

Anglo-Chinese School (Independent)

Year 5 (2022) IBDP Chemistry HL



TOPIC 4 CHEMICAL BONDING AND STRUCTURE

(IBDP syllabus Topic 4)

- 4.1 Ionic bonding and structure
 - Essential Idea: ionic compounds consist of ions held together in lattice structures by ionic bonds.
- 4.2 Covalent bonding
 - Essential Idea: covalent compounds form by the sharing of electrons.
- 4.3 Covalent structures
 - Essential Idea: Lewis (electron dot) structures show the electron domains in the valence shell and are used to predict molecular shape.
- 4.4 Intermolecular forces
 - Essential Idea: the physical properties of molecular substances result from different types of forces between their molecules.
- 4.5 Metallic bonding
 - Essential Idea: metallic bonds involve a lattice of cations with delocalised electrons

Introduction

- A <u>chemical bond</u> is a force which holds two or more atoms or ions together.
- All chemical reactions involve bond breaking followed by bond making.
 - o The breaking of bonds requires (absorbs) energy endothermic process.
 - The formation of bonds releases energy exothermic process.

The feasibility of a reaction depends on the energy transfers associated with the breaking and making of bonds. Hence, by forming bonds with each other, atoms become part of a more stable system.

- All types of bonding involve interactions between opposite charges and they are electrostatic in nature.
 - lonic bond attraction between some positively charged particles (cations) and negatively charged particles (anions)
 - o Covalent bond attraction between nuclei and shared electrons
 - **Metallic bond** attraction between metal ions and delocalised electrons
- The electrons involved in the chemical bond formation usually come from the outermost shells of the atoms. These electrons are called **valence electrons**. The nuclei of the atoms are unaffected. The valence electrons rearrange to attain a state of minimum energy.
- Usually, atoms achieve stability by acquiring the nearest noble gas electronic configuration. This means possessing a completely filled valence shell with 8 outermost shell electrons. This is known as **octet configuration**. Helium is an exception because it has only two electrons.
- Bonding affects the chemical and physical properties of compounds.



4.1 Ionic Bonding and Structure

ØNature of science:

Use theories to explain natural phenomena – molten ionic compounds conduct electricity, but solid ionic compounds do not. The solubility and melting points of ionic compounds can be used to explain observations. (2.2)

Understandings:

- Positive ions (cations) form by metals losing valence electrons.
- Negative ions (anions) form by non-metals gaining electrons.
- The number of electrons lost or gained is determined by the electron configuration of the atom.
- The ionic bond is due to electrostatic attraction between oppositely charged ions.
- Under normal conditions, ionic compounds are usually solids with lattice structures.

Applications and skills:

- Deduction of the formula and name of an ionic compound from its component ions, including polyatomic ions.
- Explanation of the physical properties of ionic compounds (volatility, electrical conductivity and solubility) in terms of their structure.

Guidance:

Students should be familiar with the names of these polyatomic ions: NH₄⁺, OH⁻, NO₃⁻, HCO₃⁻, CO₃²⁻, SO₄²⁻ and PO₄³⁻.

4.1.1 Definition

The ionic or electrovalent bond refers to **the electrostatic attraction** experienced between the electric charges of a **cation** (positive ion) and an **anion** (negative ion).

Therefore,

- when an atom loses electrons it becomes a positively charged ion (cation);
- when an atom gains electrons it becomes a negatively charged ion (anion);
- these ions will usually have the nearest noble gas electronic configurations;
- and these oppositely charged ions will have electrostatic attraction for one another. This is the **ionic bonding**.

lonic compounds are usually formed between two elements of very different electronegativities (usually a difference in electronegativity of greater than 1.8). The highly electronegative element (non-metal) will gain electrons to form the anion while the element with low electronegativity (metal) will lose its valence electrons forming the cation.

4.1.2 Dot and Cross Diagrams

Example: NaC1







- (b) MgC ½
- Mg²⁺ 2 Cl
- (c) Na₂O



(d) Al₂O₃



4.1.3 Nature of Ionic Bonding

lonic bonds are the strong electrostatic attraction between ions of opposite charges. They are

- Electrostatic in nature;
- Usually strong, therefore ionic compounds generally have high melting and boiling points;
- Non-directional i.e. equally strong in any direction.

4.1.4 Ionic Bond Strength and Lattice Energy

The interactions between these charged particles give rise to the electrostatic attraction. The strength of this electrostatic attraction is indicated by its **lattice energy**.

Lattice energy of an ionic compound is defined as the enthalpy change when one mole of a solid ionic compound is separated into gaseous ions under standard conditions.

Its magnitude is proportional to the charges on the ions (q_+ and q_-) and inversely proportional to the distance separating them ($r_+ + r_-$) i.e.



From the graph:

- Electrostatic attraction between the two ions increases when r decreases, i.e., they come closer.
- But the repulsion of the electron clouds prevents the inter–nuclear distance from being smaller than r.
- At an inter–nuclear distance of r, the system reaches a minimum potential energy and the ions experience the strongest electrostatic attraction.

Generally, decreasing the size and increasing the charge of the ion will increase the strength of the ionic attraction; leading to higher melting and boiling points. But there are exceptions. For example, the melting point of $A \ge O_3$ is 2072 °C and this is lower than that of MgO which is 2852 °C.

E.g. 1 Melting point of KF > KC1 and MgO > Na_2O

E.g. 2 Melting point of MgO > Melting point of NaC1 $(Mg^{2+}O^{2-})$ $(Na^{+}CI)$

The 3–dimensional arrangement of alternating cations and anions usually results in the formation of a crystalline structure called a lattice. The ions in an ionic compound attract one another to form giant ionic lattices where the positive ions are surrounded by the negative ions and vice versa.





However, the strength of an ionic bond can also be affected by:

- arrangement of the ions in the crystal structure and
- degree of covalent character in the ionic bond.

4.1.5 **Properties of Ionic Compounds**

lonic compounds possess a giant crystal lattice structure, where the oppositely charged ions are assembled so that the **strong ionic bonds extend throughout the structure.** The properties of the ionic compounds result from **both** the structure and the bonding.

The typical properties of ionic compounds are:

- High melting and boiling points
- Hard but brittle
- Good conductors of electricity in molten and aqueous state
- Soluble in polar solvents but insoluble in non-polar solvents

This table shows the properties of ionic lattices (compounds) and the explanations of these properties.

Property	Explanation
High melting point and boiling point	The melting and boiling points of ionic compounds are high because a large amount of thermal energy is required to overcome the separate the strong electrostatic attractive forces between oppositely–charged ions.
Hard	Most ionic compounds are hard; the surfaces of their crystals are not easily scratched. This is because the ions are bound strongly to the lattice and are not easily displaced.

Property	Explanation			
Brittle	Brittleness refers to the ease of shattering or fracturing under stress. Under sharp blows, i.e. high stress forces, slight distortion can occur along a plane in the ionic solid. This happens because distortion causes ions of like charges to come close together and they sharply repel.			
	Force			
Electrical conductor in molten and aqueous state	Solid state: The strong electrostatic attractive forces prevent the movement of charged ions. Since the ions are unable to move, they cannot carry the electrical charges.			
conductor in solid state	Molten and aqueous state: There are free mobile ions present to carry the electrical charges.			
Solubility in water and	The formation of ion–dipole attractions results in the release of energy that causes the detachment of ions from the crystal lattice for solvation			
polar solvents	Some ionic crystals dissolve readily in water. Since water is a polar molecule, it attacks an ionic lattice and pulls it apart. Once removed from the lattice, an ion is quickly surrounded by the water molecules. These water molecules are strongly attracted to the ions because of electrostatic ion–dipole attraction.			
	δ^+ $\delta^ \delta^ \delta^ \delta^ \delta^ \delta^ \delta^ \delta^-$			
Solubility in non-polar solvents	Non–polar solvents like hexane and benzene, do not have strong dipoles to pull the ions away from the lattice and the compound does not dissolve in such solvents.			

4.2 Covalent Bonding

ØNature of science:

Looking for trends and discrepancies—compounds containing non-metals have different properties than compounds that contain non-metals and metals. (2.5)

Use theories to explain natural phenomena – Lewis introduced a class of compounds which share electrons. Pauling used the idea of electronegativity to explain unequal sharing of electrons. (2.2)

Understandings:

- A covalent bond is formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei.
- Single, double and triple covalent bonds involve one, two and three shared pairs of electrons respectively.
- Bond length decreases and bond strength increases as the number of shared electrons increases.
- Bond polarity results from the difference in electronegativities of the bonded atoms.

Applications and skills:

• Deduction of the polar nature of a covalent bond from electronegativity values.

Guidance:

- Bond polarity can be shown either with partial charges, dipoles or vectors.
- Electronegativity values are given in the data booklet in section 8.

4.2.1 Definition

The covalent bond is the **electrostatic attraction** between **a shared pair of electrons** and the **nuclei** of the atoms being bonded.

4.2.2 Electron Sharing in Covalent Bonds

- Usually between atoms of non-metals (typically between two elements with an electronegativity difference of less than or equal to 1.8).
- By sharing electrons, the atoms achieve the noble gas electronic configurations.
- A covalent bond is formed between two atoms when electrons are shared by them.
- The probability distribution of the shared electrons is relatively high in the region between the two nuclei. The electrostatic attraction between the nuclei and shared bonding electron pair holds the two nuclei together.

4.2.3 Overlapping of Atomic Orbitals

- In order to form a covalent bond, the two atoms must come close enough for their atomic orbitals with unpaired electrons to overlap.
- Too large an overlap will result in a strong repulsion between the bonding nuclei. The most stable situation is achieved by partial overlapping of the two atomic orbitals.



4.2.4 Two Ways of Electron Sharing

- <u>Normal covalent bonds</u>: The electrons in the shared pair originate from the two atoms involved in bonding (one electron from each).
- <u>Coordinate (Dative) covalent bonds</u>: Both the electrons in the shared pair originate (is donated) from the same atom. (see Section 4.2.7)
- In sharing the electrons, each atom achieves the nearest noble gas electronic configuration.

