** (ionic bonding) or **sharing electrons** (covalent bonding).

2.3.1 Dot-and-Cross Diagrams

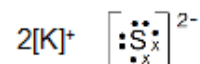
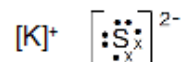
(b) describe, including the use of 'dot-and-cross' diagrams:

(i) ionic bonding as in sodium chloride and magnesium oxide

Dot-and-Cross diagrams are used to represent the valence electrons of individual atoms in an ionic compound.

General Guidelines for dot-and-cross diagrams of an ionic compound.


1. For the metal, determine the valence electrons lost from the metal and indicate it as the charge on the cation i.e.
2. For the non-metal, use dot to represent the correct number of valence electrons. Use cross to represent the additional electrons needed to achieve octet configuration. Indicate the number of electrons gained as the charge on the anion i.e.
3. Write coefficient to the square bracket to represent the number of cations/anions in the chemical formula i.e.



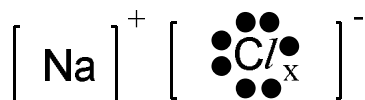
Note: Do NOT draw concentric circles



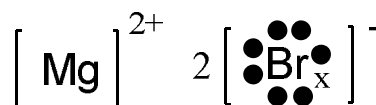
Exercise 3:

 Draw the dot-and cross diagram of the following compounds:

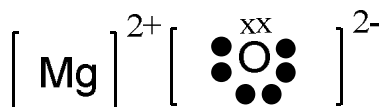
(a) NaCl



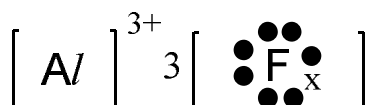
(b) MgBr_2



((c))MgO



(d) AlF_3



Thinking Process:

- Is the compound ionic (gaining and losing of electrons to form ions) or covalent (sharing of electrons)?
- For ionic compound, what is the charge on the ions?

2.4 Strength of Ionic Bonds

The strength of ionic bonds is related to the **lattice energy** of the ionic compound.

Definition: Lattice energy is the energy evolved when **1 mole** of a pure ionic solid is **formed** from its **constituent gaseous ions**.

$$\text{Strength of ionic bonds: } |LE| \propto \left| \frac{q^+ q^-}{r^+ + r^-} \right|$$

The magnitude of lattice energy depends on the two factors: **ionic charge** and **ionic size**.

- Effect of ionic charge (q): The **greater the charge of the ions**, the **greater** the magnitude of the lattice energy and the **stronger** the ionic bonds.
- Effect of ionic size (r): The **bigger the ions**, the greater the sum of the ionic radii, the **smaller** the magnitude of the lattice energy and thus the **weaker** the ionic bonds.

2.5 Physical properties

(n) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

(a) High melting and boiling points

- Ionic compounds are held together by strong electrostatic forces of attraction between oppositely charged ions. Hence, **a lot of energy** is required to overcome these strong attractions resulting in ionic compounds having high melting and boiling points.
- Many ionic compounds have melting points greater than 500 °C and hence are solids at room temperature.
- The **greater the magnitude of the lattice energy**, the **stronger** the ionic bonds, the **higher** the melting point.

**Exercise 4**

Explain why MgO has a higher melting point than CaO.

Answer:

- Both have **giant ionic lattice** structures with **strong electrostatic forces of attraction between oppositely charged ions**.
- Since $|LE| \propto \left| \frac{q^+ q^-}{r_+ + r_-} \right|$
- Both Mg^{2+} and Ca^{2+} has the **same charge**
- Mg^{2+} has **smaller ionic radius** Ca^{2+} ion.
- This leads to **stronger electrostatic forces of attraction** with O^{2-} anion / **more exothermic lattice energy**.
- Hence, **more energy** is required to overcome the **stronger ionic bonds** in MgO as compared to CaO.



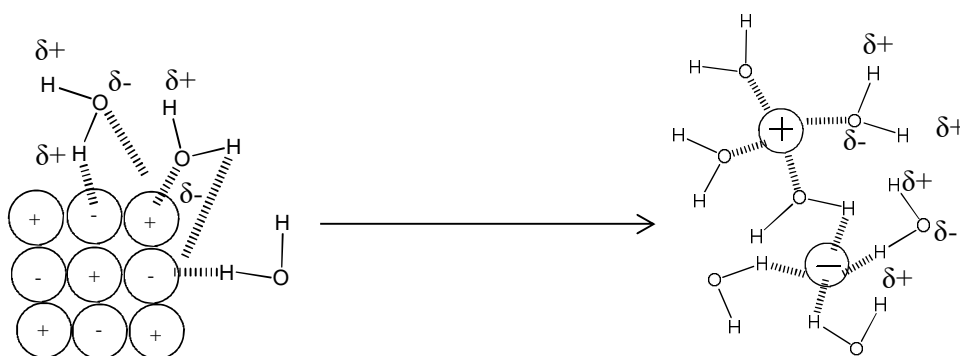
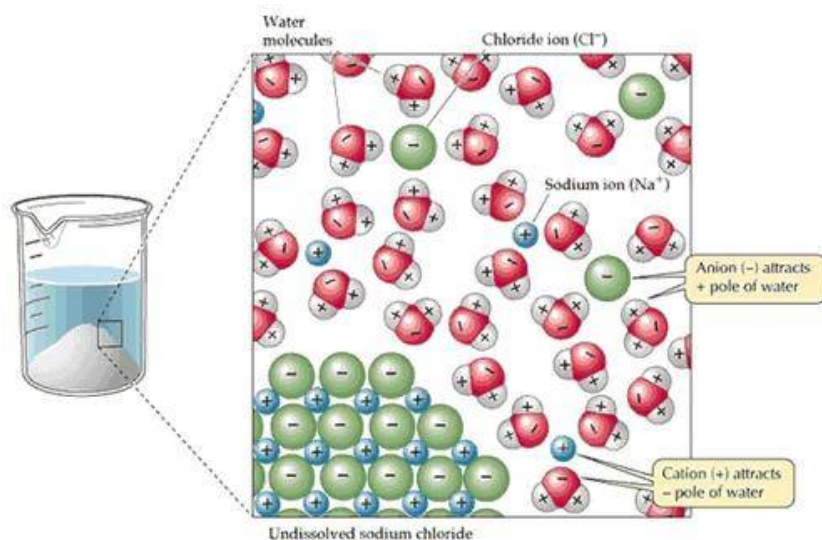
Remember to compare the cations (Mg^{2+} and Ca^{2+}) and **not** Mg and Ca which are atoms.

Thinking Process:

- What structures do they have?
- What bonds must be broken during melting?
- What factors affect the strength of this type of bonds broken?
- Comparison of mp: SIA format

(b) Soluble in polar solvent but insoluble in non-polar solvent

- When bonds or interactions are formed, **energy is released**. When bonds or interactions are broken, energy is **taken in**.
- When an ionic compound dissolves, the crystal lattice must be broken down and this requires a lot of energy. This energy can be offset by a release of energy caused by **solvation** (if the solvent is water, this is known as **hydration**). (Refer to *Energetics* notes)
- When an ionic compound is placed in water, the water molecules can penetrate the crystal lattice and interact with the ions via **ion-dipole** attractions (the cations are surrounded by the (δ^-) oxygen end of the water molecule while the anion is surrounded by the (δ^+) hydrogen end of the water molecule).
- This **ion-dipole** attractions **may release sufficient energy** to **overcome** the **strong ionic bonds**. The salt will hence dissolve and the hydrated ions are free to move about.



| | |
|---------------------------------|------------------------------------------------------|
| Strong ionic bonds between ions | Ion-dipole attractions formed between ions and water |
|---------------------------------|------------------------------------------------------|

- (v) However, not all ionic compounds are soluble in water. This happens when the ionic bonds in the lattice is so strong i.e. high lattice energy that the energy released from forming ion-dipole is **insufficient** to overcome strong ionic bonds.
- (vi) Ionic compounds are not soluble in non-polar solvents as the **ion-induced dipole** attractions are too weak, releasing too little energy to overcome the strong electrostatic attractions between the ions in the crystal lattice.

Video: Dissolution of NaCl

<https://www.youtube.com/watch?v=CLHP4r0E7hg>




Exercise 5: N2010/11/4(a),(b) modified

Explain, with the aid of a diagram, why MgSO_4 dissolves in water.

Thinking Process:

What is the type of interactions between ions and water (solvent)?

Steps:

1. Identify the solute-solute interaction, solvent-solvent interaction and the solute-solvent interaction
2. Compare the strengths of the interaction
3. Conclude Solubility

If the energy released from solute-solvent interaction is sufficient to overcome the solute-solute and solvent-solvent interaction => SOLUBLE

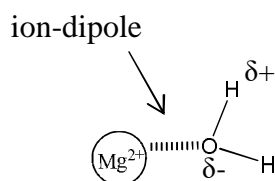
If the energy released from the solute-solvent interaction is insufficient to overcome the solute-solute and solvent-solvent interaction => INSOLUBLE

Solubility Template: (not required in answer)

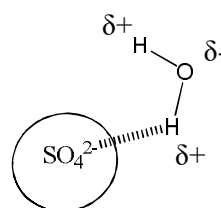
| | Type of bonds/interactions |
|----------------------------------------------------------------------------------------------------------------|----------------------------|
| Solute – Solute MgSO_4 | Ionic bonding |
| Solvent – Solvent water-water | Hydrogen-bonding |
| Solute – Solvent Mg^{2+} – water SO_4^{2-} – water | Ion-dipole |

Answer: MgSO_4 forms ion-dipole attractions with water. The ion-dipole attractions release sufficient energy to overcome the strong ionic bonds between oppositely-charged ions and the hydrogen bonding between water molecules, hence it dissolves.

Mg^{2+} cation



SO_4^{2-} anion

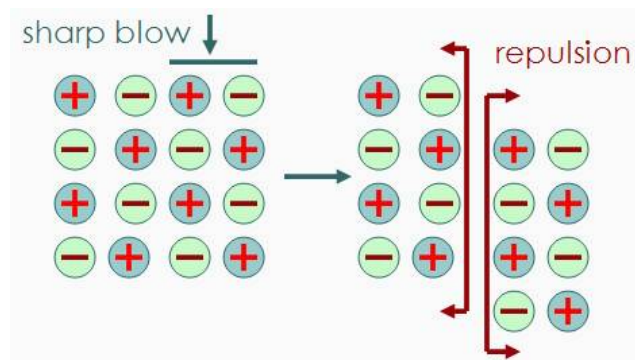


(c) Conducts electricity in molten and aqueous states but not in solid state

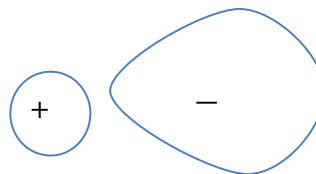
- Ionic compounds conduct electricity in the molten and aqueous states as there are **mobile ions** to conduct electricity.
- However in the solid state, the ions are held at fixed position and unable to act as mobile charge carriers. Hence, ionic compounds do not conduct electricity when in the solid state.

(d) Hard, rigid and brittle

- Ionic compounds are hard due to the strong ionic bonds between the oppositely charged ions. Hence ionic compounds are difficult to cut.
- On applying stress to solid, repulsion between similarly charged ions in neighbouring crystal planes causes the crystal to fracture. Thus, ionic compounds are brittle.

**2.6 Covalent character in Ionic Bonds**

The attraction of the cation for the valence shell electrons of the anion causes distortion (polarisation) of the electron cloud in the anion, pulling it into the region between the two nuclei. This distortion of electron cloud results in the ionic bond having some **covalent character**.

Ionic bond with covalent character

Fajan's rule: The **more polarised** the anion, the **higher** the degree of covalent character.

Degree of covalent character depends on:

- Polarising power** of the **cation** (i.e. ability to polarise the anion).
 - This depends on its charge density (= charge / size).
 - The **higher the charge** and the **smaller the cation**, the **stronger** is its polarising power.
- Polarisability** of the **anion** (i.e. ease of being polarised).
 - This depends on its **size**.
 - The larger the size and the higher the charge, the more polarizable it is.

In short, an ionic compound has high degree of covalent character if:

- (i) the **cation** is **small and highly charge**,
- (ii) the **anion** is **large**



Exercise 6

(1) Explain why LiCl has more covalent character than NaCl .

Answer:

The smaller Li^+ has a **higher** charge density than Na^+ . Hence it is able to **distort the anionic electron cloud of Cl^- more**, (polarisation) giving rise to more covalent character.

(2) Explain why AlCl_3 is covalent while AlF_3 is ionic.

Answer:

The electron cloud of Cl^- is **larger** than that of F^- . Hence, Cl^- anion is **more readily polarised** by the **high charge density of Al^{3+} cation** giving rise to covalent character.

Thinking Process:

- What kind of compound are they?
- What is the difference in both compounds?
- What causes covalency in the compounds?