4.2.5 Dot and Cross Diagrams

Representation of covalent bonds can be done by the use of dot and cross diagrams which illustrate clearly the electrons that orbit around each covalently bonded atom. Sometimes the Lewis (electron dot) structure is useful as well.

The terms 'bond pair' and 'lone pair' will be used to describe valence electrons in an atom/molecule. **Bond pairs are shared pairs of electrons between two atoms** whilst **lone pairs are pairs of electrons not shared**.

Compound	Dot and Cross Diagram	Lewis (Electron–Dot) Structure
HC1	H*Cl:	
H ₂	H∗H	
CĿ	× Č]*Č]:	
H ₂ O	H∗O∗H	

Exercise 2: Complete the following table by drawing the relevant diagrams

Compound	Dot and Cross Diagram	Lewis (Electron–Dot) Structure
CO2	$\sum_{xx}^{xx} \cdot C \cdot \cdot O_{xx}^{xx}$	
CC1	$\begin{array}{c} \overset{xx}{\underset{xx}{\overset{xx}{\underset{xx}{\overset{xx}{\underset{xx}{\overset{xx}{\underset{xx}{\overset{xx}{\underset{xx}{\underset{xx}{\overset{xx}{\underset{xx}{x}{x}{x}{x}{x}{x}{x}{x}{x}{x}{x}{x}$	
NH3	H × Z× H	
O ₂	.xx .xx xx ≍ : Ö	

Compound	Dot and Cross Diagram	Lewis (Electron–Dot) Structure
C ₂ H ₄	⊥ ×Ο×⊥ ו ו ⊥×Ο×⊥	
PCl₃	$ \overset{xx}{\underset{xx}{\overset{xx}}{\overset{xx}{$	
N ₂	×NX:N:	

4.2.6 Limitations to Octet Rule in Determining Covalent Bond Structures

Octet Rule: In forming chemical bonds, atoms in period 2 tend to achieve the stable noble gas electronic configuration with 8 electrons in the valence shell. This can be done by gaining, losing or sharing of electrons.

Exceptions:

- Molecules whose central atoms have fewer than 8 electrons after bonding.
 E.g. BF₃, AIC 1₃ (usually compounds of Group 2 and 13 elements).
- Molecules whose atoms have more than 8 electrons after bonding.
 E.g. SF₆, PF₅ (usually compounds of Period 3 elements onwards)
- Molecules with an odd number of electrons.
 E.g. NO, NO₂ (note that N has 5 valence electrons).

Compound	'Dot-and-cross' diagram	Comments
BeC⊉	×Č: ×x * Be * Č:×	After bonding, Be has only 4 assigned electrons. After bonding, B has only 6 assigned electrons. Be and B are Period 2 elements with a n = 2 shell which can hold a maximum of $2n^2 = 8$ electrons.
BF3	× F × × F × × F × B × F ×	 Be and B form covalent compounds due to the high I.E. involved in forming Be²⁺ and B³⁺ respectively. They often have incomplete valence shells (< 8 e⁻) in their compounds. These electron–deficient compounds are very reactive.
PCኔ	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	After bonding, P has 10 assigned electrons. After bonding, S has 12 assigned electrons. P and S are Period 3 elements with an n = 3 shell which can hold a maximum of 2n ² = 18 electrons. There are vacant d–orbitals
SF ₆	$\stackrel{xx}{\stackrel{\times}{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{$	to hold the extra electrons. P and S can expand their valence shell.

Examples of molecules without the noble gas configuration.

4.2.7 Coordinate Covalent Bonds (Dative Covalent Bonds)

A coordinate covalent bond or dative covalent bond is a covalent bond in which the shared pair of electrons is **contributed by only one of the bonded atoms**. This atom donates both electrons to the shared pair.

Criteria for the formation of coordinate covalent bond:

- Donor atom: possesses an unshared pair or lone pair of electrons. This atom can donate that pair of electrons for sharing.
- Acceptor atom: possesses an empty orbital in its valence shell. This empty orbital can then receive a pair of electrons from the electron donor.

The symbol ' \rightarrow ' is used to indicate the coordinate covalent bonds in Lewis Structure. It always point from the donor atom to the acceptor atom.



Example 1: $H_3N \rightarrow BF_3$

For the $H_3N:\rightarrow BF_3$ molecule, a coordinate covalent bond is formed between N and B in which N donates both electrons for sharing.



The Lewis structure can also be used to represent coordinate covalent bonding. The coordinate covalent bond is represented by an arrow " \rightarrow " which represents the bond pair electrons donated by the nitrogen atom.



Example 2: NH4⁺



After the coordinate covalent bond formation, all four N–H bonds in the ammonium ion are equivalent and the origin of the coordinate covalent bond cannot be distinguished.

While the +1 charge is now on the entire ion, it can be formally assigned to the N atom.



Coordinate covalent bonding may also exist in covalent compound complexes involving only **one** compound where the central atom has less than 8 electrons in its valence shell. This means that it is available to accept a pair of electrons from other atoms with available lone pairs. E.g. $AICI_3$ (dimeric) and $BeCI_2$ (polymeric).

Example 3: Al2Cl6

Aluminium chloride in solid state is ionic (unusual, as it is covalent at higher temperatures), it should be represented by $A^{3+} \cdot 3C^{\perp}(s)$.

In the vapour phase at high temperatures, AlC $_{3}$ exists as discrete molecules (M_r = 133.5).



At lower temperatures, however, the AlCl₃ *dimerises* (i.e. to form a *dimer*, a molecule made from two smaller identical ones) to form molecules of Al₂Cl₆ ($M_r = 267$).



Two of the aluminium–chlorine bonds are coordinate covalent bonds, which hold the two ALC1₃ units together. The dative covalent bond is made from chlorine atoms (donor of a pair of electrons) to aluminium atoms (acceptor of a pair of electrons).

4.2.8 Intermediate Type of Bonding

A bond simply refers to the attractive force between two particles.

Pure ionic compounds are usually formed through the complete transfer of electrons from metallic atoms to non–metallic atoms; forming cations and anions.

Pure covalent compounds are formed by <u>equal sharing</u> of electrons between covalently bonded atoms.

Pure ionic and covalent bonds are two extreme types of electron distribution.

However, compounds are rarely purely ionic or covalent. In fact, chemical bonds are mostly partially ionic and/or partially covalent.



Intermediate types of bond arise from:

- Polarisation of ionic bond due to incomplete electron transfer
- **Polarisation of covalent bond –** due to electronegativity difference between the bonded atoms.

4.2.8.1 Covalent Character in Ionic Bonding

Assumptions of ionic bonding

Theory of ionic bonding is oversimplified because

- the electron is assumed to be completely transferred from one atom to another;
- the charge of the ions is assumed to be evenly distributed in the ions;
- the cations and anions are assumed to be point charges.

Formation of ionic bond with covalent character

When cations and anions come together to form a crystal lattice, the nett positive charge on the cations can attract the electrons in the outer shells of the anions.

This results in a sharing of electrons between the cation and anion.

Electron transfer from the metallic atom to non-metallic atom is therefore "incomplete".

This diagram shows the transition from pure ionic bond to polarised ions - and eventually a polar covalent bond.



Important definitions:

Term	Definition			
Polarity	Separation of positive and negative charge			
Polarisation	Distortion of the anion's electron cloud by positively charged cation			
Polarising power	The ability of the cation to distort (or to polarise) the anion's electron			
	cloud			
Polarisability	The ease with which the anion's electron cloud can be distorted			
	(polarised)			

Comparing the ionic bonds in NaCl and $A \ge O_3$

In the ideal ionic bond between the two ions in NaCl, the electron involved is transferred completely from one atom to another such that the valence electron density resides completely on the negative ion.



However, in $A \ge O_3$ where the cation is small and highly charged (**high charge density**), the A^{3+} ion will have a strong attraction on the electron cloud of the anion O^{2-} . This can be so strong that it pulls the cloud to itself and distorts it.



The ionic bond will now have some covalent character because of the **polarisation** of anion. The electron cloud of the anion is distorted by the cation.

Because of polarisation, the transfer of electrons from metals to non-metals to form cations and anions is considered incomplete.

If the electron cloud of the anion is large, it will become more easily distorted. E.g. ALC 13



This distortion of electron density from the anion means that valence electron density is now not exclusively found on the anion. The electron density actually moves to a region between the cation and anion. The bond becomes more like a covalent bond. In this way, the ionic bonds take on a covalent character.

In fact, for AlCl₃, the covalent character becomes so predominant that aluminium chloride can exists as covalent molecules in the gaseous state.

Factors affecting the degree of polarisation:

• Charge and size of cation (Polarising power of cation)

The higher the cationic charge, the greater is the polarising power. E.g. $Na^+ < Mg^{2+} < Al^{3+}$

This explains why many aluminium compounds have covalent character, E.g. aluminium halides (AlCl₃, AlBr₃ etc).

The smaller the ionic radius of the cation, the greater the polarising power. E.g. Effect of size of cation: $Li^+ > Na^+ > K^+$

• Charge and size of anion (Polarisability of anion)

The higher the anionic charge, the greater is the polarisability. E.g. $N^{3-} > O^{2-} > F^-$

The larger the ionic radius of the anion, the greater the polarisability. E.g. Effect of size of anion: $I^- > Br^- > C \square > F^-$

An ionic compound will have a considerable amount covalent character if

- Anion is large \Rightarrow high polarisability;
- Cation is small ⇒ high polarising power;
- Either the cation or anion is highly charged.

Factors Affecting Ionic Bond Strength

• Lattice energy (See section 4.1.4)

Lattice energy of an ionic compound is defined as the enthalpy change when one mole of a solid ionic compound is separated into gaseous ions under standard conditions.

Its magnitude is proportional to the charges on the ions (q+ and q–) and inversely proportional to the distance separating them (r + r -) i.e.

$$|\text{Lattice Energy}| \propto \left| \frac{q_+q_-}{r_+ + r_-} \right|$$

Where q_+ = charge of cation

- q_{-} = charge of anion
 - r_{+} = radius of cation
 - r_{-} = radius of anion

Covalent character

The introduction of covalent character into an ionic bond increases the strength of the ionic bond.

E.g. AgC1has a larger magnitude of lattice energy compared to NaC1

Based on the formula $|\text{Lattice Energy}| \propto \left| \frac{q_+q_-}{r_++r_-} \right|$ Charge of cation, q_+ : Ag⁺ = Na⁺ Charge of anion, q_- : same anion for both compounds Radius of cation, r_+ : Ag⁺ > Na⁺ Radius of anion, r_- : same anion for both compounds

Therefore, AgC1should have a lower magnitude of lattice energy and hence, weaker ionic bond strength than NaC1 This does not agree with the statement above.

The magnitude of lattice energy of AgC1 is greater due to the presence of covalent character in ionic bond

Properties of Ionic Compounds with Covalent Character

• Ionic compounds with a high degree of covalent character may be soluble in organic solvent.

e.g. LiClis very soluble in ethanol and diethyl ether, while NaCl(nearly purely ionic) is insoluble.

• Ionic compounds with a high degree of covalent character such as AIC la exist as simple molecules instead of giant ionic lattice. They have low boiling points and melting points.

Exercise 3:

Use ideas of polarisation to predict which of the following compounds will be more ionic, and which more covalent. State your reasons clearly.

(a) BeCl₂ and MgCl₂

More ionic: MgCl₂ More covalent: BeCl₂ Size of cation: Be²⁺ < Mg²⁺ Polarising power of cation: Be²⁺ > Mg²⁺ Extent of distortion of anion electron cloud in BeCl₂ > MgCl₂ Extent of covalent character: BeCl₂ > MgCl₂

(b) AIF₃ and AIC l₃

More ionic: $A \mathbb{I} \mathbb{F}_3$ More covalent: $A \mathbb{I} \mathbb{C} \mathbb{I}_3$ Size of anion: $\mathbb{F}^- < \mathbb{C} \mathbb{T}$ Polarisability of anion: $\mathbb{F}^- < \mathbb{C} \mathbb{T}$ Extent of distortion of anion electron cloud in $A \mathbb{I} \mathbb{F}_3 < A \mathbb{I} \mathbb{C} \mathbb{I}_3$ Extent of covalent character: $A \mathbb{I} \mathbb{F}_3 < A \mathbb{I} \mathbb{C} \mathbb{I}_3$

(c) MgC_{12} and $A_{1C_{13}}$

More ionic: MgCl₂ More covalent: AlCl₃ Size of cation: Mg²⁺ > Al³⁺ Charge and charge density of cation: Mg²⁺ < Al³⁺ Polarising power of cation: Mg²⁺ < Al³⁺ Extent of distortion of anion electron cloud in MgCl₂ < AlCl₃ Extent of covalent character: MgCl₂ < AlCl₃

(d) FeCl₂ and FeCl₃

More ionic: FeCl₂ More covalent: FeCl₃ Charge of cation: Fe²⁺ < Fe³⁺ Polarising power of cation: Fe²⁺ < Fe³⁺ Extent of distortion of anion electron cloud in FeCl₂ < FeCl₃ Extent of covalent character: FeCl₂ < FeCl₃

(e) PbO and PbO₂

More ionic: PbO More covalent: PbO₂ Charge of cation: Pb²⁺ < Pb⁴⁺ Polarising power of cation: Pb²⁺ < Pb⁴⁺ Extent of distortion of anion electron cloud in PbO < PbO₂ Extent of covalent character: PbO < PbO₂

4.2.8.1.1 Electronegativity of Elements

Definition

Electronegativity is defined as the relative attraction that an atom has for the shared pair of electrons in a covalent bond.

Electronegativity Values (Pauling's scale)



- In Pauling's scale, a value of 4.0 is assigned to the most electronegative element Fluorine.
- The more electronegative elements are on the top right-hand corner of the periodic table: F, O, N, C1 They gain electrons from atoms of other elements and are powerful oxidizing agents.
- Metallic elements tend to lose electrons to form positive ions. They have low electronegativity values and are said to be electropositive.

Trends of Electronegativities

Across a period (left to right),

- The atoms get smaller, resulting in decreased distance between bonding electrons and the nuclei.
- Nuclear charge increases but shielding effect remains relatively constant since the inner quantum shells of electrons remain the same.
- Effective nuclear charge increases.
- As a result, electrostatic attraction between the bonding electrons and the nuclei increases as the atoms get smaller.
- Therefore, electronegativity increases.

Down a group (top to bottom),

- The atoms get larger, resulting in increased distance between bonding electrons and the nuclei.
- This increase in distance results in a decrease in electrostatic attraction between the bonding electrons and the nuclei of the atoms.
- Therefore, electronegativity decreases.

4.2.8.2 Ionic Character in Covalent Bonding

Assumptions of covalent bonding

• The model of covalent bonding assumes that the pair of electrons in a covalent bond is shared equally between two atoms; the electron density lies in an equidistant region from both nuclei.

Non-polar covalent bond



In a bond between identical atoms e.g. H_2 or C_2 , the bonding electrons are shared equally thus the electron density is symmetrically distributed between the bonded atoms.



Polar covalent bond in HC1



- In a polar bond, electrons are shared unequally because of the difference in the electronegative values of the 2 atoms in the molecule.
- When these two atoms with different electronegativities form a covalent bond, the valence electron density distorts towards the atom with the higher electronegativity.
- This distortion of the valence electron cloud is also called polarisation.
- A covalent bond that is polarised is said to be a polar bond.
- The polar bond will have partial electrical charges on the two ends of the bonds due to the uneven distribution of electrons.

Dipole moment

- The more electronegative atom with a high electron density will have a partial negative charge: denoted as δ -.
- The less electronegative atom with a lower electron density will have a partial positive charge, denoted as δ +.
- This separation of charges therefore creates a dipole (two equal and opposite charges separated over a distance).
- The polar bond will therefore possess a small dipole moment (μ), which measures the polarity of the bond. Dipole moment is a vector quantity that encompasses both magnitude and direction.
- For a molecule like HC1, the dipole moment can be illustrated as follows:



Polar bond and polar molecules

 Many molecules with polar bonds are themselves polar and have a permanent dipole. Molecular polarity is a vector quantity. Therefore vector addition can be used to sum up all the dipole moments present to establish whether there is a net dipole moment, μ, for the molecule. If there is a net dipole, the molecule is polar.



• However, some molecules with polar bonds are non-polar as their bond polarities cancel each other out. So the net dipole = 0. Hence, a molecule can possess polar bonds and still be non-polar. If the polar bonds are evenly (or symmetrically) distributed, the bond dipoles cancel and do not create a molecular dipole.

For a covalent molecule to be polar

- there must be at least one polar bond;
- the polar bonds must not cancel out so that there will be a net dipole.

Relationship between the type of bond and difference in electronegativity between two bonded atoms

Bond	Difference in electronegativity between the two bonded atoms	Type of bond
Cl-Cl	3.0 - 3.0 = 0	Covalent
C1-C	3.0 - 2.5 = 0.5	Polar covalent
C⊩H	3.0 - 2.1 = 0.9	Polar covalent
F–Li	4.0 - 1.0 = 3.0	Ionic

When the difference in electronegativity of the two atoms increases, the polarity of • covalent bond between them increases until a stage when the electron pair essentially resides with the more electronegative atom, giving rise to an ionic bond.



- The difference in electronegativity between two bonding atoms may be used to predict • whether the bond is ionic or covalent.
- Note: In an attempt to classify the ionic character of covalent bonds, the values used • are arbitrary cut-off values which is inconsistent with the gradation of ionic character observed experimentally. (Silberberg in "Chemistry - The Molecular Nature of Matter and Change")
- Electronegativity difference = 0 •
- Electronegativity difference < 0.4
- Electronegativity difference 0.4 to 1.8
- \Rightarrow non–polar covalent bond
- \Rightarrow mostly covalent bond
- \Rightarrow polar covalent bond
- Electronegativity difference > 1.8 •
 - \Rightarrow mostly ionic bond Del innia hut DeCl : equalent

E.g.	BeF ₂ : ionic	but	BeC₂: covalent
	AlF₃ : ionic	but	AlCl3: covalent

Factors affecting covalent bond strength

Bond dissociation energy is a means to measure covalent bond strength.

Bond strength is affected by the following factors:

Bond Length



Bond length is measured from the centre of one atom to the centre of another atom.

- The longer the bond length, the further from the shared pair of electrons the nuclei are. Therefore, a larger bond length translates to a lower bond energy and strength.
- However, the fluorine–fluorine bond in a F₂ molecule is relatively weak even though it is shorter than the bond lengths of the heavier dihalogen molecules. This is a result of the relatively large electron and inter–nuclear repulsions and the relatively small overlap of bonding orbitals arising from the small size of the atoms.

• Bond multiplicity

- This refers to the presence of multiple covalent bonds between 2 atoms. The presence of multiple bonds increases the overall bond strength between the 2 atoms.
- For example:

	C–C	C=C	C≡C
Bond Length (nm)	0.154	0.133	0.120
Bond dissociation energy (kJ mol ⁻¹)	350	610	837

Bond polarity

• An increase in polarity also means an increase in the ionic character of the bond. This usually results in an increase in bond strength and energy.