🔑 Self- Check: Q1-3

3 Covalent Bonding

- (a) show understanding that all chemical bonds are electrostatic in nature and describe:
 - (ii) covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei
- (m) describe, in simple terms, the lattice structure of a crystalline solid which is:
 - (ii) simple molecular, as in iodine

Definition: Covalent bonding is the **electrostatic attraction** between a **shared pair of electrons and the positively charged nuclei**.

- Covalent bonds usually occur between **non-metals**.
- There are two classes of covalent molecules
 - i. **Giant Covalent Molecules** (Section 8)
 - ii. **Simple Covalent Molecules**

(b) describe, including the use of 'dot-and-cross' diagrams:

- (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

3.1 Dot-and-Cross Diagram

Dot-and-cross diagrams are also used to represent the valence electrons of individual atoms in a covalent molecule. The octet rule is the basis of drawing dot-and-cross diagrams. However there are exceptions to the Octet Rule.

General guidelines in drawing dot-and-cross diagrams

- 1 Identify the central atom. (Usually the least electronegative atom.)
- 2 Identify the number of valence electrons for each element. Decide on the type of bond (single, double, triple or dative) for the atom to achieve octet configuration.
- 3 Check that the terminal atom achieve octet configuration. Check if the central atom is period 3 (or above) element which can expand octet configuration (have more than 8 electrons) if there is a need to. (Section 3.5 – pg 22)

Note: Do NOT draw concentric circles.

3.2 Diagram to show the shape of the structure

When the question is phrased like this:

“Draw the structure and suggest the shape of H_2O ” or “Draw a diagram to show the shape of H_2O ”, students should not draw dot-and-cross diagrams. Instead, do the following:

- Replace each bond pair of electrons with a line to represent a bond (–).
- Two lines represent a double bond. ($=$)
- Three lines represent a triple bond. (\equiv)
- Dative bond is represented by an arrow (\rightarrow) that points from the atom donating the lone pair of electrons to the atom accepting it. (Section 3.4)
- Lone pair(s) of electrons on central atom (if any) has to be shown.

**Exercise 7****Thinking Process:**

- Is the compound ionic (gaining and losing of electrons to form ions) or covalent (sharing of electrons)?
- Which is the central atom?
- Which period is the central atom found? Can it expand octet configuration?
- If it can't, how to make them achieve octet configuration?

1. Draw the dot-and-cross diagram for each of the following molecules.
2. Draw a structure to show the shape for each of the following molecules.

| | Q1 | Q2* |
|---------------------|----|-----|
| a) CH ₄ | | |
| b) CO ₂ | | |
| c) H ₂ O | | |

*Shapes will be covered in Section 4.1

3.3 Sigma and Pi Bonds (σ and π Bonds)

(c) describe covalent bonding in terms of orbital overlap (limited to s and p orbitals only), giving σ and π bonds (see also *Introduction to Organic Chemistry* notes)

(a) **Atomic orbitals** are regions of space around the nucleus of an atom where an electron is likely to be found. During bond formation, **two atomic orbitals overlap to form a molecular orbital containing an electron pair**.

(b) The overlapping of orbitals can occur in two different ways giving rise to:

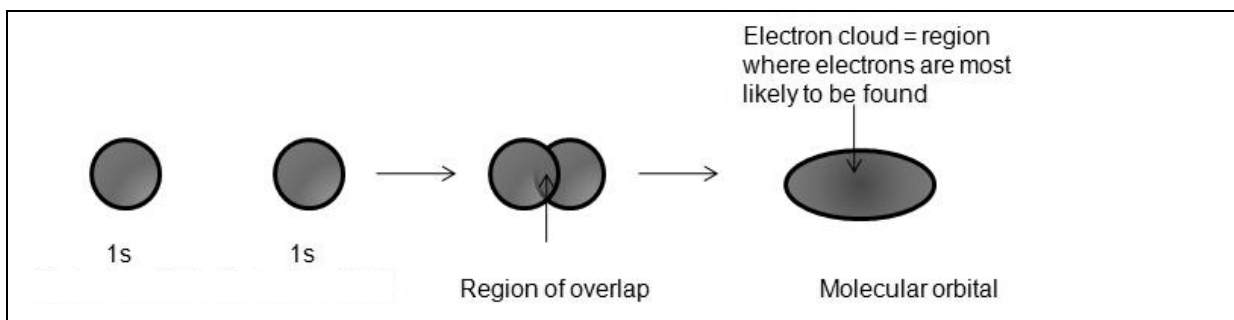
- i. **sigma** (σ) bonds
- ii. **pi** (π) bonds

3.3.1 Formation of Sigma (σ) Bonds

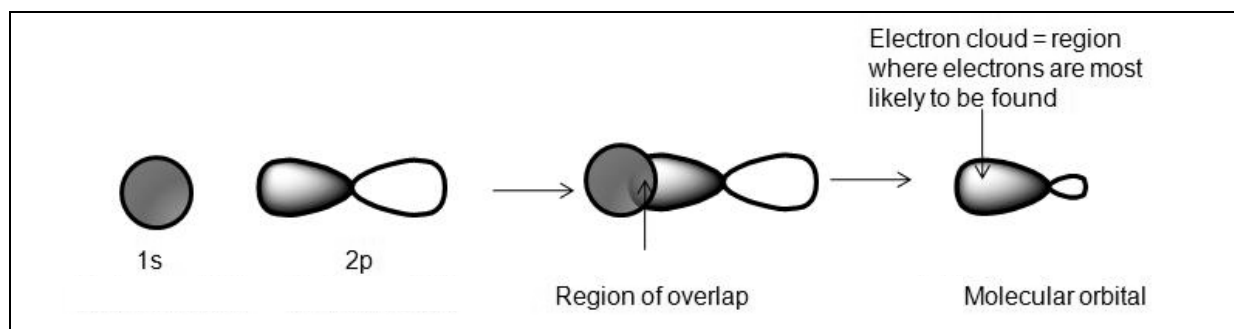
A sigma bond is formed when atomic orbitals overlap in a **head-on** manner. There can only be **one** sigma bond between two atoms.

Sigma bonds can be formed between:

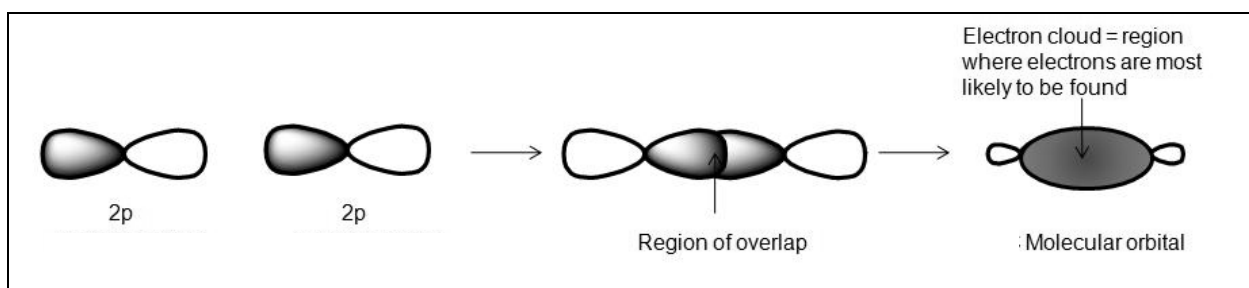
i. s and s orbitals



ii. s and p orbitals



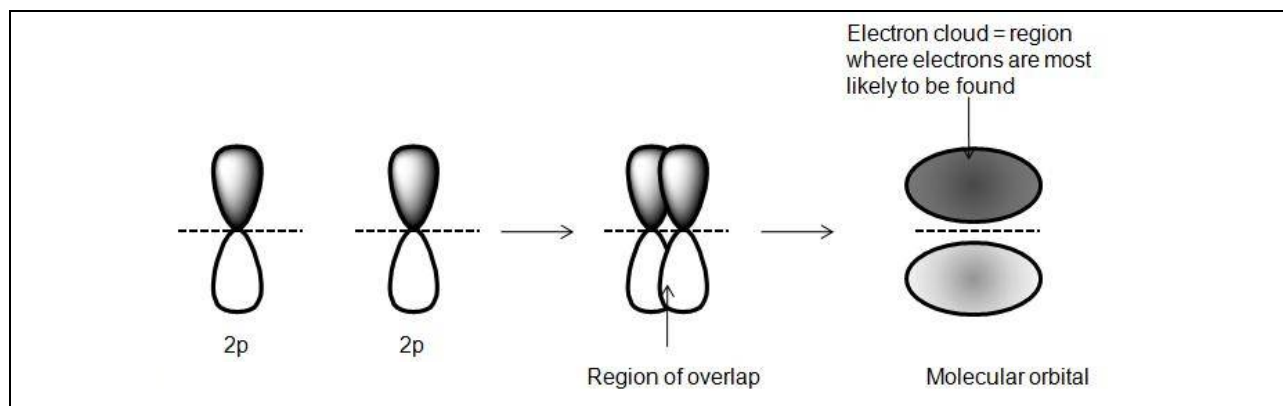
iii. p and p orbitals



3.3.2 Formation of Pi (π) Bonds

- (a) A π bond is formed when two orbitals (can be p or d) overlap in a **side-on** manner (above and below the line drawn through the 2 nuclei).
- (b) A π bond is **weaker** than a sigma bond due to the **less effective** 'side-on' overlap compared to the 'head-on' overlap.
- (c) π bond can only exist after a σ bond is formed.
- (d) π bonds occur in compounds containing **multiple** (double or triple) bonds.

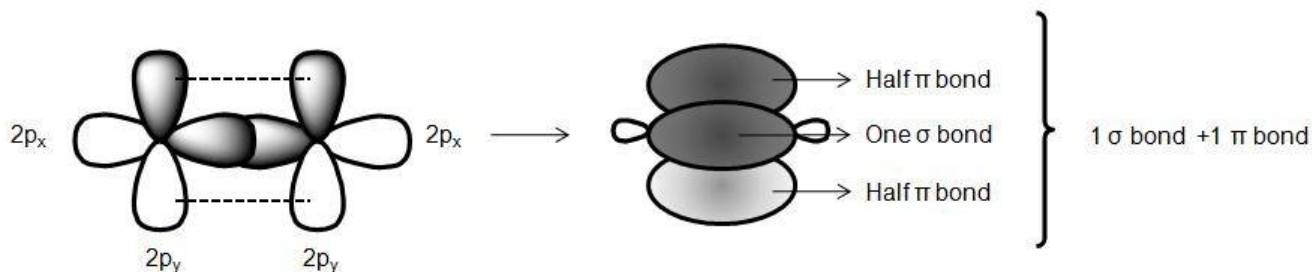
i. p and p orbital



Example 1: Formation of oxygen molecule, $\text{O}=\text{O}$

Head-on overlap between two $2p_x$ orbitals produces a **sigma** (σ) bond

Side-on overlap between two $2p_y$ orbitals produces a **pi** (π) bond.



Summary

| Number of electron pairs shared | Name | Type of bonds formed |
|---------------------------------|-------------|----------------------|
| 1 | Single bond | 1 σ |
| 2 | Double bond | 1 σ , 1 π |
| 3 | Triple bond | 1 σ , 2 π |

Self-check Q4

Video: Sigma & pi-bonds in Fluorine, Nitrogen & Oxygen
<https://www.youtube.com/watch?v=avW70VpzUec>



3.4 Dative Bonds

(b) describe, including the use of 'dot-and-cross' diagrams:

(iii) co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al_2Cl_6 molecule

(a) A co-ordinate or dative bond is a covalent bond which is formed when one atom **donates a lone pair of electrons** for sharing with another atom.

(b) Criteria for dative bonding:

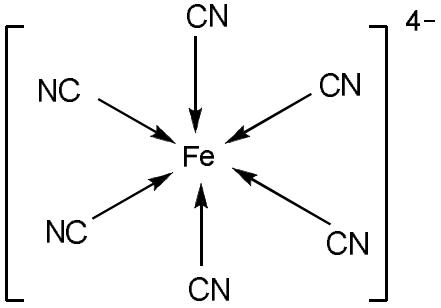
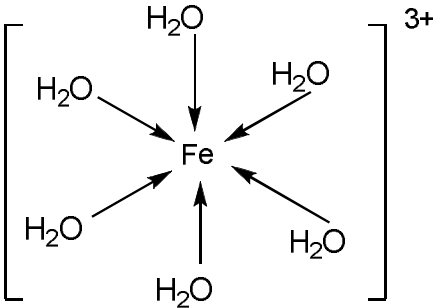
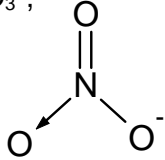
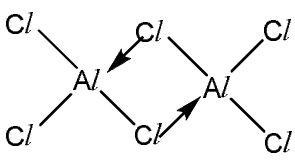
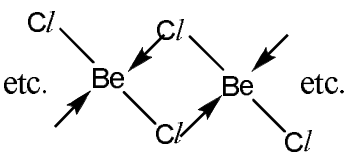
- Donor atom has a **lone pair of electrons**
- The acceptor atom must have an **empty orbital** in the valence shell
- The dative bond is represented by the symbol \rightarrow . The arrow points from the donor atom towards the acceptor atom.