4.3 Covalent Structure

ØNature of science:

Scientists use models as representations of the real world – the development of the model of molecular shape (VSEPR) to explain observable properties. (1.10)

Understandings:

- Lewis (electron dot) structures show all the valence electrons in a covalently bonded species.
- The "octet rule" refers to the tendency of atoms to gain a valence shell with a total of 8 electrons.
- Some atoms, like Be and B, might form stable compounds with incomplete octets of electrons.
- Resonance structures occur when there is more than one possible position for a double bond in a molecule.
- Shapes of species are determined by the repulsion of electron pairs according to VSEPR theory.
- Carbon and silicon form giant covalent/network covalent structures.

Applications and skills:

- Deduction of Lewis (electron dot) structure of molecules and ions showing all valence electrons for up to four electron pairs on each atom.
- The use of VSEPR theory to predict the electron domain geometry and the molecular geometry for species with two, three and four electron domains.
- Prediction of bond angles from molecular geometry and presence of nonbonding pairs of electrons.
- Prediction of molecular polarity from bond polarity and molecular geometry.
- Deduction of resonance structures, examples include but are not limited to C_6H_6 , CO_3^{2-} and O_3 .
- Explanation of the properties of giant covalent compounds in terms of their structures.

Guidance:

- The term "electron domain" should be used in place of "negative charge centre".
- Electron pairs in a Lewis (electron dot) structure can be shown as dots, crosses, a dash or any combination.
- Allotropes of carbon (diamond, graphite, graphene, C₆₀ buckminsterfullerene) and SiO₂ should be covered.
- Coordinate covalent bonds should be covered.

Solution Nature of science (Refer to page 104 of Chemistry Course Companion)

4.3.1 Understanding the Shapes of Molecules

- Non-metal atoms achieve a stable octet electron configuration by sharing of electrons with one another. Covalent bonding is the electrostatic attraction between the shared electrons and the bonded nuclei.
- Due to overlapping of atomic orbitals, covalent bonds are directional and therefore lead to molecules with specific shapes.
- The **shapes** of covalent molecules and polyatomic ions refer to the geometric arrangement of atoms within the molecules or ions.
- The study of the shapes of molecules will help to decide
 - o the polarity of molecules. This will help answer why CC¼ is non–polar despite having polar C–C1bonds.
 - o their physical properties
 - their chemical properties.
- The overall shape of a molecule or polyatomic ion is determined by its
 - o bond angles
 - number of electron domains (refer to <u>both</u> bonding electron pairs and non-bonding lone pairs).

4.3.2 Valence Shell Electron Pair Repulsion (VSEPR) Model

Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

- The shape of a covalent molecule can be predicted using the Valence Shell Electron Pair Repulsion Theory.
- The theory states that the electron domains or regions that surround the central atom of a molecule or ion would adopt an arrangement such that they are as far apart as possible to minimise electron–electron repulsion.
- In applying this theory,
 - any atom in a molecule or ion bonded to more than one atom is known as a <u>central</u> <u>atom</u>.
 - e.g. $H_2O \rightarrow O$ is a central atom.
 - each bonded atom or lone pair of electrons joined to the central atom constitutes an <u>electron domain</u>.
 - e.g. $H_2O \rightarrow O$ has 4 electron domains (i.e. 2 bonding pairs and 2 lone pairs).
 - a multiple bond (i.e. double or triple bonds) is to be considered as an electron domain for the purpose of determining the overall geometry.

no. of lone pairs = $\frac{(\text{no. of electrons in valence shell}) - (\text{no. of electrons in bonding pairs})}{2}$

S Interpreting the VSEPR model (Refer to page 110 of Chemistry Course Companion)

Principles of VSEPR Theory

- **Electron pairs** (both bond pairs and lone pairs) around the central atom arrange themselves as far as possible to **minimise repulsion**.
- The strength of repulsion decreases in the order:

Lone pair – Ione pair	>	Lone pair – bond pair >	Bond pair – bond pair
repulsion		repulsion	repulsion

- This is due to the bonded pair electrons being localised between the two nuclei while the lone pair electrons are not localised and extend to a greater region of space.
- Thus the lone pair region would push away neighbouring bonded electron pair regions, forcing them closer together, i.e. decreasing the bond angle.

Steps to Predict the Shapes of Molecules and Ions

1. Draw the dot-and-cross diagram

- a. If ion has negative charge(s), add electron(s) to the more electronegative element
- b. If ion has positive charge(s), subtract electron(s) from the less electronegative element

2. Count the total no. of electron pairs around the central atom.

- a. A single bond, double bond, triple bond & dative bond is counted as 1 electron pair
- b. A lone pair is also counted as 1 electron pair





- 3. Determine the basic shape: determined by the total number of electron pairs around the central atom.
- 4. Determine the actual shape: determined by the exact number of bond pairs and lone pairs around the central atom.
- 5. Draw the structure (if required)



Electron Domain Geometry and Molecular Geometry:

Total no. of electron domains	0 Ione pair (Electron domain geometry)	1 Ione pair	2 lone pairs	
2	180° Iinear			
3	trigonal planar	V–shaped / bent	Scan view a on V the	me to video SEPR ory
4	tetrahedral	< 109.5°	< 109.5° V–shaped / bent	
5	90° 90° 120° trigonal bipyramid	"see-saw" or	T-shaped	
		saw horse / distorted tetrahedral * lone pairs will replace th first to minim	e <u>equatorial</u> electron pairs ise repulsion.	
6	90°			
0	octahedral	square pyramidal	square planar	
		* the first lone pair can be as they are all equivalent pair, it will be assigne (opposite) to the first lone	e assigned to any position If there is a second lone ed to the position <u>trans</u> pair to minimise repulsion.	



Predicting the shape of NH₃ and CH₃[−]

	Steps	NH ₃	CH₃⁻
1	Draw the dot–and–cross diagram	N is in Group 15 → 5 valence electrons around N H + H H H	C is in Group 14 → 4 valence electrons around C C • ★ H H H H
2	Add electron if ion is negatively charged (anion). Subtract electron if ion is positively charged (cation).	No charge ➔5 available electrons around N atom.	One single –ve charge → 5 available electrons around C atom.
3	Count the total no. of electron pairs around the central atom.	4 electron pairs:3 bond pairs, 1 lone pair	4 electron pairs: 3 bond pairs, 1 lone pair
4	Determine the electron domain geometry : determined by the total number of electron pairs around the central atom.	Tetrahedral	Tetrahedral
5	Determine the actual shape : determined by the exact number of bond pairs and lone pairs around the central atom.	Trigonal Pyramidal	Trigonal Pyramidal

_					Ŀ	7
	6	Deduce bond angle (if required) Note: Only angles between bond pairs!	107°	107º		6

Exercise 4: PhET Simulation on Shapes of Molecules

(a) Beryllium chloride, BeC12

Central atom	:	Be
Electron pairs	:	2
Bond pair	:	2
Lone pair	:	0
Electron domain geometry	:	Linear
Shape	:	Linear
Bond angle	:	180°

(b) Carbon dioxide, CO₂ (explore on PhET)

Central atom	:	С
Electron pairs	:	2
Bond pair	:	2
Lone pair	:	0
Electron domain geometry	:	Linear
Shape	:	Linear
Bond angle	:	180°

Be

Scan me to

access the PHET

simulation for this activity

••

-**C**l:

As each of the double bonds is treated as an electron domain, each carbon atom in a carbon dioxide molecule has two electron regions. The shape of a carbon dioxide molecule is thus **linear** for maximum charge separation.

(c) Boron trifluoride, BF₃ (explore on PhET)

Central atom	:	В	:F:
Electron pairs	:	3	1
Bond pair	:	3	
Lone pair	:	0	
Electron domain geometry	:	Trigonal planar	:F F:
Shape	:	Trigonal planar	•• ••
Bond angle	:	120 [°]	

(d) CH₃⁺

Central atom	:	С	
Electron pairs	:	3	· · · ·
Bond pair	:	3	
Lone pair	:	0	
Electron domain geometry	:	Trigonal planar	H´ `H
Shape	:	Trigonal planar	L _
Bond angle	:	120°	

(e) Sulfur dioxide, SO₂ (explore on PhET)

Central atom	:	S	•	•
Electron pairs	:	3	//S	;
Bond pair	:	2	:0	``0 ∶
Lone pair	:	1	••	••
Electron domain geometry	:	Trigonal planar		
Shape	:	V-shaped / bent		
Bond angle	:	117.5°.		

(f) Ethene, $CH_2=CH_2$

		н н
:	С	$\langle \rangle$
:	3	C=C
:	3	
:	0	H H
:	Trigonal planar	
:	Trigonal planar	
:	120°	
	:	C 3 3 0 Trigonal planar Trigonal planar 120°

The bonding electrons in the C=C bond are treated as one electron cloud and therefore there are three electron clouds surrounding each carbon atom in the molecule. According to the electron pair repulsion theory, the arrangement of the three electron clouds around each carbon atom is trigonal planar.

(g) CH₄ (explore on PhET)

Central atom Electron pairs Bond pair Lone pair Electron domain geometry Shane	:	C 4 4 0 Tetrahedral Tetrahedral	H H ^{WW} C H
Shape	:	Tetrahedral	Н
Bond angle	:	109.5 °	
) CH₂-			

С

(h) CH3

Central atom	:
Electron pairs	:
Bond pair	:
Lone pair	:
Electron domain geometry	:
Shape	:
Bond angle	:

4 3 1 Tetrahedral **Trigonal pyramidal** 107°

H

(i) Ammonium ion, NH4⁺

			г ¬+
Central atom	:	Ν	u
Electron pairs	:	4	
Bond pair	:	4	
Lone pair	:	0	
Electron domain geometry	:	Tetrahedral	
Shape	:	Tetrahedral	
Bond angle	:	109.5°	
CH, CH ⁻ and NH ⁺ are iso	electro	nic so they have the s	ame shane

 CH_4 , CH_3^- and NH_4^+ are isoelectronic so they have the same shape.

(j) Ammonia, NH₃ (explore on PhET)

Central atom	:	Ν	 N
Electron pairs	:	4	
Bond pair	:	3	ЧП
Lone pair	:	1	
Electron domain geometry	:	Tetrahedral	
Shape	:	Trigonal pyramidal	
Bond angle	:	107°	

The lone pair is closer to the nitrogen nucleus than the bond pairs and so it repels them strongly. i.e. it pushes the N–H bonds closer to each other. The H–N–H angle is therefore 107° which is smaller than 109.5° .

`0`

(k) Water, H₂O (explore on PhET)

:	0
:	4
:	2
:	2
:	Tetrahedral
:	V-shaped / Bent
:	104.5°
	:

The two bond pairs escape from the lone pair repulsion by moving together slightly. The H–O–H angle is 104.5°

(I) NH₂⁻

Central atom	:	Ν	[: <u>N</u> :]
Electron pairs	:	4	
Bond pair	:	2	[
Lone pair	:	2	
Electron domain geometry	:	Tetrahedral	
Shape	:	V-shaped / Bent	
Bond angle	:	104.5°	

 NH_2^- and H_2O are isoelectronic. NH_2 have the same shape as H_2O .

(m)Phosphorus pentachloride, PC₁ (explore on PhET)

Electron pairs Bond pair	:	5 5	:C <i>l</i> ////// P──C <i>l</i> :
Lone pair Electron domain geometry	:	0 Trigonal bipyramid	:Cl
Shape Bond angle	:	Trigonal bipyramid 120° (equatorial) , 90°	(axial)

(n) SF₄ (explore on PhET)

Central atom	
Electron pairs	:
Bond pair	
Lone pair	
Electron domain geometry	
Shape	

: F S 5 4 1 Trigonal bipyramid See-saw / Saw horse / **Distorted tetrahedral**

117.5° (equatorial), <90° (axial)

Bond angle

(o) $C \mathbb{F}_3$ (explore on PhET)

Central atom	
Electron pairs	
Bond pair	
Lone pair	
Electron domain geometry	
Shape	
Bond angle	



(p) XeF₂ (explore on PhET)

:	Xe
:	5
:	3
:	2
:	Trigonal bipyramid
:	Linear
:	180°
	:

:

:

:

:

:

:

•

(q) Sulfur hexafluoride, SF₆ (explore on PhET)

Central atom	:	S
Electron pairs	:	6
Bond pair	:	6
Lone pair	:	0
Electron domain geometry	:	Octahedral
Shape	:	Octahedral
Bond angle	:	90 °



:F:

: F

: F :

: F :

Xe

(r) BrF₅ (explore on PhET)

:	Br	 : F :
:	6	· · · · · · · ·
:	5	
:	1	Br
:	Octahedral	: F▼ ·· ▼F :
:	Square pyramidal	•• ••
:	<90°	
		Br 6 5 1 Octahedral Square pyramidal \$90 °

(s) XeF₄ (explore on PhET)

Control atom		Xo	··· ··
	•	<u>Ae</u>	· F /// · · · · · · ·
Electron pairs	:	6	·· ´Xe`` ·
Bond pair	:	4	
Lone pair	:	2	
Electron domain geometry	:	Octahedral	
Shape	:	Square planar	
Bond angle	:	90 °	

Exercise 5:

Molecule / ion	Dot–and–cross diagram	Lewis structure	Total no. of electr on doma ins	No. of bond pairs	No. of Ione pairs	Shape
SO₃	O ××× O ××× S ××O		3	3	0	Trigonal planar
H₃O⁺			4	3	1	Trigonal pyramida I
CıF₃	•F• •F *C-* ** ** **		5	3	2	T– shaped
I ₃ -			5	2	3	Linear
NO ₂	Ö*×N×Ö:		3	2	1	Bent

4.3.3 Types and Properties of Covalent Compounds

A. Giant covalent structures (e.g. diamond, silicon dioxide)



- In giant covalent structures, the strong covalent bonds extend between all atoms throughout the solid. Their physical properties are determined by the nature of the strong covalent bonds.
 - ✓ Hard because strong covalent bonds hold all the atoms in place (except for graphite).
 - ✓ High melting and boiling points because a lot of energy is needed to break all the strong covalent bonds holding the atoms in place. This is necessary in order to achieve a liquid state.
 - ✓ Insoluble in polar solvents and water.
 - ✓ Low electrical conductivity, due to absence of mobile ions and electrons, except in the special case of graphite.
- Silicon dioxide, SiO₂ is also known as silicon(IV) oxide. Crystalline silicon has the same structure as diamond. To create silicon dioxide, the silicon structure can be modified by including some oxygen atoms. Notice that each silicon atom is bridged to its neighbours by an oxygen atom. One silicon atom is bonded to 4 oxygen atoms while each oxygen atom is bonded to 2 silicon atoms. See diagram above.
- B. Discrete or simple covalent molecules (e.g. I₂, CO₂)
- These compounds exist as simple discrete covalent molecules. The strong covalent bonds are within the molecules. Between the molecules, there are only intermolecular forces which are weaker than covalent bonds.



- These compounds have the following properties:
 - ✓ Usually soft or brittle.
 - ✓ Low melting and boiling points because the intermolecular forces of attraction are easy to overcome.
 - Their solubilities in water and organic solvent depend on the nature of the molecules (whether they are polar or non-polar).
 - ✓ Low electrical conductivity, due to absence of mobile charged particles.

4.3.4 Allotropes

Allotropes are different forms of an element in the same physical state.

A. Diamond

- Hardest known natural mineral.
- It is an allotrope of carbon all the C atoms are sp³ hybridised.
- Giant macromolecular covalent structure with every
- carbon atom tetrahedrally bonded to four others.Applications: jewellery, drilling and cutting tools.

B. Graphite

- Common allotrope of carbon and all the C atoms are sp² hybridised.
- Giant macromolecular covalent structure where each carbon atom uses only 3 of its 4 valence electrons in covalent bonding to three other carbon atoms in a trigonal plane.
- Each carbon atom then contributes one electron to a delocalised system of electrons. The delocalised
- electrons are free to move throughout this plane.
- For this reason, graphite conducts electricity along the planes of carbon atoms, but not in the direction

at right angles to the plane.

- The layers are held together by London (dispersion) forces hence the layers can slip easily.
- Applications: dry lubricant and electrodes in electrolysis.



Scan me to view a video on allotropes of carbon



C. C₆₀ Buckminsterfullerene (or Fullerene)

- This is not a giant macromolecular covalent structure.
- Each carbon atom is covalently bonded to three others and all the C atoms are sp² hybridised.
- Composed entirely of carbon. Fullerenes vary in sizes and take the form of a hollow sphere, ellipsoid, or tube.
- Buckminsterfullerenes or bucky balls are spherical or ellipsoid fullerenes and got their names for the resemblance of their allotropic structure to the geodesic dome structures devised by the scientist and architect Richard Buckminster Fuller.
- C₆₀ fullerene is composed of individual molecules with strong covalent bonds but weak London forces between the molecules.
- In the C_{60} polyhedron cage there are 20 hexagonal surfaces and 12 pentagonal surfaces, and each carbon atom is covalently bonded to three others. The coordination number is 3 but the shape of the molecule is not planar.
- Fullerenes are black solids and are not soluble in water. They dissolve in organic solvents to form coloured solutions.
- Though fullerene contains delocalised electrons, it does not conduct electricity as the electrons are not able to move from one fullerene molecule to the next.
- Carbon nanotubes, also called bucky tubes, are cylindrical fullerenes. They exhibit extraordinary strengths and have unique electrical properties.

D. Graphene

- Graphene is a thin layer of pure carbon; an almost transparent sheet and one atom in thickness. It is a single, tightly packed layer of carbon atoms that are bonded together in a hexagonal honeycomb lattice.
- It is an allotrope of carbon and its atoms are sp² hydridised.
- Layers of graphene stacked on top of each other to form graphite. If a graphene sheet is rolled up, it forms a carbon nanotube. When it is folded up into a sphere, it becomes fullerene.
- It is the thinnest compound known to man, the lightest material known, the strongest compound discovered, the best conductor of heat at room temperature and also the best conductor of electricity.



 Hence graphene is an incredible material because of its superb electrical conductivity, strength, flexibility and transparency. Uses of graphene include replacing metals in the aerospace industry (low density and high strength) and in liquid crystal display (LCD) and flexible touch screens in mobile devices (flexibility, 	
transparency and electrical conductivity).	

4.4 Intermolecular Forces

ØNature of science:

Obtain evidence for scientific theories by making and testing predictions based on them – London (dispersion) forces and hydrogen bonding can be used to explain special interactions. For example, molecular covalent compounds can exist in the liquid and solid states. To explain this, there must be attractive forces between their particles which are significantly greater than those that could be attributed to gravity. (2.2)

Understandings:

- Intermolecular forces include London (dispersion) forces, dipole-dipole forces and hydrogen bonding.
- The relative strengths of these interactions are London (dispersion) forces < dipoledipole forces < hydrogen bonds.

Applications and skills:

- Deduction of the types of intermolecular force present in substances, based on their structure and chemical formula.
- Explanation of the physical properties of covalent compounds (volatility, electrical conductivity and solubility) in terms of their structure and intermolecular forces.

Guidance:

• The term "London (dispersion) forces" refers to instantaneous induced dipole-induced dipole forces that exist between any atoms or groups of atoms and should be used for non-polar entities. The term "van der Waals" is an inclusive term, which includes dipole-dipole, dipole-induced dipole and London (dispersion) forces.

4.4.1 Introduction to Intermolecular Forces of Attraction

- <u>Intermolecular</u> forces are forces that exist **BETWEEN molecules**. It is *DIFFERENT* from <u>intramolecular</u> forces, which refer to the forces that hold atoms together **WITHIN** a molecule, e.g. covalent bonds.
- Intermolecular forces are usually weaker than covalent bonds.