(c) Once a dative bond is formed, it is exactly like a covalent bond in character. i.e. strong and shared by the two bonded atoms.

(d) The dative bond is represented by the symbol \rightarrow . The arrow points from the donor atom towards the acceptor atom.

Examples: Dative bonding can exist in different classes of substances


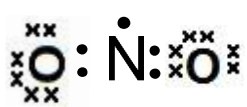

| Classes | Examples |
|----------------------------------|----------------------------------------------------------------------------------------|
| Simple covalent molecules | Carbon monoxide, $\cdot\text{C}\equiv\text{O}$ $\text{BCl}_3\cdot\text{NH}_3$, |

| | | |
|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| Between positive metal ions and lone pair of electrons from ligands | $[\text{Fe}(\text{CN})_6]^{4-}$,  | $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$,  |
| Between atoms in ions | NO_3^- ,  | Try: Can you draw NH_4^+ and H_3O^+ also? |
| In certain covalent metal chlorides which are dimerised in the gaseous states | Al_2Cl_6 ,  | $(\text{BeCl}_2)_n$  |

3.5 Exceptions to Octet Rule

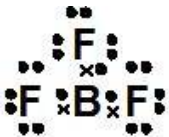


(a) Odd electron species

- Such species are called radicals and are very reactive. Not all electrons are paired. E.g. NO , NO_2 , ClO_2 .

| | | |
|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| NO  | NO_2  | ClO_2  |
|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|

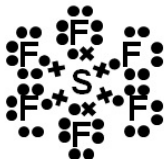
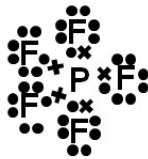

(b) Electron deficient species

- Molecules with fewer than 8 valence electrons, e.g. BF_3 , AlCl_3 , BeCl_2 .

| | | |
|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| BF_3  | AlCl_3  | BeCl_2  |
|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|

(c) Species with more than 8 valence electrons (**expansion of octet configuration**)

- Elements in **Period 3 and after** where they have **energetically accessible empty d-orbitals** to accommodate more than 8 electrons

| | | |
|----------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| SF_6  | PF_5  | XeF_4  |
|----------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|

**Exercise 8**

Why does SF_6 exist but not OF_6 ?

Thinking Process:

- What is the difference in these 2 compounds?
- How does the position of the central atom in the Periodic Table affect the number of electrons that is allowed around it?

Answer:

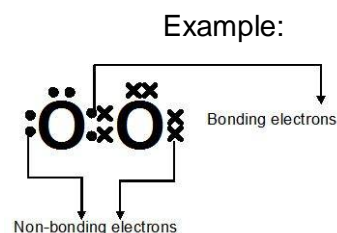
- O and S belong to Group 16, but O is in Period 2 while S is in Period 3.
- S can use its **energetically accessible empty 3d orbitals** to accommodate the extra electrons to form SF_6 whereas oxygen does not have/cannot expand its octet structure.

4 Shapes of Molecules and Molecular Ions

- (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)

- (a) Covalent bonds are **directional**. Hence covalent molecules or ions with covalent bonds have **definite** shapes.
- (b) The arrangement of atoms in space determines the shapes of molecules and molecular ions and is governed by the **V**alence **S**hell **E**lectron **P**air **R**epulsion (**VSEPR**) Theory
- (c) There are two types of electron pairs around the atom.

- i. **Bonding** electrons
- ii. Non-bonding electrons or **lone pair** electrons

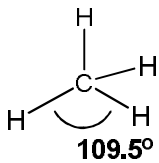
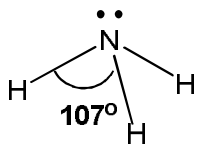


(d) **3 Basic principles:**

- i. Electron pairs **repel** each other and **arrange themselves as far apart as possible to maximise stability** and **minimise electrostatic repulsion**.
- ii. Orbitals containing lone pairs are larger than those containing bond pairs or an odd electron. They take up **more space** around the central atom and are, on average, closer to the nucleus. Hence, they have a **greater repulsive effect** than the bond pairs.
- iii. The order of the extent of repulsion is:



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

Example: CH₄, NH₃

| | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| CH ₄ | NH ₃ |
|  |  |
| Both covalent molecules have the same number of electron pairs; however, NH ₃ has a <u>smaller</u> bond angle than CH ₄ because of the <u>greater repulsion</u> between lone pair and bond pair of electrons. This forces the bond pairs closer together and hence a smaller bond angle of <u>107°</u> . | |

- iv. Repulsion between electron pairs is increased by increase in **electronegativity** of the central atom and vice versa.

Example: H₂O and H₂S

| | |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| H ₂ O | H ₂ S |
|  |  |
| Both H ₂ O and H ₂ S are covalent molecules with the bent shape (2 bond pairs of electrons and 2 lone pairs of electrons). In H ₂ O, oxygen has a <u>greater</u> electronegativity than sulfur in H ₂ S. Hence, the bond pair of electrons are more <u>strongly</u> attracted to oxygen, resulting in <u>greater</u> repulsion between the bond pairs in water. Hence, the H-S-H bond angle in H ₂ S is <u>less than 105°</u> . | |

**Exercise 9****Thinking Process:**

- What is the difference in these 2 compounds?
- How does electronegativity affect the bond angle?

Between PH₃ and PF₃, which molecule has a smaller bond angle?

Answer:

F is more electronegative than H. In PF₃, the bond pairs of electrons are attracted more towards F and **further away** from P. This results in **less repulsion** and **smaller bond angle**.

(e) Steps in predicting shapes:

- (i) Determine the central atom.
- (ii) Determine the **number of sigma (σ) bond pairs** and **lone pairs of electrons** around **the central atom**.
- (iii) Follow the assignment of shapes according to the VSEPR theory.

4.1 Shapes of Neutral species**i. Two electron pairs**

Electron pair geometry: Linear

| | |
|-----------------------------------------|--------------------------|
| | N_2O |
| No. of bond pairs (around central atom) | 2 |
| No. of lone pairs | 0 |
| Shape of molecule | Linear |
| Bond angle | 180° |

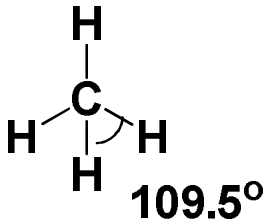
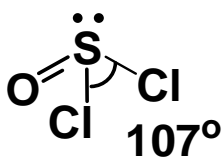
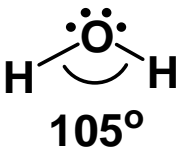
ii. Three electron pairs

Electron pair geometry: Trigonal Planar

| | | |
|-----------------------------------------|------------------------|-----------------------------|
| | BF_3 | SO_2 |
| No. of bond pairs (around central atom) | 3 | 2 |
| No. of lone pairs | 0 | 1 |
| Shape of molecule | Trigonal planar | Bent |
| Bond angle | 120° | Bond angle: 110-120° |

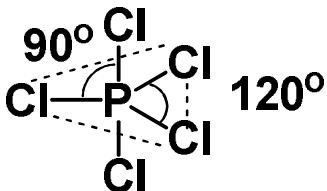
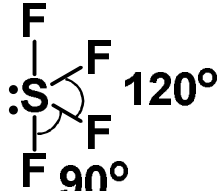
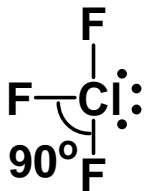
i. Four electron pairs

Electron pair geometry: Tetrahedral

| | | | |
|-----------------------------------------|----------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| | CH_4  | SOCl_2  | H_2O  |
| No. of bond pairs (around central atom) | 4 | 3 | 2 |
| No. of lone pairs | 0 | 1 | 2 |
| Shape of molecule | Tetrahedral | Trigonal pyramidal | Bent |
| Bond angle | 109.5° | 107° | 105° |

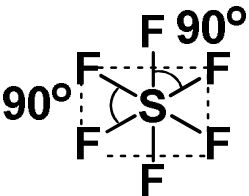
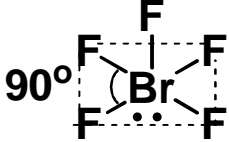
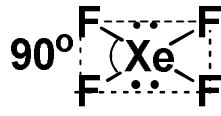
iv. Five electron pairs

Electron pair geometry: Trigonal Bipyramidal

| | | | |
|-----------------------------------------|-------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------|
| | PCl_5  | SF_4  | ClF_3  |
| No. of bond pairs (around central atom) | 5 | 4 | 3 |
| No. of lone pairs | 0 | 1 | 2 |
| Shape of molecule | Trigonal bipyramidal | See-Saw or distorted tetrahedral | T-shaped |
| Bond angle | 90° and 120° | 90° and 120° | 90° |

v. Six electron pairs

Electron pair geometry: Octahedral

| | | | |
|-----------------------------------------|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| | SF_6  | BrF_5  | XeF_4  |
| No. of bond pairs (around central atom) | 6 | 5 | 4 |
| No. of lone pairs | 0 | 1 | 2 |
| Shape of molecule | Octahedral | Square pyramidal | Square planar |
| Bond angle | 90° | 90° | 90° |

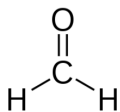
**Exercise 10** [N2017/P1/3(modified)]**Thinking Process (for both questions):**

- Which is the central atom?
- How many bond pairs and lone pairs are around the central atom?
- What is the shape according to VSEPR theory?

Valence Shell Electron Pair Repulsion theory can be used to predict the bond angles in methanol CH_2O . Which bond angle will this theory predict for the H-C-H bond angle in methanal?

A 104.5°**B** 107°**C** 109.5°**D** 120°

Ans: (D)



Methanal has a 3 bond pairs, hence, have the shape of trigonal planar. The bond angle is 120°.

Video: Shapes of species (viewed in 3D)

https://www.youtube.com/watch?time_continue=18&v=keHS-CASZfc

**Interactive animation:**

https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html



4.2 Shapes of Charged species



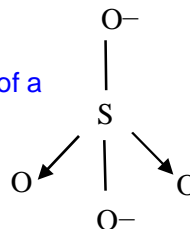
- TIP**
- For **positively charged species**, electrons are **removed** from the **less** electronegative atoms
 - For **negatively charged species**, electrons are **added** to the **more** electronegative atoms.

| | | | |
|-----------------------------------------------|------------------------|-------------------------|----------------------|
| | NO_3^- | SO_4^{2-} | NH_4^+ |
| | | | |
| No. of sigma bond pairs (around central atom) | 3 | 4 | 4 |
| No. of lone pairs | 0 | 0 | 0 |
| Shape of molecule | Trigonal planar | Tetrahedral | Tetrahedral |
| Bond angle | 120° | 109.5° | 109.5° |
| | BrF_4^+ | I_2Cl^- | ICl_4^- |
| | | | |
| No. of sigma bond pairs (around central atom) | 4 | 2 | 4 |
| No. of lone pairs | 1 | 3 | 2 |
| Shape of molecule | See-saw | Linear | Square planar |
| Bond angle | 90°, 120° | 180° | 90° |

Thinking Question:

1. Why is this structure for SO_4^{2-} not accepted?

A dative bond is considered a single bond. Formation of a dative bond releases less energy than a double bond. Hence, this proposed structure is less stable.



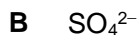
2. What shapes are considered to be planar?

Linear, bent, trigonal planar, T-shaped, square planar



Exercise 10

1. Which of the following ions is planar?



NO_2^- : 2 b.p., 1 l.p. = Bent (Planar)

SO_4^{2-} : 4 b.p., 0 l.p. = Tetrahedral (Non-planar)

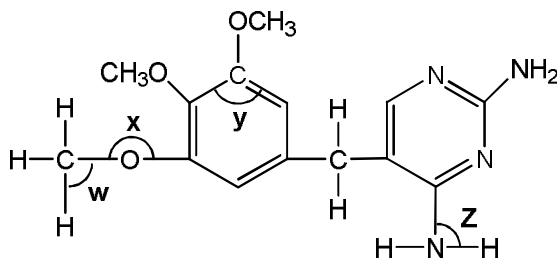
H_3O^+ : 3 b.p., 1 l.p. = Trigonal pyramidal (Non-planar)

PCl_4^+ : 4 b.p., 0 l.p. = Tetrahedral (Non-planar)

Thinking Process:

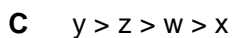
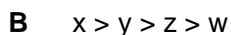
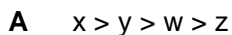
- Which is the central atom?
- How many bond pairs and lone pairs are around the central atom?
- What is the shape according to VSEPR theory?

2. Trimethoprim (TMP) is used for the treatment and prevention of urinary tract infections, traveller's diarrhoea, respiratory and middle ear infections. It has the structure as shown on the right :



Trimethoprim (TMP)

In which sequence are the bond angles quoted in decreasing order?