Compare	$HCl(g) \rightarrow H(g) + Cl(g)$	Δ H = +431 kJmol ⁻¹
	$HC1(1) \rightarrow HC1(g)$	Δ H = +16 kJmol ⁻¹

More energy is required to break the covalent bonds between H and Clatoms than to overcome the intermolecular forces of attraction between the HClmolecules during vaporisation.

• Change of state is related to the strength of intermolecular forces of the molecular substances. Intermolecular forces are the forces that must be OVERCOME during the melting and boiling processes of simple molecular substances.

Note: DURING MELTING AND BOILING, COVALENT BONDS ARE <u>NOT</u> BROKEN.



- The intermolecular forces present are dependent on the nature of the molecules, i.e. the **polarity** of the molecules (polar or non–polar).
- The types of intermolecular forces of attraction will also influence some of the physical properties of simple covalent substances, such as melting and boiling points and solubility in polar and non-polar solvents.
- There are three main types of forces between molecules i.e. the intermolecular forces:
 - London (dispersion) forces which is based on the instantaneous induced dipole-induced dipole interactions
 - Dipole-dipole forces
 - Hydrogen bonding

S Theories of intermolecular forces. (Refer to page 123 of Chemistry Course Companion)

4.4.2 Types of Dipoles

- The intermolecular forces of attractions between atoms and molecules are due to:
 o permanent dipoles
 - o temporary (instantaneous induced) dipoles
 - o induced dipoles

Permanent dipole

A permanent dipole exists in all polar molecules as a result of the difference in electronegativity of the bonded atoms. The more electronegative atom (e.g. C1) tends to attract the bonded electron pair to itself and becomes slightly negatively charged (δ-). The less electronegative atom (e.g. H) will then be electron deficient, and becomes slightly positively charged (δ+).



Instantaneous induced dipole

• In non-polar molecules (e.g. the halogens, noble gases, oxygen and tetrachloromethane), there are no permanent dipoles because the electron clouds are symmetrically distributed around the molecule. However, due to the fluctuation of electron clouds, positive and negative charges can arise temporarily, giving rise to **instantaneous** induced dipoles (or **temporary** dipoles).



Induced dipole

• When a molecule having a dipole (permanent or instantaneous) comes close to a non-polar molecule, the non-polar molecule will be **induced** to form a dipole temporarily.



4.4.3 Instantaneous Dipole–Induced Dipole Interactions (London Dispersion Forces)

Introduction

- London (dispersion) forces exist in all molecules. However, they are the only dominant attractive forces existing between <u>non-polar molecules</u> such as CO₂, C₂.
- London forces are also called dispersion forces or instantaneous induced dipoleinduced dipole forces.
- These interactions explain the liquefaction of non-polar molecules / atoms, such as noble gases, nitrogen at low temperatures as there is attractive forces.

Formation of instantaneous dipole-induced dipole interactions

- The electron density on a non–polar molecule is usually evenly distributed, giving a symmetrical electron cloud.
- However, the electrons in a molecule are in continual motion. <u>Temporary fluctuations</u> in the electron density of the molecule result in a non–symmetrical electron cloud and an <u>instantaneous (or temporary) induced dipole</u>
- This temporary dipole can **induce** a similar dipole in a neighbouring molecule so that the molecules attract each other.
- Due to the temporary and fluctuating nature of such dipole attractions, they are **generally weak** when compared to covalent bonds; and are called instantaneous (or temporary) induced dipole–induced dipole interactions.
- These instantaneous induced dipole–induced dipole interactions also exist between atoms of inert gases, e.g. He, Ar. For the monoatomic noble gases, random fluctuations of the electron cloud may occur. The resulting dipole can induce a dipole in a neighbouring atom to bring about an attraction between the dipoles.



instantaneous dipole–induced dipole attraction (weak intermolecular forces of attraction)

Factors affecting the strength of instantaneous induced dipole-induced dipole interactions

• Size of electron cloud / Number of electrons

 With an increase in the number of electrons, the size of electron cloud also increases. Larger electron clouds are more easily polarised. Therefore, instantaneous induced dipoles are formed more readily and more strongly, and the dispersion forces between molecules will be stronger.

Example 1:

The boiling point of noble gases increases down the group in the periodic table, i.e. from helium to argon.

Atom	Boiling point (°C)	No. of electrons	Remarks
Helium	-269	2	Moro cleatrona
Neon	-246	10	Nore electrons
Argon	-186	18	

As the size of atom and number of electrons increases DOWN the group,

- o the size of electron cloud increases (more polarisable);
- the <u>strength</u> of instantaneous induced dipole–induced dipole interactions increases;
- o and more energy is required to separate the molecules.

Example 2:

Molecule	Boiling point (°C)	No. of electrons
Fluorine	-188	18
Chlorine	-35	34
Bromine	59	70

As the size of molecule and number of electrons increases DOWN the group,

- the size of electron cloud increases (more polarisable);
- the <u>strength</u> of instantaneous induced dipole–induced dipole interactions increases;
- o and more energy is required to separate the molecules.

As a result, boiling point increases down the halogen group.

- o F_2 and C_2 exist as gases.
- \circ Br₂ as liquid and I₂ as solid at room temperature.

Example 3:

Molecule	Boiling point (°C)	Remarks
Methane (CH ₄)	-162	Carbon abain increases
Ethane (CH ₃ CH ₃)	-89	Carbon chain increases
Propane (CH ₃ CH ₂ CH ₃)	-42	

As the size of molecule becomes bigger

- o the size of electron cloud increases (more polarisable);
- the <u>strength</u> of instantaneous induced dipole–induced dipole interactions increases;
- o and more energy is required to separate the molecules.

As a result, the boiling point increases as the carbon chain increases. There will be a change of physical state from gas to liquid.

• Surface area of contact

 Straight chain molecules have an elongated electron cloud whilst branched molecules have a more compact spherical electron cloud. An elongated electron cloud allows more contact with a neighbouring molecule over a greater surface area than a spherical one. As a result, straight chain molecules are able to form stronger intermolecular forces (instantaneous induced dipole – induced dipole interactions / London dispersion forces) between the molecules.

Branched isomers of organic compounds have lower boiling points than straight chain isomers of organic compounds.

Example 4:

Molecule	Boiling point (°C)	No. of electrons	Remarks
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	36	72	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	28	72	More branching
CH ₃ CH(CH ₃)CH ₂ CH ₃ 2–methylbutane			→ lower bp
H H H H H H H H H H	9	72	

Pentane, 2–methylbutane and 2,2–dimethylpropane are three isomers with molecular formula C_5H_{12} .



- They have the same number of electrons, but they have different surface area of contact.
- Both pentane and 2,2–dimethylpropane have simple molecular structures
- Pentane has a straight chain but 2,2-dimethylpropane has a branched chain
- Extent of surface area of contact:
 - pentane > 2,2–dimethylpropane
- Extent of distortion of the electron cloud:
 - pentane > 2,2–dimethylpropane
- Extent of weak intermolecular instantaneous dipole-induced dipole attractions: pentane > 2,2–dimethylpropane
- Energy required to overcome intermolecular instantaneous dipole-induced dipole attractions:

pentane > 2,2–dimethylpropane.

• Hence boiling point of pentane is higher than that of 2,2-dimethylpropane

4.4.4 Dipole–Dipole Forces

Polar and non-polar molecules

- The **dipole moment**, μ , is a measure of the charge separation and distribution within a molecule.
- This dipole moment of a molecule is the vector sum of the individual bond dipoles.
- Polarity of a molecule depends on the polarity of the bond(s) and shape of the molecule.
- Non–polar molecules are
 - o molecules without polar bonds (e.g. H_2 , C_2) **OR**
 - \circ $\,$ molecules with symmetrically arranged polar bonds and their dipole moments cancel out.

Molecule	Shape	Structure
Carbon dioxide (CO ₂)	Linear	ö ≕c ≕ö
Boron trifluoride (BF ₃)	Trigonal planar	· · · · · · · · · · · · · · · · · · ·
Tetrachloromethane (CC₄)	Tetrahedral	:C/: :C/: :C/: :C/:
Phosphorus(V) chloride (PCե)	Trigonal bipyramidal	:C/: :C///////P
Sulfur hexafluoride (SF ₆)	Octahedral	• F • F • F • • F • • • F • • • F • • • • • F •

Examples of non-polar molecules with non-zero bond dipoles but zero net dipole moment:

- The occurrence of polarity in a molecule is mainly due to:
 - Difference of electronegativity between the bonding atoms and the resultant dipole moment of the whole molecule which is non-zero.
 - Non-symmetrical shape of molecule
- All polar molecules are said to have net dipole moments.

Example 1:

The net dipole moment of three C–C1and one C–H is non–zero.



Example 2:

In propanone $(CH_3)_2CO$, the oxygen atom is more electronegative than carbon. The net dipole moment of propanone is non-zero.



Example 3:

The presence of unpaired electron. Usually a molecule with lone pair is polar. In water molecule, there are two lone pairs on the electronegative oxygen atom. The net dipole moment of water is non-zero.



Exercise 6:

Molecule	Polarity of bond	Polarity of molecule	Shape
SO ₂	S=O : Polar	Polar	Bent
NH₃	N–H : Polar	Polar	Trigonal pyramidal
H ₂ O	O–H : Polar	Polar	Bent
CHCla	C–H : Non–polar C–C1: Polar	Polar	Tetrahedral

Dipole-dipole forces

The electrostatic attraction between the oppositely charged ends of two **polar molecules** with permanent dipoles is called the dipole–dipole forces.



permanent dipole-permanent dipole attraction (relatively stronger intermolecular forces of attraction)

• These permanent dipole-dipole attractions are electrostatic in nature.

Factor affecting strength of dipole-dipole forces

The strength of the dipole-dipole forces depends on the polarity of the molecule.

• The greater the electronegativity difference between the bonded atoms, the larger the bond dipoles δ +/ δ -, and the stronger the attraction between the oppositely charged dipoles.

Example: The boiling point of CH_3F is higher than that of CH_3Cl



• F is <u>more electronegative</u> than C1, giving rise to a <u>larger dipole moment</u> in CH₃F and therefore a <u>stronger dipole – dipole forces.</u>

Strength of instantaneous induced dipole-induced dipole interactions versus dipoledipole forces

• In general, for molecules of similar molecular mass (or number of electrons), a polar molecule will normally have higher melting and boiling points than a non-polar molecule as a result of the additional dipole-dipole forces.

Example:

lodine monochloride IC1has a similar M_r as Br_2 , but its boiling point is nearly 40 °C higher than that of Br_2 . Explain.

Molecule	Boiling point	No. of electrons
Br ₂	97	70
ICl	59	70

- Br₂ is a <u>non-polar</u> molecule with <u>weaker London (dispersion) forces</u> between the molecules. IC1 is a <u>polar molecule</u> (due to the electronegativity difference between I and C1) with additional <u>stronger dipole dipole forces</u> between the molecules
- which require more energy to break
- and hence possesses a higher boiling point.

The term van der Waals force is a 'broad' term which includes:

- the force between two permanent dipoles,
- the force between a permanent dipole and a corresponding induced dipole and
- the force between two instantaneously induced dipoles (London dispersion force).

4.4.5 Hydrogen Bonding

As recommended by IUPAC in 2011, a hydrogen bond is defined as an attractive interaction between a hydrogen atom from a molecule or a molecular fragment, X–H, in which X is more electronegative (N, O, F) than H, and an atom or group of atoms (N, O, F) in the same or different molecule, in which there is evidence of bond formation.

• A typical hydrogen bond may be shown as:

• Hydrogen bonds can occur in water molecules (H₂O), ammonia molecules (NH₃), hydrogen fluoride molecules (HF) and also between water molecules (H₂O) and dimethyl ether molecules ((CH₃)₂O). The physical properties and structure of substances are often affected by the presence of hydrogen bonding.

Formation of hydrogen bonding

- Essential requirements for the formation of hydrogen bond between two molecules:
 - For one molecule:

A **hydrogen atom is attached to** a highly electronegative atom, such as **N**, **O** or **F**.

• For another molecule:

There is at least one **Ione-pair of electrons on** the electronegative atom **N**, **O or F**.

• When a hydrogen atom is bonded to a highly electronegative atom such as fluorine, oxygen or nitrogen, the bonding electron pair is drawn towards the electronegative atom.



• The electron density of the hydrogen atom is reduced and it becomes slightly positively charged (δ +). The highly electronegative atom of <u>another</u> molecule, possessing lone pairs of electrons, can approach this slightly positively charged hydrogen atom without much repulsion and share some of its electron density.



 The strong electrostatic attraction between the slightly positively charged hydrogen atom (δ+) and the lone pair on the electronegative atom (δ-) is called the hydrogen bonding.



- The number of hydrogen bonds formed per molecule depends on the:
 - number of lone pairs available on the electronegative atom
 - o number of H atoms covalently bonded to N, O or F on another molecule.

Generally, the number of hydrogen bonds formed per molecule depends on which is limiting either the number of lone pairs or number of H atoms.

Examples of molecules with hydrogen bonding

Compound	Boiling point (°C)
NH ₃	-33
H ₂ O	100
HF	19

- F is the most electronegative atom and the H–F bond is the most polarised (i.e. largest dipoles δ+, δ–). HF would therefore have the strongest hydrogen bonding and highest boiling point. However, it is observed that H₂O has the highest boiling point instead.
- Note that each hydrogen bond has to be formed between <u>exactly</u> an electron–deficient hydrogen atom and a lone pair on the electronegative atom (N, O, F).
- Notice that each H₂O molecule has two H^{δ+} and two lone pairs on the O atom, and can form two hydrogen bonds per water molecule. There are exactly the right numbers of H^{δ+} and lone pairs so that every one of them can be involved in hydrogen bonding (average of two hydrogen bonds per molecule).



• In the case of NH₃, the extent of hydrogen bonding is limited by the fact that each N has only one lone pair but three H^{δ +}. In a group of NH₃ molecules, there are not enough lone pairs to go around to bond with all the H^{δ +} so each NH₃ molecule forms an average of one hydrogen bond per molecule.



Intermolecular hydrogen bonding and intramolecular hydrogen bonding

- Intermolecular hydrogen bonding: Occurs between a hydrogen atom (covalent bonded to a highly electronegative atom) in one molecule and the lone pair on a highly electronegative atom (N, O, F) of another molecule.
- Intramolecular hydrogen bonding: Occurs between a hydrogen atom (covalent bonded to a highly electronegative atom) in one molecule and the lone pair on a highly electronegative atom (N, O, F) of another part of the same molecule.

Example 1:

Molecule	Boiling point (°C)	Remarks
2–nitrophenol	216	Intramolecular hydrogen bonding
4-nitrophenol	259	Intermolecular hydrogen bonding



- In 2–nitrophenol, the –OH and –NO₂ groups are close to each other, hence intramolecular hydrogen bonding occurs.
- Extent of **intra**molecular hydrogen bond: 2-nitrophenol > 4-nitrophenol
- Extent of **inter**molecular hydrogen bond: 2-nitrophenol < 4-nitrophenol (as there is less availability of the lone pair of electrons on O of NO₂ group in 2–nitrophenol for intermolecular hydrogen bonding)
- 4-nitrophenol has a higher boiling point than 2-nitrophenol because more energy is required to overcome the more extensive **intermolecular hydrogen bonding** (while weak London forces operate between molecules of 2-nitrophenol)

Example 2:

Will hydrogen bonding be present in ethanal CH₃CHO?



- Both hydrogen atom and highly electronegative atom are present, but the hydrogen is not directly bonded to the highly electronegative O, therefore only dipole-dipole forces and not hydrogen bonding.
- Note: The hydrogen atom involved in hydrogen bonding MUST be bonded to a highly electronegative atom.

Effects of hydrogen bonding

1. Dimerisation of ethanoic acid in benzene or in CC14



Intermolecular hydrogen bonds

- Ethanoic acid (or acetic acid) CH₃COOH has M_r = 60, but M_r of ethanoic acid in benzene or CC₁ shows a M_r value that is twice this value, i.e. 120.
- This is the consequence of <u>very strong intermolecular hydrogen bonding</u> between two acid molecules to form a dimer.
- The acid is a polar compound whereas the organic solvent is non-polar. The solutesolvent interactions are weaker than the hydrogen bonds formed between the acid molecules. The acid molecules therefore dimerise via hydrogen bonds.



• M_r of ethanoic acid in water remains at 60. This is because no dimerisation occurs due to extensive hydrogen bonding with water molecules.

2. Structure of ice

- In ice, each water molecule is connected to other water molecules through hydrogen bonding in a rigid but open 3–dimensional tetrahedral structure. There is a lot of empty space between the water molecules. Therefore, ice has a lower density than water and floats on water.
- As ice melts, some of the hydrogen bonds break and the water molecules move into the empty spaces that were in the ice structure. As a result, the water molecules are closer together in liquid water than in ice.



- As such,
 - Water is denser than ice.
 - At 4 °C, water molecules pack most compactly, and the density of water reaches a maximum. (1 g cm⁻³)



Scan me to view a video on the arrangement of water in solid, liquid, and gaseous states



4.4.6 Effects of Intermolecular Forces on Physical Properties of Simple Covalent Substances

• The strength of covalent bonds, hydrogen bonds, dipole-dipole forces and instantaneous induced dipole-induced dipole forces are compared in the following table below:

Bonding	Bond strength (kJ mol ⁻¹)	
Covalent bond	100 – 500	
Hydrogen bond	2 – 50	
Dipole-dipole forces	5 – 12	
Instantaneous dipole-induced dipole	a wide range depending	
(London (dispersion) forces)	on size of molecule	

- Similarities between instantaneous induced dipole–induced dipole, dipole–dipole forces & hydrogen bonds:
 - o all are electrostatic in nature
 - o all are dipole-dipole interactions

Melting / boiling point

 In general, the strength of intermolecular forces for molecules of comparable sizes is as follows:

Hydrogen bonding > Dipole-dipole forces	> Instantaneous induced dipole-induced
	dipole forces
strongest	weakest

Solubility in polar solvents (e.g. water) **and non–polar solvents** (e.g. organic solvents: benzene, tetrachloromethane CC₁

 Substances whose molecules can <u>form hydrogen bonding with polar water molecules</u> are usually <u>soluble in water</u>, e.g. ammonia (NH₃), ethanol (C₂H₅OH). They have a hydrogen atom attached to a highly electronegative atom (N, O, F).



- Substances whose molecules are non-polar are soluble in non-polar solvents but insoluble in polar solvents.
 - The weak instantaneous induced dipole–induced dipole attractions between iodine molecules is similar in strength / compatible to the weak instantaneous induced dipole–induced dipole attractions between benzene molecules.
 - Strong hydrogen bonding between water molecules is not compatible to the weak instantaneous induced dipole–induced dipole interactions between non–polar molecules

Melting and boiling point variation of hydrides in Groups 14, 15, 16 and 17



• **Observation 1**: The boiling point of Group 14 hydrides (CH₄, SiH₄, GeH₄, SnH₄) are lower than the rest of the hydrides.

Explanation:

- Group 14 hydrides are tetrahedral, non–polar molecules whereas the hydrides of the other groups are polar.
- Therefore, the intermolecular forces are instantaneous induced dipole–induced dipole forces as compared to the rest which are dipole–dipole forces.
- **Observation 2**: There is a general increase in boiling point of the hydrides
 - Group 14: $CH_4 < SiH_4 < GeH_4 < SnH_4$
 - Group 15: $PH_3 < AsH_3 < SbH_3$
 - Group 16: $H_2S < H_2Se < H_2Te$
 - Group 17: HC1< HBr < HI

Explanation:

- As the relative molecular mass increases the instantaneous induced dipoleinduced dipole forces between the molecules also increase as the electron clouds of the molecules increases in size and hence in polarisability.
- More energy is required to overcome the increasing strength of the instantaneous induced dipole–induced dipole forces down the group.
- Therefore, the boiling points of the hydrides within a group generally increase.
- **Observation 3**: NH₃, H₂O and HF have much higher boiling point than those hydrides from their corresponding groups.