$w = 109.5^\circ$, $x = 105^\circ$, $y = 120^\circ$, $z = 107^\circ$

Self- Check: Q5

Reference: Summary Table of Shapes (Pg 59)

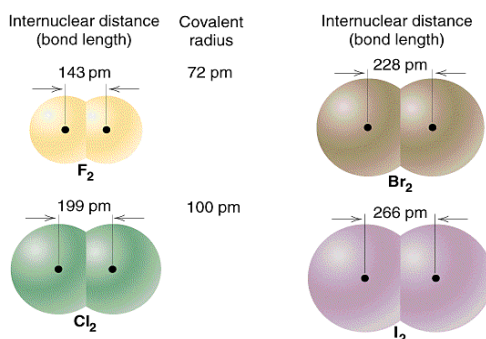
5 Covalent Bond Strength

(k) explain the terms *bond energy* and *bond length* for covalent bonds
 (l) compare the relativities of covalent bonds in terms of bond energy, bond length and bond polarity

(a) Bond length and bond energy gives an indication of the strength of a covalent bond.

- Bond length** is the distance between the nuclei of the two bonded atoms when their atomic orbitals overlap to form molecular orbitals.

Example:



- Bond energy** is the energy required to break 1 mole of a covalent bond between 2 atoms in the gaseous state.

Example: $A - B(g) \rightarrow A(g) + B(g)$

Bond Energy = + x kJ mol⁻¹

(b) Factors affecting covalent bond strength:

(I) Bond length & bond energy

- Smaller atoms can approach each other more closely
- More effective overlap of atomic orbitals
- Shorter bond length → stronger bond (larger bond energy)

| | Cl – Cl | Br – Br | I – I |
|------------------------------------|----------------|----------------|--------------|
| Bond Length / nm | 0.199 | 0.228 | 0.266 |
| Bond Energy / kJ mol ⁻¹ | 244 | 193 | 151 |

(II) Bond order (number of chemical bonds between a pair of atoms)

- Multiple bonds have larger bond energy than single bonds

Example:

| | C – C | C = C | C ≡ C |
|------------------------------------|--------------|--------------|--------------|
| Bond Energy / kJ mol ⁻¹ | 346 | 610 | 837 |

(III) Bond polarity

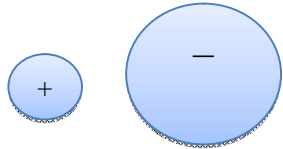
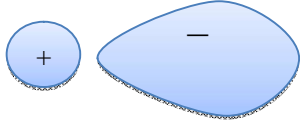

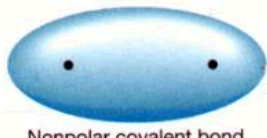
- When bond length is comparable, the strength of the bond can be determined by the polarity of the bond. The **greater the electronegativity difference** between the bonding atoms, the **more polar** the bond, the **stronger** the bond. (Recap: Electronegativity is the ability of an atom in a molecule **to attract the shared electrons** in a covalent bond.)

Example:

| | N – H | O – H | F – H |
|------------------------------------|-------|-------|-------|
| Bond Length / nm | 0.099 | 0.098 | 0.092 |
| Electronegativity Difference | 0.9 | 1.4 | 1.9 |
| Bond Energy / kJ mol ⁻¹ | 388 | 463 | 562 |

6 Effect of electronegativity difference on bond type

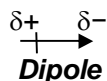
Bonding is rarely entirely ionic or covalent, it is usually some mixture of the two.

| | | | |
|------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|--------------------------------------------------------------------------------------|-----------------------|
| Pure ionic bond | Complete transfer of electrons |  | EN difference >1.7 |
| Ionic bond with covalent character (results from polarisation of anions by cations) | Partial transfer of electrons |  | 0.4–1.7 |
| Covalent bond with ionic character (results from unequal sharing of bonding electrons due to the difference in electronegativity of atoms) | Unequal sharing of electrons |  | <0.4 |
| Covalent bond | Equal sharing of electrons |  | 0 |

6.1 Bond Polarity

- (f) explain and deduce bond polarity using the concept of electronegativity
[quantitative treatment of electro-negativity is **not** required]
- (g) deduce the polarity of a molecule using bond polarity and its molecular shape
(analogous to those specified in (d));

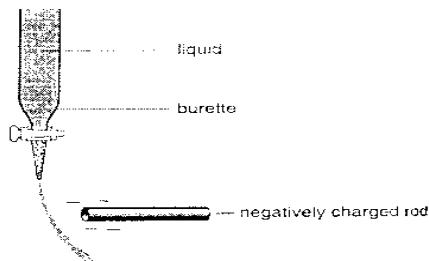
- i. When two different atoms of different electronegativity are covalently bonded, the **more electronegative atom** pulls the electrons of the covalent bond towards itself and acquires a **small negative charge (δ^-)** while the other atom acquires a **small positive charge (δ^+)**. This results in **charge separation (dipole)** and the bond is **polar**. E.g. H – Br



- ii. The polarity of a bond is measured by **dipole moment, μ** (usually represented by an arrow pointing towards the more electronegative atom). Dipole moments are like vectors.

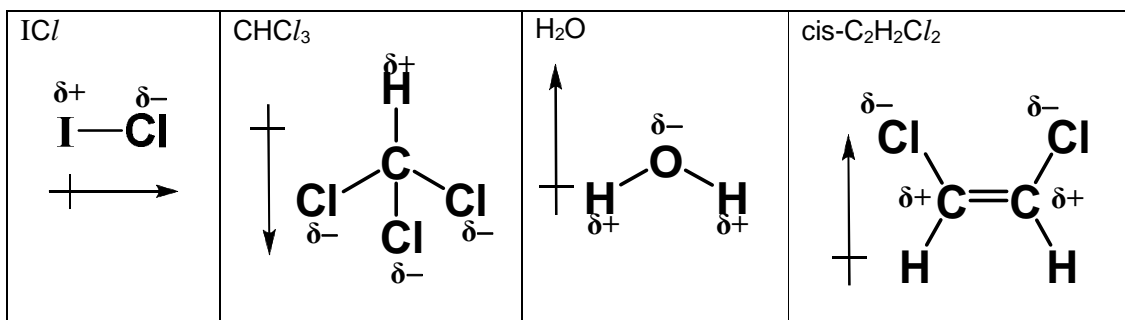
6.2 Polar Molecules

- i. A molecule is polar only if it has dipole(s) where the distribution of charge in the molecule is **nonsymmetrical** (i.e. the individual dipoles do not cancel each other). Hence a polar molecule has an **overall dipole moment**.
- ii. Thus, the bonding electrons will not be evenly shared, giving rise to a permanent dipole in the molecule, giving rise to a polar covalent bond.
- iii. A covalent bond has some ionic character.
- iv. In the presence of an electric field, the polar molecule will orientate themselves due to the partial charges.



The diagram (taken from J97/P3/3) above illustrates how trichloromethane flowing from a burette will be deflected when a charged rod is brought near the flow.

Examples of polar molecules:



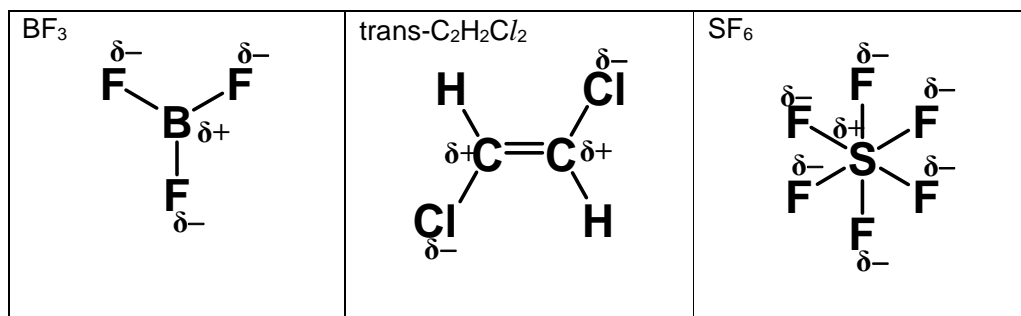
Note: Arrows in the diagrams above represent overall dipole moment.

6.3 Non-Polar Molecules

A **non-polar molecule** is one that has **no overall dipole**. This can be due to:

- no polar bond** in the molecule i.e. when all the atoms are the same e.g. Cl_2
- polar bonds in the molecule. But if two **dipoles** have the same magnitude and are opposite in directions, they **cancel each other**. The molecule has a **zero overall dipole moment**.

Examples of non-polar molecules:



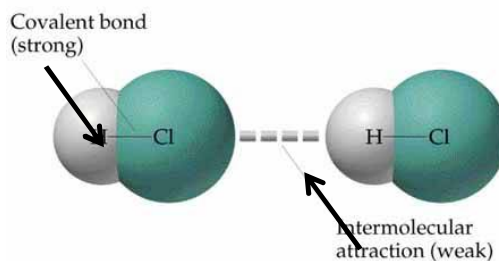
Self-Check: Q6 & 7

7 Physical properties of Simple Covalent Molecules

- (n) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances
- (o) suggest the type of structure and bonding present in a substance from given information

Simple covalent molecules are attracted to each other by weak intermolecular forces. The forces of attraction are much weaker than ionic, metallic and covalent bonds.

Take hydrogen chloride, HCl for example, between H and Cl atoms, strong covalent bond exists. **Between HCl molecules**, intermolecular forces exist, which affects the physical properties of the covalent compounds.



The molecular structure and type of bonding give rise to the following physical properties.

- Melting point and boiling point
- Solubility
- Electrical Conductivity

7.1 Intermolecular forces

(h) describe the following forces of attraction (electrostatic in nature):

- intermolecular forces, based on permanent and induced dipoles, as in liquid and gaseous CHCl_3 ; Br_2 and the noble gases
- hydrogen bonding, using ammonia and water as examples of molecules containing -NH and -OH groups

- The type of intermolecular forces present within the simple molecules are:
 - Instantaneous dipole-induced dipole attractions (id-id)
 - Permanent dipole-permanent dipole attractions (pd-pd)
 - Hydrogen bonding (an extreme form of pd-pd)
- Comparison in strength of the forces for molecules **comparable in total number of electrons**:

id-id attractions < pd-pd attractions < hydrogen bonding

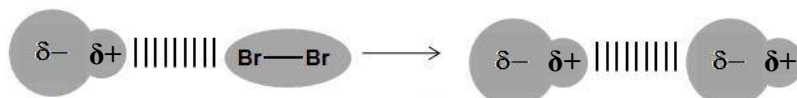
7.2 Instantaneous dipole-induced dipole attractions (id-id)

- Id-id forces of attraction exist for **all molecules**. **Non-polar molecules** experiences id-id attractions only.
- In a non-polar molecule, like Cl_2 or Br_2 , there is no difference in the electronegativity of the two bonding atoms and electrons are evenly distributed.
- As electrons are constantly moving, there could be an **instantaneous dipole** formed when there are more electrons on one side of the molecule. Hence there could be a small partial charge of δ^+ on one atom and δ^- on another atom. This occurs even for a monoatomic element such as Ne.

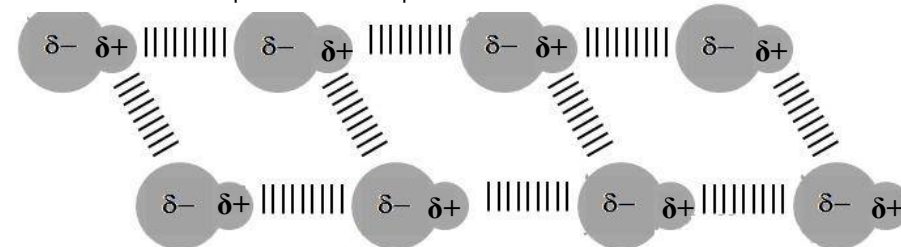
- When another neighbouring molecule approaches, the **instantaneous dipole** can **induce** a **temporary dipole** in this neighbouring molecule by attracting/repelling its electrons.
- These temporary weak intermolecular forces of attraction between the two molecules with opposite partial charges are called **instantaneous dipole-induced dipole attractions**.
- Id-id attractions are weak and short ranged. Hence, they operate between portions of molecules that are close to each other only.



1. Formation of instantaneous dipole



2. Instantaneous dipole induces a dipole in another molecule



3. Formation of network of instantaneous dipole-induced dipole attractions in a simple molecule structure

- The diagram above shows how a whole lattice of molecules could be held together using instantaneous dipole-induced dipole attractions.
- Non-polar** molecules only has instantaneous dipole-induced dipole attractions.

7.2.1 Factors affecting strength of instantaneous dipole – induced dipole attraction

(I) Number of electrons

- Molecules which have **more electrons** will cause the molecular electron clouds to be **more easily polarised**, resulting in stronger id-id attractions.

Example: Comparison of id-id attractions across period 3

| Element | Phosphorus, P ₄ | Sulfur, S ₈ | Chlorine, Cl ₂ | Argon, Ar |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|------------------------|---------------------------|-----------|
| M _r | 124 | 256.8 | 71.0 | 39.9 |
| Boiling point /°C | 277 | 445 | –34 | –186 |
| Note: Although higher M _r implies a larger number of electrons but comparison of M _r is not a marking point in your answer. Use “ number of electrons ” instead. | | | | |

**Exercise 11****Thinking Process:**

- What structures do they have?
- What bonds/interactions need to be broken during boiling?
- What are the factors that affect the strength of such interactions?
- Comparison of b.p: SIA format

1. Which molecule, SiH₄ or CH₄, has a higher boiling point (less volatile)?

Explain.

Answer:

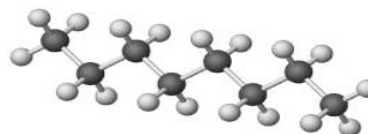
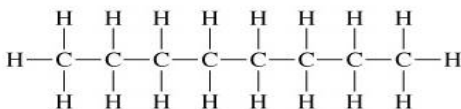
Both SiH₄ and CH₄ are non-polar simple covalent molecules with instantaneous dipole-induced dipole (id-id) attractions between the molecules. SiH₄ has a larger number of electrons than CH₄ and forms stronger id-id attractions. More energy is required to overcome the stronger id-id in SiH₄. Hence, SiH₄ has a higher boiling point than CH₄.

(II) Surface area

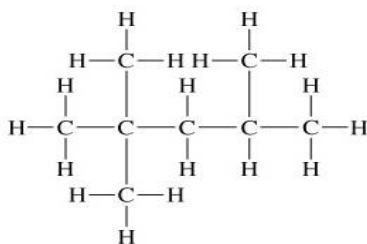
- For different molecules with the same number of electrons, id – id attractions are more extensive in molecules with greater surface area for molecular interactions/attractions.
- Straight chain molecules have a more open structure and hence greater surface area for molecular attractions compared to branched chain isomers which are more compact and spherical. The id-id attractions are hence more extensive in straight chain molecules.

Example: octane and 2,2,4-trimethylpentane

(a) Octane
CH₃(CH₂)₆CH₃
melting point -56.8 °C
boiling point 125.7 °C



(b) (Isooctane)
2,2,4-Trimethylpentane
CH₃C(CH₃)₂CH₂CH(CH₃)₂
melting point -104.7 °C
boiling point 99.2 °C





Exercise 12

Explain the difference in the boiling points between butane and 2-methylpropane

| Compound | Structure | M_r | Boiling point |
|-----------------|------------------------------------------------------------------------------------------------------------------------------|-------|---------------|
| Butane | <pre> H H H H H — C — C — C — C — H H H H H </pre> | 58.0 | -0.5°C |
| 2-methylpropane | <pre> H H H H—C—C—C—H H H H </pre> | 58.0 | -11.7°C |

Thinking Process:

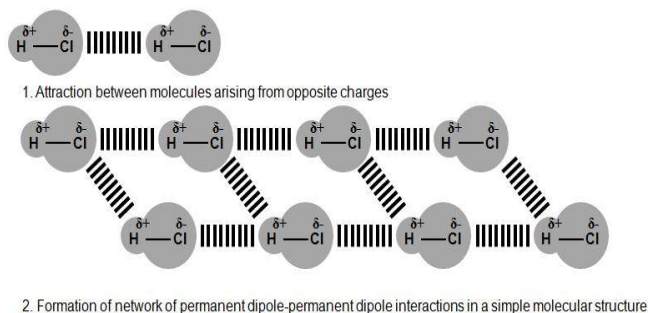
- What kind of compounds are they?
- What bonds/interactions need to be broken during boiling?
- What are the factors that affect the strength of such interactions?
- Comparison of b.p. SIA format

Answer:

Both butane and 2-methylpropane are **non-polar simple covalent molecules** with **instantaneous dipole-induced dipole (id-id) attractions** between the molecules. They are isomers with the same number of electrons. The butane molecules have a **larger surface area** and hence can form **more extensive** id-id attractions. **More energy** is required to overcome the more extensive attractions between butane molecules than 2-methylpropane. Butane has a higher boiling point.

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

- **All** molecules experience id-id attractions.
- **Polar** molecules such as CHCl_3 , CH_3CHO , NCl_3 have additional **permanent dipole-permanent dipole attractions** between them due to the **non-symmetrical** distribution of electrons within the molecule as the atoms have different electronegativity. The more electronegative atom will attract electrons towards itself and acquire a partial negative charge, whereas the less electronegative atom will have a partial positive charge.



Case studies:

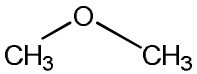


Exercise 13

Thinking Process:

- What structures do they have?
- What bonds/interactions need to be broken during boiling?
- From the data, what is the factor here that affects the b.p?
- Comparison of b.p: SIA format

1. Explain why $(\text{CH}_3)_2\text{O}$ has a higher boiling point than $\text{CH}_3\text{CH}_2\text{CH}_3$.

| Compound | $(\text{CH}_3)_2\text{O}$ | $\text{CH}_3\text{CH}_2\text{CH}_3$ |
|------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------|
| Structure |  | $\text{CH}_3\text{CH}_2\text{CH}_3$ |
| M_r | 46 | 44 |
| Boiling point / $^{\circ}\text{C}$ | 34.6 | -42.0 |

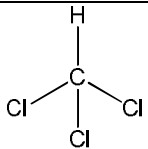
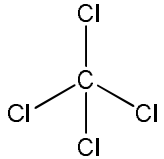
Answer:

Both compounds are simple covalent molecules. $\text{CH}_3\text{CH}_2\text{CH}_3$ is non-polar with instantaneous dipole-induced dipole (id-id) attractions while $(\text{CH}_3)_2\text{O}$ is polar with additional permanent dipole-permanent dipole (pd-pd) attractions. More energy is required to overcome the pd-pd attractions and hence $(\text{CH}_3)_2\text{O}$ has a higher boiling point.

2) Explain the difference in the boiling points between trichloromethane, CHCl_3 , and tetrachloromethane, CCl_4 .

| Molecule | M_r | Boiling point / $^{\circ}\text{C}$ |
|-----------------|-------|------------------------------------|
| CHCl_3 | 119.5 | 61.2 |
| CCl_4 | 154 | 76.8 |

• Thinking Process:

| Compound | Shape of Molecule | Type of molecule | B.p / $^{\circ}\text{C}$ | id-id | pd-pd |
|-----------------|-------------------------------------------------------------------------------------|------------------|--------------------------|-------|-------|
| CHCl_3 |  | Polar | 61.2 | ✓ | ✓ |
| CCl_4 |  | Non-polar | 76.8 | ✓ | |

Answer:

Both CHCl_3 and CCl_4 are **simple covalent molecules**. CCl_4 is non-polar with **instantaneous dipole-induced dipole (id-id) attractions** while CHCl_3 is polar with additional **permanent dipole-permanent dipole (pd-pd) attractions**.

However, CCl_4 contains **more electrons** than CHCl_3 resulting in **stronger id-id attractions**.

More energy is required to overcome the stronger id-id attractions in CCl_4 . Hence CCl_4 has a higher boiling point.

Learning point:

Polar molecules have both id-id and pd-pd attractions. Its boiling point is only higher than non-polar molecules with **comparable number of electrons**. However, a larger non-polar molecule could have higher boiling point than a smaller polar molecule as its number of electrons is significantly larger and hence, id-id is significantly stronger and requires more energy to overcome.

7.4 Hydrogen bonding

(h) describe the following forces of attraction (electrostatic in nature):

- (ii) hydrogen bonding, using ammonia and water as examples of molecules containing $-\text{NH}$ and $-\text{OH}$ groups

Hydrogen bonding is an **extreme** form of permanent dipole-permanent dipole attractions. It is the **electrostatic force of attraction** between a **hydrogen** atom **covalently bonded** to a **highly electronegative atom** (F, O or N) and the **lone pair of electrons of another highly electronegative atom** (F, O or N).

When H atom is covalently bonded to a highly electronegative atom, it becomes almost **bare** or the nucleus of the H atom becomes very exposed. The attraction between the δ^+ of H atom with the lone pair of electron of another highly electronegative atom (F, O or N) is then particularly **strong**.

- The criteria for forming hydrogen bonding is
 - **H atom covalently bonded to F, O or N** and
 - **lone pair of electrons on another F, O or N**

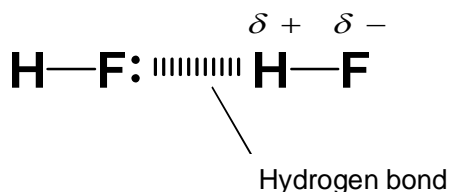
Examples: HF , NH_3 and H_2O

7.4.1 Intermolecular hydrogen bond

There are 3 ways of forming hydrogen bonds between 2 molecules:

1. Between 2 identical molecules
2. Between 2 different molecules
3. Between a molecule with H bonded to F, O or N and a **hydrogen bond acceptor**

1. Formed between **identical molecules** e.g. between HF molecules:

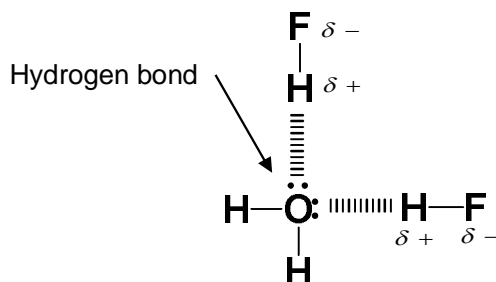


Checklist for representing hydrogen bond:

- ☒ $\delta+$ on H, and $\delta-$ on electronegative atoms
- ☒ Lone pair of electron on F, O or N
- ☒ Dotted line and label to

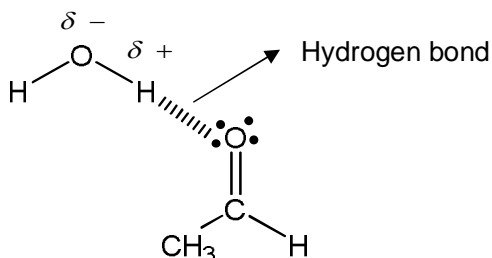
2. Formed between different types of molecules (e.g. between HF and H₂O).

Example:



3. Formed between a molecule (that has a hydrogen atom covalently bonded to F, O or N) and a **hydrogen bond acceptor**. A hydrogen bond acceptor is a molecule that has lone pair of electrons on F, O or N. It need not have hydrogen atom directly bonded to F, O or N.

Example:



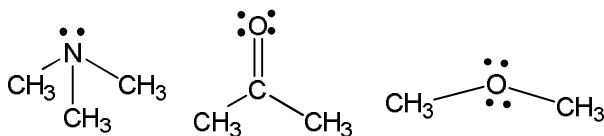
Think!

Can CH3CHO form intermolecular hydrogen bonds with itself?

Larger amount of energy is required to overcome the hydrogen bonding present between molecules, as compared to id-id and pd-pd attractions **for molecules of comparable number of electrons**. The energies of hydrogen bonds typically range

from about 4 to 25 kJ mol⁻¹, which are still **weaker than the covalent bonds** which easily have bond energies greater than 100 kJ mol⁻¹.

Other examples of hydrogen bond acceptors:

**Exercise 14** [N2017/P1/4]

Water has a much higher boiling point than methane.

What are the **major** reasons for this?

- 1 Strong hydrogen bonds exist between water molecules.
- 2 The O-H bonds in water are stronger than the C-H bonds in methane.
- 3 The water molecules contains more electrons than the methane molecule.

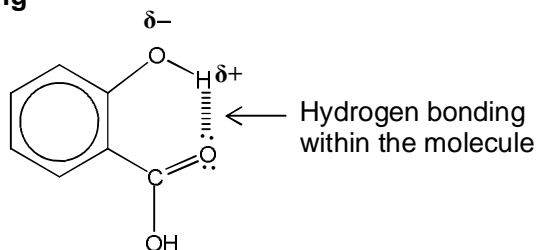
A 1,2 and 3 **B** 1 and 2 only **C** 1 only **D** 2 and 3 only

Ans: C (1 only)

During boiling, only the intermolecular bonding are broken. Hence, covalent bonds such as O-H and C-H are not affected.

The no. of electrons that water and methane molecules have are comparable. Hence, the id-id attractions are similar. The hydrogen bonding that existing between water molecules requires a larger amount of energy to overcome compared to the id-id between the CH₄ molecules, hence higher boiling point.

7.4.2 Intramolecular hydrogen bonding



- Hydrogen bonding not only occurs between molecules, but can also exist **within** the molecule due to the **proximity** of the substituents.
- Such compounds undergo **intramolecular hydrogen bonding**.
- Since the 2 substituents are used for intramolecular hydrogen bonding, they have less tendency to attract neighbouring molecules by intermolecular hydrogen bonding, resulting in **less extensive intermolecular hydrogen bonding**.
- The boiling point of the compound would be lower than expected.

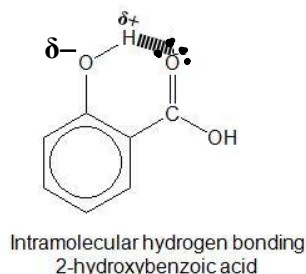


Exercise 15

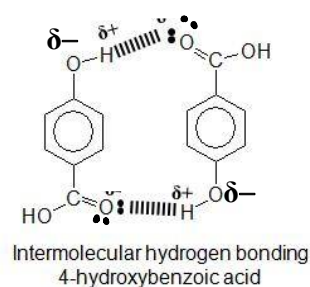
Thinking Process:

- What is the difference in the structures of A and B?
- What interactions need to be broken during boiling?
- From the data, what is the factor here that affects the b.p?
- Comparison of b.p: SIA format

1. Why is the boiling point of compound **A** lower than compound **B**?



A:



B:

Answer:

Both compounds are polar simple covalent molecules, capable of hydrogen bonding.

Due to the proximity of the 2 functional groups ($-\text{OH}$ and $-\text{COOH}$) in **A**, it forms intramolecular hydrogen bonding. Hence, it has less extensive intermolecular hydrogen bonding.

Boiling point of **A** is lower than **B** as less energy is required to overcome the less extensive intermolecular hydrogen bonding.

7.4.3 Factors affecting strength of Hydrogen bonding

Boiling points of HF , H_2O and NH_3 are listed in the table below:

| Compound | Boiling Point ($^{\circ}\text{C}$) |
|----------------------|--------------------------------------|
| HF | 20.0 |
| H_2O | 100 |
| NH_3 | -33.0 |

(i) Electronegativity difference between H and F, O or N

- The **larger** the difference \Rightarrow the **stronger** the hydrogen bond

| Element | Fluorine | Oxygen | Nitrogen |
|-------------------|----------|--------|----------|
| Electronegativity | 3.98 | 3.44 | 3.04 |

Example: Compare the boiling points between HF and NH_3

- F, being **more electronegative** than N, is able to attract electrons from H atom more effectively. This results in a stronger attraction between the H atom and the

F atom of the neighbouring molecule. Hence a larger amount of energy to overcome the forces of attraction between HF molecules.

Therefore, boiling point: $\text{HF} > \text{NH}_3$

(ii) Extent of hydrogen bonding

Example: Compare the boiling points between HF, NH_3 and H_2O

- Number of hydrogen bonds formed per molecule

| Molecule | No. of H bonded to F/O/N | No. of lone pairs on F/O/N connected to H | No. of hydrogen bonds per molecule |
|----------------------|--------------------------|-------------------------------------------|------------------------------------|
| HF | 1 | 3 | 1 |
| NH_3 | 3 | 1 | 1 |
| H_2O | 2 | 2 | 2 |

- The expected boiling point is $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$.
- However, the boiling point of H_2O is found to be **highest**.
- This can be explained by the fact that there is an average of **2 hydrogen bonds per H_2O molecule** due to the **presence of 2 lone pairs and 2 H atoms bonded to O**. In both HF and NH_3 , there is only **one** hydrogen bond per molecule. Hence, **the extent of H-bonding** in H_2O is greater.
- The actual order of boiling point is **$\text{H}_2\text{O} > \text{HF} > \text{NH}_3$** .

☞ Self- Check: Q8

Effects of hydrogen bonding

(a) Anomaly in Boiling points

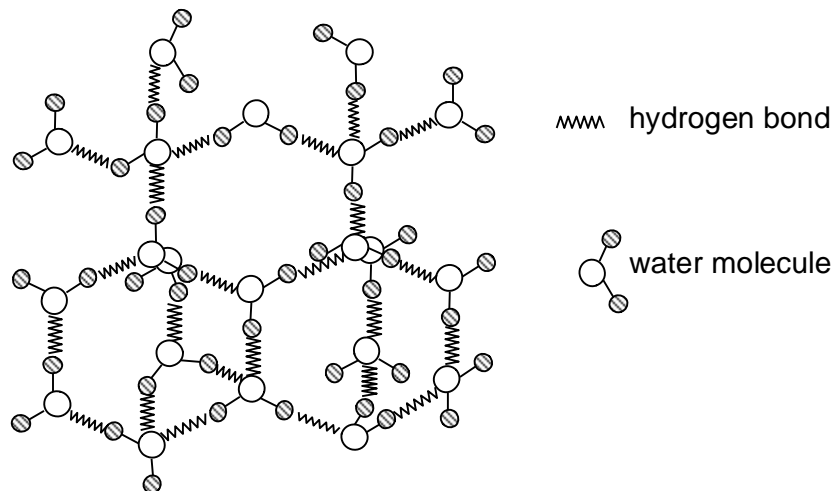
HF, H_2O and NH_3 have boiling points which are much higher than expected compared to the compounds form from the elements in the same group.

(b) Structure and properties of ice

(j) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water

(m) describe, in simple terms, the lattice structure of a crystalline solid which is:

(iv) hydrogen-bonded, as in ice



- Most liquids become denser when they change into their solid forms. Not so with water: ice floats on water!
- The lower density of ice than water is due to the **highly ordered 3-dimensional structure in ice** which arises from **hydrogen bonding**.
- Each oxygen atom in ice is **tetrahedrally bonded** to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. This enables the water molecules in ice to form **rigid, open, 3-dimensional networks** as shown above.
- This highly ordered 3-dimensional arrangement of H₂O molecules in ice creates a very **open** structure and prevents the molecules from getting too close to one another.
- This open structure occupies a larger volume for the same mass of liquid water. Hence ice is less dense than liquid water.

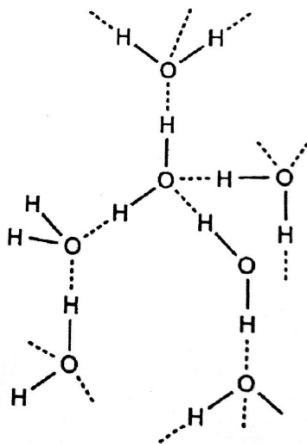
Video: Why ice floats on water?

<https://www.youtube.com/watch?v=UukRgqzk-KE>




Exercise 19 [N2007/P1/7]

The diagram shows the structure of part of a crystal of ice.


Thinking process:

What type of bonding is present in ice?

Which statement is correct?

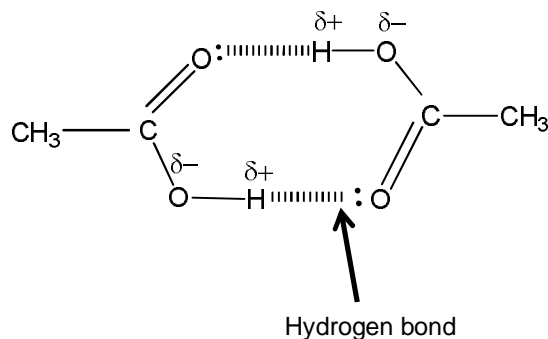
- A** All the bond angles surrounding each oxygen atom are 120° .
- B** Four electrons from each oxygen are involved in forming hydrogen bonds.
- C** The hydrogen bonds, shown by the dotted lines, are stronger than the O–H covalent bonds.
- D** The open structure of ice causes ice to be denser than water.

Ans: B

- A** All the bond angles surrounding each oxygen atom are 109.5° .
- B** 2 hydrogen bond per water molecule. Each hydrogen bond is formed from the interaction of a δ^+H atom and a lone pair of electrons on O.
- C** The hydrogen bonds are weaker than the O–H covalent bonds.
- D** The open structure of ice causes ice to be less dense than water.

(c) Anomalous relative molecular mass

- Hydrogen bonding can occur between two molecules of carboxylic acids, e.g. ethanoic acid, CH_3COOH to form a **dimer**.
- When dissolved in a non-polar organic solvent or in the gaseous phase, the apparent M_r of ethanoic acid is 120 instead of 60.



Summary Table of intermolecular forces for simple covalent molecules

| | | | |
|-----------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| Type of intermolecular forces | instantaneous dipole – induced dipole (id-id) attractions | Permanent dipole – permanent dipole (pd-pd) attractions | Hydrogen bonding |
| Type of molecules where IMF is present | Between all molecules (both non-polar and polar) | Between polar molecules | Between a molecule with H bonded to F, O or N and a molecule with lone pair of electrons on F, O or N |
| Factors affecting IMF | 1. No. of electrons 2. Surface area | Not applicable | 1. Number of hydrogen bonds per molecule 2. Electronegativity difference |
| Examples | Ne, H ₂ , CO ₂ , CH ₄ | CHCl ₃ , CH ₃ CHO, PCl ₃ | H ₂ O, NH ₃ , HF, C ₂ H ₅ OH |

7.5 Melting point and boiling point of simple molecules

- Melting and boiling points of simple molecules are relatively **low** since both melting and boiling processes involve **overcoming of the weak intermolecular forces**.

For molecules with **similar number of electrons**, strength of intermolecular H-bonds > pd-pd attractions > id-id attractions

7.6 Solubility of Simple Molecules

- When bonds or interactions are formed, energy is **released**.
- When bonds or interactions are broken, energy is **taken in**.

**Format of answering solubility questions:**

Energy released from forming solute-solvent interactions is sufficient / insufficient to overcome solute-solute interactions and solvent-solvent interactions. Hence, soluble / insoluble.

*Note: You **MUST SPECIFY** the type of interactions involved.

- Simple covalent molecules which are non-polar are usually **soluble in non-polar solvents**. Both the solute and the solvent are likely to have molecules attracted to each other by instantaneous dipole-induced dipole attractions. When the solute-solute, solvent-solvent and solute-solvent interactions are **all comparable** in strength, the solute is able to dissolve i.e soluble in the solvent.

Example: iodine in CCl_4

Energy released when forming **weak instantaneous dipole-induced dipole (id-id) attractions between iodine and CCl_4 molecules** is sufficient to overcome the id-id attractions between CCl_4 molecules and id-id attractions between iodine molecules.

- Simple molecules which are non-polar are usually **insoluble in polar solvents such as water**.

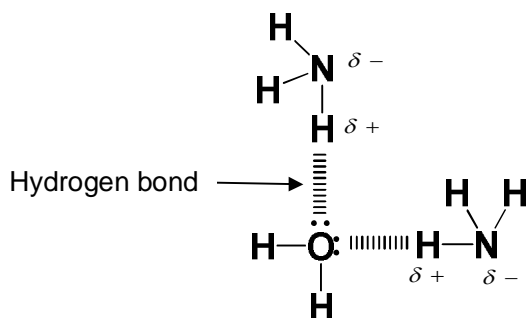
Example: iodine in water

Energy released when forming **weak instantaneous dipole-induced dipole (id-id) attractions between iodine and water molecules** is insufficient to overcome the hydrogen bonding between water molecules and id-id attractions between iodine molecules.

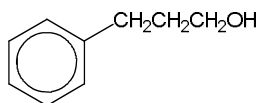
- Molecules which can form hydrogen bonding are usually soluble in water. The more extensive the hydrogen bonding formed, the more soluble the compound.

Example: Ammonia in water

Energy released when forming hydrogen bonding between ammonia and water molecules is sufficient to overcome the hydrogen bonding between water molecules and hydrogen bonding between ammonia molecules.



- Molecules will usually be **insoluble** when they have a **large non-polar group** where the **id-id** will be the predominant forces of attraction between molecules.



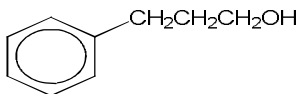
Example: $\text{CH}_3\text{CH}_2\text{OH}$ is soluble but

is insoluble in water

although both can form hydrogen bonding.



Exercise 16



Explain why

(3-phenylpropan-1-ol) is insoluble in water.

Thinking process:

What are the solute-solute, solvent-solvent and solute-solvent interactions?

Solution:

As 3-phenylpropan-1-ol has a **large** non-polar alkyl group, its **predominant forces are id-id attractions**. Energy released from forming **hydrogen bonding between water and 3-phenylpropan-1-ol** is **insufficient** to overcome the **hydrogen bonding between water** and the **id-id attractions between 3-phenylpropan-1-ol**.

Self- Check: Q9

7.7 Electrical Conductivity

Molecular substances are usually **non-conductors** of electricity due to the absence of mobile particles such as ions or electrons.

- The **electrons are usually localised** in the covalent bonds.

- However, if the molecule ionises in water, e.g. HCl , AlCl_3 , NH_3 , it may conduct electricity due to presence of charge carriers.

7.8 Liquefaction of Gases

(i) outline the importance of intermolecular forces to the liquefaction of gases when subjected to high pressure and / or low temperature

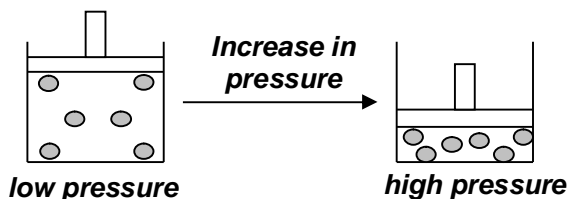
Liquefaction of gases is the process by which substances in their gaseous state are converted to the liquid state (condensation). A major commercial application of liquefaction is the liquefaction of air to allow separation of the constituents, such as oxygen, nitrogen, and the noble gases.

Liquefaction of gases occurs when the kinetic energy of the gas particles is not strong enough to overcome the intermolecular forces of attraction between the gas molecules. A combination of high pressure and low temperature allows gases to be liquefied. The ease of liquefaction of gases generally depends on the strength of intermolecular forces.

(1) At low Temperature

- The kinetic energy of the gas particles decreases and the particles move slower. The particles do not have sufficient energy to overcome the forces of attraction between each other. This causes the attractive forces between the particles to become more significant.
- Most gases can be liquefied by only lowering the temperature at standard pressure e.g. oxygen and nitrogen which has only weak instantaneous dipole – induced dipole intermolecular forces of attraction.

(2) At high Pressure



- The gas particles are closer together and the attractive forces between them become more significant. The particles do not have sufficient energy to overcome the forces of attraction between each other.

- Gases with stronger intermolecular forces (e.g. hydrogen bonding or more significant id-id) can only be liquefied by applying pressure at room temperature e.g. ammonia and butane.

(3) At high pressure and low temperature

This condition is required for gases with very weak forces e.g. helium (interatomic id-id).

🔗 Self- Check: Q10

8 Giant Covalent Molecule

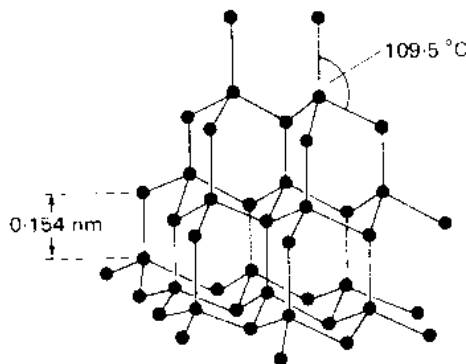
(m) describe, in simple terms, the lattice structure of a crystalline solid which is:

(iii) giant molecular, as in graphite; diamond

- A solid with a giant molecular structure is made up of atoms, usually non-metals, held together in an extensive network by **covalent bonds**.
- Such solids are said to be giant covalent molecules (**macromolecules**). E.g. diamond, graphite and quartz (silicon dioxide).
- Such substances usually have **high melting points** and exist as solids.

8.1 Diamond

- The structure of diamond is a three-dimensional array of carbon atoms.

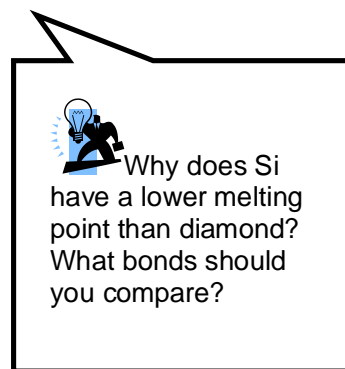
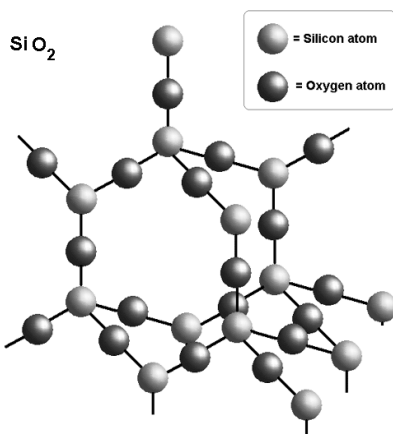


- Each carbon atom is covalently bonded to **4 other carbon atoms**. Hence, the geometry is tetrahedral with bond angles of 109.5° around each carbon atom. This tetrahedral arrangement is **repeated** throughout the entire molecule giving rise to interlocking hexagonal units so that the resultant structure is extremely strong and rigid. Diamond is the hardest natural occurring substance and is used in drill bits and glass cutters.
- Diamond **does not conduct electricity** as it **does not possess delocalised electrons**.
- Diamond has a melting point of 3550°C due to the **strong covalent bonds** between all the carbon atoms.

- Diamond **does not dissolve in water** or any other solvent as a lot of energy is required to overcome the strong covalent bonds between the carbon atoms. This amount of energy is not compensated by the solvation energy released if diamond dissolves in water or other solvents.
- Silicon has the same structure as diamond and is also hard. However, the covalent bonds between the silicon atoms are **weaker** than those between the carbon atoms in diamond. Thus, silicon's melting point is lower at 1410 °C.

8.2 Quartz (Silicon Dioxide)

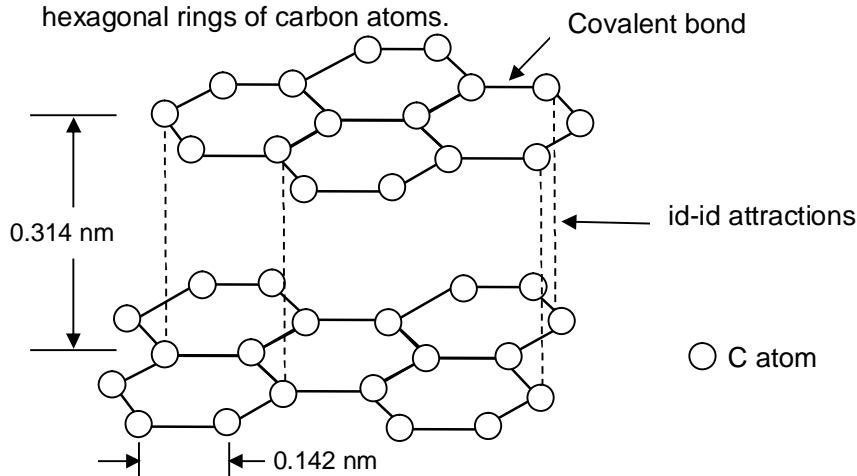
- (i) Quartz is silicon dioxide and has the following structure:



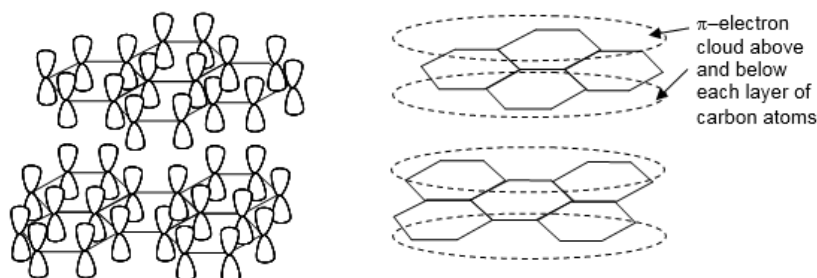
- (ii) From the diagram, each silicon atom is bonded to 4 oxygen atom while each oxygen atom is bonded to 2 silicon atoms. The arrangement of silicon atoms in quartz is similar to that of carbon in diamond. The only difference is that for quartz, there is an oxygen atom between 2 silicon atoms.

8.3 Graphite

- Graphite has a **layered** structure and is made up of planes of interconnected hexagonal rings of carbon atoms.



- Each carbon atom forms **3 σ bonds** with 3 other carbon atoms. Hence, the geometry is trigonal planar with bond angles of 120° around each carbon atom.
- Each carbon has a p-orbital, which contains a single electron, that will overlap sideways with the p-orbitals of its immediate neighbouring carbon atoms. This results in an extended **π -electron cloud** above and below the plane containing the carbon atoms.



- These π -electrons are delocalised **within** each layer and hence, graphite **only conduct electricity in a direction parallel to the layers**. As the delocalised electrons cannot jump across the layers, graphite is an **insulator** in a direction **perpendicular** to the layers.
- Graphite has a high melting point of 3730°C due to the presence of **strong covalent bonds within each layer**, which requires a lot of energy to overcome. Hence, graphite is used as crucibles for molten metals and reentry nose cones of rockets.
- The bonds within each layer are **covalent** but between each layer is **instantaneous dipole-induced dipole attractions**. These id-id attractions are weak. Hence, it allows each layer to glide over each other. Thus, graphite is **soft** and used in pencils and as lubricants.

Summary Table of All Types of Structures

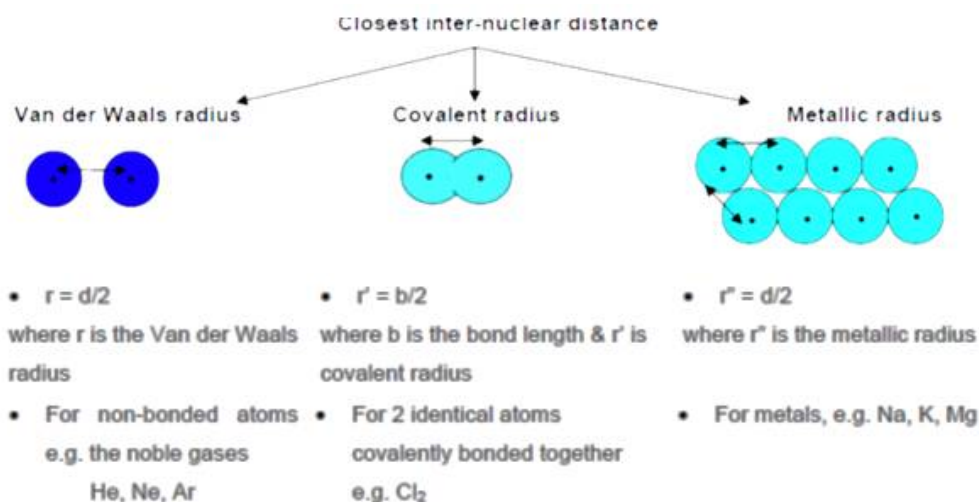
| Physical properties | Structures | | | |
|---------------------------|-----------------------------------------------------------------------------|--------------------------------------------------------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| | Giant metallic lattice | Giant ionic lattice | Giant covalent molecule | Simple covalent molecule |
| Physical state at rtp | Solid except for mercury which is a liquid | Solid | Solid | Mostly liquid/gases Some solids |
| Melting and boiling Point | High melting and boiling point due to the breaking of strong metallic bonds | High melting and boiling point due to the breaking of strong ionic bonds | High melting and boiling point due to the breaking of strong covalent bonds | Low melting and boiling point due to the breaking of weak intermolecular forces of attraction |
| Hardness | Hard but malleable and ductile | Hard and brittle | Hard except for graphite which is soft and slippery | Soft |

| | | | | |
|--------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------|------------------------------------|----------------------------------------------------------------------------------------------|
| Solubility | Insoluble in polar and non-polar solvents | Depends on lattice energy and hydration energy | Insoluble in all solvents | Depends on strength of solute-solute, solvent-solute and solute-solvent interactions. |
| Electrical conductivity | Good conductors in all states | Good conductors in liquid/molten and aqueous state Non-conductors in solid state | Non-conductors except for graphite | Non-conductors in all states. Some exceptions are those molecules which ionises in solution. |



Appendix I: Types of radius

- There are some problems to measuring atomic radius as atoms are not spheres with well-defined surface and radius. Also, it would be quite difficult to measure the radius of an atom which is in the order of nanometers (10^{-9}m). What we can determine experimentally are inter-nuclear distances and the radius of an atom is, therefore, taken to be *half* the closest inter-nuclear distance.



Question: Using the Data Booklet, explain why is the radius of Ar larger than Cl?

covalent radius of Cl: 0.099 nm ; van der Waals radius of Ar: 0.192 nm

Cl_2 exists as a diatomic molecule where its covalent radius measured is half the inter-nuclear distance of the two atoms with overlapping orbitals. On the other hand, Ar exists as monoatoms and its van der Waals radius is half the distance between the nuclei of two non-bonded Ar atoms, which includes the large space in between them. Hence, the van der Waals radius of Ar is much larger than the covalent radius of Cl.

**Appendix II: Nature of Science****History of the chemical bond**

The development of the conceptual understanding of a chemical bond is closely intertwined with the development of the atomic model. The discovery of electrons by J. J. Thomson led to the acceptance that electrons, in particular valence electrons, were involved in chemical bonding. He noted that the number of valence electrons can vary between zero and eight, and that the atom becomes stable when the number reaches eight. Thomson also observed that the number of valence electrons in an atom of an element corresponded to the element's Group number in Mendeleev's Periodic Table.

Lewis first proposed that a chemical bond (in organic compounds) involved a shared pair of electrons between two atoms (rule of two). Two theories were subsequently proposed based on the quantum mechanical model of the atom. Pauling's Valence Bond Theory (VBT) proposed that a covalent bond is formed from the overlap of (hybridised) atomic orbitals with a pair of electrons located between the two atoms. Mulliken's Molecular Orbital (MO) Theory proposed that the number of molecular orbitals should be the same as the number of atomic orbitals used to form the chemical bond. There were limitations to the VBT; it could not explain certain properties that the MO theory could (e.g. the paramagnetic properties of O_2). Despite its limitations, the VBT is more intuitive and easily applied to the drawing of structures of molecules.

Octet rule

Lewis noted that his rule of two led to many atoms in molecules (except hydrogen) having a valence shell of eight electrons and in particular four pairs, which he called the rule of eight (the term **octet rule** was later coined by Langmuir). But there were also exceptions to the octet rule in species with the following:

- an odd number of valence electrons, e.g. NO
- more than eight valence electrons, e.g. PCl_5
- less than eight valence electrons, e.g. BH_3

It is hence important to remember that the octet rule is based on empirical observation. It applies strictly only to the period 2 elements, C, N, O and F, due to the availability of 2s and 2p orbitals in the valence shell. The octet rule can be used to identify chemical structures that are likely to be stable but cannot be used to explain the stability. The explanation for stability is based on minimisation of energy.

Video: A brief introduction to Molecular Orbital Theory

<https://www.youtube.com/watch?v=PEhe1zV5Bps>



- Scientific theories are explanations for observable phenomena which have been developed over time. These ideas are subject to revision and improvement in light of new evidence.
- Scientific knowledge is reliable and durable, yet subject to revision in the light of new evidence.
- Scientists use of models to explain concepts, solve problems and make predications.



Refer to Topic 9.1 Nanomaterials AO b(ii)

Appendix III: Why a Gecko's Feet can Stick to Almost Anything

It has been observed since the 4th century BC that geckos have the ability to climb walls, hang upside down, and apparently “stick” to anything. Aristotle was the first known to have commented on the phenomenon, stating gecko's have the ability to “run up and down a tree in any way, even with the head downwards.” It wasn't until recently that it was discovered what gave them this spider-man-like ability.

Gecko's have millions of tiny hairs on their toes called setae (“setae” being Latin for “bristle”). All combined, these hair-like tissues give a washboard type appearance to a gecko's toes. Each one of these seta have thousands

of thinner hair-like structures that have flat caps at the ends called spatulae (yes the same meaning as the thing that flips our pancakes). These spatulae use what is called “van der Waals” force to allow the gecko's feet to adhere to objects.

More specifically, all of these seta and spatulae combined give the gecko's feet an extremely large surface area, compared to its size. This surface area allows the gecko to take advantage of attraction caused by van der Waals' force. Van der Waals' force, simply stated, is the combined attractive forces between molecules. Normally, the force between molecules is too minute to matter; however, given the light weight nature of a gecko (approximately 2.5 ounces) and the extreme number of spatulae (which are about the size of a bacterium), the combined force allows the gecko to “stick” to almost anything. This surface area is so great that it has been shown that if a mature gecko were to have all of their setae in contact with a surface at one time, it could potentially support up to 290 lbs.

There may be even more going on here as well, though it's still up for debate. A study published in the Journal of the Royal Society Interface in the summer of 2011 has shown



that geckos leave footprints in the form of Phospholipid residue. Phospholipids are a type of lipid (molecule that forms fats and waxes) that can form with 2 layers. These layers allow it to both attract water on one side and repel it on the other. This study suggests that there might be more going on with a gecko's ability than we currently realize and it is thought by its publishers that these phospholipids might also play a role in a gecko's sticky talent.

While the discovery of phospholipids in the gecko's footprint brings a new factor to the equation, the ancillary evidence that a gecko cannot "stick" to Teflon is a strong indication that van der Waals force is the main mediator in their abilities. Teflon (Polytetrafluoroethylene) is mainly carbon and fluorine. Fluorine itself is highly electronegative, meaning it really really likes to attract electrons to itself. Because of this, it tends to mitigate what is known as the "London dispersion force". This force is thought to usually be the dominate player in the van der Waals force. A gecko, who is dependent on the sum total of all of the factors of van der Waals force, would find it extremely difficult to stick to anything that eliminates its ability to utilize the force. As such, geckos cannot "stick" to Teflon.

Source:

<http://www.todayifoundout.com/index.php/2011/11/why-a-geckos-feet-can-stick-to-almost-anything/>

Note: van der Waals force includes:

- force between permanent dipoles
- force between a permanent dipole and a corresponding induced dipole
- force between instantaneously induced dipoles

Other readings on Nature of Science:

Scientific modelling

<http://sciencelearn.org.nz/Contexts/The-Noisy-Reef/Science-Ideas-and-Concepts/Scientific-modelling>



Models have always been important in science and continue to be used to test hypotheses and predict information. Often they are not accurate because the scientists may not have all the data. **It is important that scientists test their models and be willing to improve them as new data comes to light.**

The Scientific Method

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Quantifying_Nature/The_Scientific_Method



The Scientific Method is simply a framework for the systematic exploration of patterns in our world. The scientific process, an iterative process, uses the repeated acquisition and testing of data through experimental procedures to disprove hypotheses. A hypothesis is a proposed explanation of natural phenomena, and after a hypothesis has survived many rounds of testing, it may be accepted as a theory and used to explain the phenomena in question. Thus, the scientific method is not a linear process of steps, but a method of inductive reasoning. The scientific method is an important part of life and a grander plan that formulates a lot of theories.

A Defence of the Valence Shell Electron Pair Repulsion (VSEPR) Model by Ronald James Gillespie

<http://www.crystaloutreach.ualberta.ca/en/ScienceReasoningText/ScientificLanguage/ScientificLanguageExercises/ScientificLanguageGillespieans.aspx>



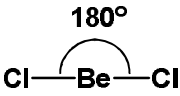
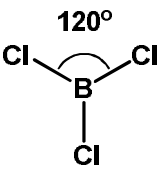
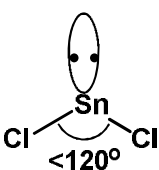
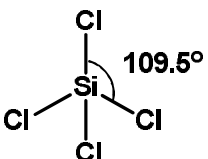
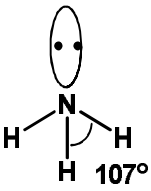
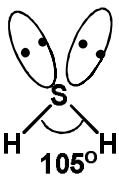
Recognise that scientific knowledge is generated from consensus within the community of scientists through a

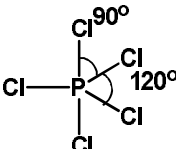
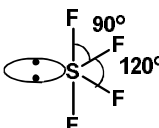
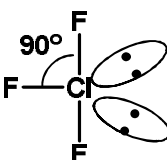
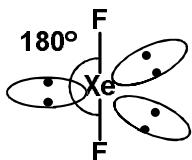
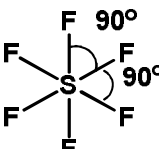
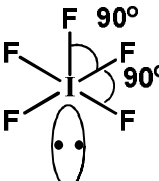
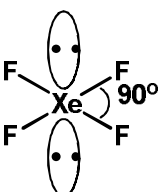
Check your Understanding by filling up the summary sheet below:



| Structure | Interactions broken during melting/boiling | Factor affecting strength of interactions |
|---------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Giant ionic lattice | Electrostatic attractions between <u>oppositely charged ions</u> . | <ul style="list-style-type: none"> $LE \propto \frac{q^+ q^-}{r_{+} + r_{-}}$ |
| Giant metallic lattice | Electrostatic attraction between a lattice of <u>positive ions and delocalised electrons</u> . | <ul style="list-style-type: none"> Number of <u>valence electrons</u> contributed to the delocalised sea of electrons / <u>Charge</u> of the cation <u>Size</u> of the cation |
| Giant covalent lattice | Strong <u>covalent bonds</u> between atoms | <ul style="list-style-type: none"> Effectiveness of <u>overlap of the orbitals</u> |
| Simple covalent molecule | <u>Instantaneous dipole-induced-dipole attractions</u> (between non-polar and polar molecules) | <ul style="list-style-type: none"> Number of <u>electrons</u> <u>Surface area</u> of interactions |
| | <u>Permanent dipole-permanent dipole attractions</u> (between polar molecules) | |
| | <u>Hydrogen bonding</u> (between polar molecules with H bonded to N, O or F) | <ul style="list-style-type: none"> <u>Electronegativity</u> difference <u>Extent</u> of hydrogen bonding |
| | For molecules with comparable number of electrons, Strength on interactions: Hydrogen bonding > <u>Permanent dipole-permanent dipole attractions</u> > <u>Instantaneous dipole-induced-dipole attractions</u> | |

Summary Table of Shapes

| No. of sigma bond pair + lone pair | Shape | Bond Angles | Example (Lewis structure with bond angle) |
|------------------------------------|------------------------------------|-------------|-------------------------------------------------------------------------------------------------------------|
| 2 + 0 | Linear | 180° | BeCl_2  |
| 3 + 0 | Trigonal planar | 120° | BCl_3  |
| 2 + 1 | Bent / V-shaped | 110° - 120° | SnCl_2  |
| 4 + 0 | Tetrahedral | 109.5° | SiCl_4  |
| 3 + 1 | Trigonal pyramidal | 107° | NH_3  |
| 2 + 2 | Bent/ V-shaped | 105° | H_2S  |

| | | | |
|-------|--------------------------------------|-----------|----------------------------------------------------------------------------------------------------|
| 5 + 0 | Trigonal bipyramidal | 90°, 120° | PCl_5  |
| 4 + 1 | See-saw | 90°, 120° | SF_4  |
| 3 + 2 | T-shaped | 90° | ClF_3  |
| 2 + 3 | Linear | 180° | XeF_2  |
| 6 + 0 | Octahedral | 90° | SF_6  |
| 5 + 1 | Square pyramidal | 90° | IF_5  |
| 4 + 2 | Square planar | 90° | XeF_4  |



Prior Knowledge in O-Levels Chemistry

| *combined science students are expected to do own bridging for highlighted AOs | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 6092 O-Level (Pure Chemistry) | 5076/78 O-Level (Combined Science) |
| <p>2.3 Structure and properties of materials</p> <p>(a) describe the differences between elements, compounds and mixtures</p> <p>(b) compare the structure of simple molecular substances, e.g. methane; iodine, with those of giant molecular substances, e.g. poly(ethene); sand (silicon dioxide); diamond; graphite in order to deduce their properties</p> <p>(c) compare the bonding and structures of diamond and graphite in order to deduce their properties such as electrical conductivity, lubricating or cutting action (candidates will not be required to draw the structures)</p> <p>(d) deduce the physical and chemical properties of substances from their structures and bonding and vice versa.</p> <p>2.4 Ionic bonding</p> <p>(a) describe the formation of ions by electron loss/gain in order to obtain the electronic configuration of a noble gas</p> <p>(b) describe the formation of ionic bonds between metals and non-metals, e.g. NaCl; MgCl₂</p> <p>(c) state that ionic materials contain a giant lattice in which the ions are held by electrostatic attraction, e.g. NaCl (candidates will not be required to draw diagrams of ionic lattices)</p> <p>(d) deduce the formulae of other ionic compounds from diagrams of their lattice structures, limited to binary compounds</p> <p>(e) relate the physical properties (including electrical property) of ionic compounds to their lattice structure.</p> <p>2.5 Covalent bonding</p> <p>(a) describe the formation of a covalent bond by the sharing of a pair of electrons in order to gain the electronic configuration of a noble gas</p> <p>(b) describe, using 'dot-and-cross' diagrams, the formation of covalent bonds between non-metallic elements, e.g. H₂; O₂; H₂O; CH₄; CO₂</p> <p>(c) deduce the arrangement of electrons in other covalent molecules</p> <p>(d) relate the physical properties (including electrical property) of covalent substances to their structure and bonding.</p> <p>2.6 Metallic bonding</p> <p>(a) describe metals as a lattice of positive ions in a 'sea of electrons'</p> <p>(b) relate the electrical conductivity of metals to the mobility of the electrons in the structure (see also 9.1(a)).</p> | <p>2.3 Structure and properties of materials</p> <p>(a) describe the differences between elements, compounds and mixtures</p> <p>2.4 Ionic bonding</p> <p>(a) describe the formation of ions by electron loss / gain in order to obtain the electronic configuration of a noble gas</p> <p>(b) describe the formation of ionic bonds between metals and non-metals, e.g. NaCl; MgCl₂</p> <p>(c) relate the physical properties (including electrical property) of ionic compounds to their lattice structure</p> <p>2.5 Covalent bonding</p> <p>(a) describe the formation of a covalent bond by the sharing of a pair of electrons in order to gain the electronic configuration of a noble gas</p> <p>(b) describe, using 'dot and cross' diagrams, the formation of covalent bonds between non-metallic elements e.g. H₂; O₂; H₂O; CH₄; CO₂</p> <p>(c) deduce the arrangement of electrons in other covalent molecules</p> <p>(d) relate the physical properties (including electrical property) of covalent substances to their structure and bonding</p> <p>8.1 Properties of metals</p> <p>(a) describe the general physical properties of metals as solids having high melting and boiling points, being malleable and good conductors of heat and electricity</p> <p>(b) describe <i>alloys</i> as a mixture of a metal with another element, e.g. brass; stainless steel</p> <p>(c) identify representations of metals and alloys from diagrams of structures</p> |