Explanation:

This is due to the high electronegativities of F (4.0), N (3.0) and O (3.5), which lead to the formation of intermolecular hydrogen bonds in their hydrides.

As hydrogen bonds are much stronger than the dipole–dipole forces, more energy is needed to break the hydrogen bonds in the molecules of these three hydrides. As a result, their boiling points are relatively higher.

4.4.7 Factors Affecting Melting and Boiling Points

• Ionic, covalent and metallic bonds are <u>strong bonds</u>. These strong bonds are broken on melting or boiling of ionic, giant molecular and metallic substances.

Type of bonds	Substance	Melting point (°C)	Boiling point (°C)
lonio	KC1	770	1437
IONIC	NaC1	801	1465
	C (diamond)	3550	4830
Covalent	Si	1410	_
	SiO ₂	1713	2590
	Na	98	883
Metallic	Mg	650	1110
	Al	660	2467

• High melting and boiling points

- Hydrogen bonding, dipole–dipole forces and instantaneous induced dipole–induced dipole forces are considerably weaker in comparison. These weaker intermolecular forces are broken on melting or boiling of simple covalent substances.
- Low melting and boiling points

Types of attractive forces	Substance	Boiling point (°C)
Hydrogon bondo	HF	19
Hydrogen bonds	H ₂ O	100
Dinala dinala faraga	PH ₃	-87
Dipole-dipole forces	AsH ₃	-62
Instantaneous induced dipole-	O ₂	-183
induced dipole	N ₂	-196

Example 1:

Comment on the following data.

Substance	Formula	Mr	No. of electrons	Boiling point (K)
Ammonia	NH₃	17	10	240
Fluoromethane	CH₃F	34	18	195
Phosphorus trichloride	PCl₃	138	66	347

- NH₃ molecules held together by hydrogen bonding, has a higher boiling point than CH₃F molecules which are held by the relatively weaker dipole–dipole forces.
- PC₁ molecules like the CH₃F molecules are also held by dipole–dipole forces. PC₁ has a higher boiling point because of the greater number of electrons resulting in stronger instantaneous induced dipole–induced dipole forces.

Example 2:

Comment on the following data.

Substance	Formula	Mr	No. of electrons	Boiling point (K)
Carbon dioxide	CO ₂	44	22	195 (sublimes)
Carbon disulphide	CS ₂	76	38	320
Butanone	$CH_3COC_2H_5$	72	40	353

- CO₂ and CS₂ are held together by the instantaneous induced dipole–induced dipole forces between the molecules. CS₂ has a higher boiling point because of the greater number of electrons resulting in stronger instantaneous induced dipole–induced dipole forces.
- CH₃COC₂H₅ molecules are held by the relatively stronger dipole-dipole forces.
- Hence it has the highest boiling point as more energy is required to overcome the stronger intermolecular forces.

Example 3:

The boiling points and solubilities in water of the three gases ammonia, hydrogen chloride and carbon dioxide are given in the table below:

Gas	Formula	Mr	Boiling point / °C	Solubility in water / mol dm ⁻³
Ammonia	NH_3	17	-33	18
Hydrogen chloride	HCI	36.5	-85	23
Carbon dioxide	CO ₂	44	-78	0.033

(a) Describe both the intramolecular and intermolecular bonding in each of the above compounds, relating the bonding to the boiling point where appropriate.

NH₃:	intramolecular –	covalent bonding
	Intermolecular –	hydrogen bonding (NH ₃ is <u>polar</u> due to the highly
		electronegative N, and <u>H is bonded to the highly</u>
		<u>electronegative N</u>)
HC1:	intramolecular –	covalent bonding
	Intermolecular –	dipole-dipole forces (HC1is polar due to the slightly
		electronegative C1, but H not bonded to a highly
		electronegative atom)
CO ₂ :	intramolecular –	covalent bonding
	Intermolecular –	instantaneous induced dipole-induced dipole
		forces (CO ₂ is <u>non-polar</u> although it has highly
		electronegative O because it is symmetrical and has
		a net zero dipole)

- <u>More energy</u> is required to break the <u>stronger</u> hydrogen bonding between NH₃ molecules so the highest boiling point.
- CO₂ has a larger size (electron cloud) than HC1, so London (dispersion) forces in CO₂ are <u>stronger</u> than the dipole–dipole interactions in HC1 Therefore, CO₂ has a slightly higher boiling point.

(b) Each of these gases is soluble in water because it interacts with the solvent.

(i) Write equations for any chemical reactions that occur.

 $\begin{array}{ll} \mathsf{NH}_3\left(g\right) \ + \ \mathsf{H}_2\mathsf{O}\left(1\right) \ \rightleftharpoons \ \mathsf{NH}_4^+\left(\mathsf{aq}\right) \ + \ \mathsf{OH}^-\left(\mathsf{aq}\right) \\ \mathsf{HCl}\left(g\right) \ + \ \mathsf{H}_2\mathsf{O}\left(1\right) \ \rightarrow \ \mathsf{H}_3\mathsf{O}^+\left(\mathsf{aq}\right) \ + \ \mathsf{Cl}\left(\mathsf{aq}\right) \\ \mathsf{CO}_2\left(g\right) \ + \ \mathsf{H}_2\mathsf{O}\left(1\right) \ \rightleftharpoons \ \mathsf{H}_2\mathsf{CO}_3\left(\mathsf{aq}\right) \\ \end{array} \left. \begin{array}{ll} \left[\mathsf{hydronium\ ion\ } \mathsf{H}_3\mathsf{O}^+\!\!\equiv \mathsf{H}^+\right] \\ \mathsf{H}_2\mathsf{O}\left(1\right) \ \rightleftharpoons \ \mathsf{H}_2\mathsf{OO}_3\left(\mathsf{aq}\right) \\ \end{array} \right.$

- (ii) Suggest reasons for the much higher solubility of ammonia and hydrogen chloride, compared to that of carbon dioxide.
- HC1dissociates <u>completely</u> into H⁺ and C1 ions (reacts with water) and is able to form <u>ion-dipole interactions</u> with water. Therefore it is very soluble in water.
- NH₃ reacts **<u>partially</u>** with water to form NH₄⁺ and OH⁻ ions, but NH₃ is <u>**polar**</u> and able to <u>**form hydrogen bonding**</u> with water molecules, hence soluble in water.
- CO₂ reacts only <u>partially</u> with water to form carbonic acid. Although CO₂ is <u>non-polar</u>, it is able to form hydrogen bonding with water molecules due to the presence of lone pairs on the electronegative oxygen atoms.

Exercise 7:

Predict which of the following pairs of substances is likely to have a higher boiling point, giving reasons for your choice:

(a) Ne and Ar

Higher Boling point: Ar Ar and Ne are held together by the instantaneous induced dipole–induced dipole forces between the atoms. Ar has a higher boiling point because of the greater number of electrons resulting in stronger instantaneous induced dipole–induced dipole forces.

(b) F₂ and C₁₂

Higher boiling point: C12

 F_2 and C_2 are held together by the instantaneous induced dipole–induced dipole forces between the molecules. C_2 has a higher boiling point because of the greater number of electrons resulting in stronger instantaneous induced dipole–induced dipole forces.

(c) NH₃ and PH₃

Higher boiling point: NH_3 NH_3 molecules held together by hydrogen bonding, has a higher boiling point than PH_3 molecules which are held by the relatively weaker dipole–dipole forces.

Exercise 8:

Specify the predominant bonding / intermolecular forces involved for each substance in the space immediately following the substance. Then in the last column, indicate which member of the pair you would expect to have the <u>higher boiling point</u>.

Substance no. 1	Predominant intermolecular force	Substance no. 2	Predominant intermolecular force	Substance with higher boiling point
HC1(g)	Dipole-dipole	I2	Instantaneous induced dipole– induced dipole forces	I ₂
CH₃F	Dipole-dipole	СН₃ОН	Hydrogen bonding	СН₃ОН
H ₂ O	Hydrogen bonding	H₂S	Dipole–dipole	H ₂ O
SiO ₂	Covalent bonding	SO ₂	Dipole-dipole	SiO ₂
Fe	Metallic bonding	Kr	London (dispersion) forces	Fe
СН₃ОН	Hydrogen bonding	CuO	lonic bonding	CuO
NH ₃	Hydrogen bonding	CH₄	Instantaneous induced dipole– induced dipole forces	NH_3
HC1(g)	Dipole-dipole	NaCl	lonic bonding	NaC1
SiC	Covalent bonding	Cu	Metallic bonding	SiC

Hint: Choices are metallic bonding, ionic bonding, strong covalent bonding, hydrogen bonding, dipole–dipole forces and instantaneous induced dipole–induced dipole forces.

4.5 Metallic Bonding

ØNature of science:

Use theories to explain natural phenomena – the properties of metals are different from covalent and ionic substances and this is due to the formation of non–directional bonds with a "sea" of delocalised electrons. (2.2)

Understandings:

- A metallic bond is the electrostatic attraction between a lattice of positive ions and delocalised electrons.
- The strength of a metallic bond depends on the charge of the ions and the radius of the metal ion.
- Alloys usually contain more than one metal and have enhanced properties.

Applications and skills:

- Explanation of electrical conductivity and malleability in metals.
- Explanation of trends in melting points of metals.
- Explanation of the properties of alloys in terms of non-directional bonding.

Guidance:

- Trends should be limited to s- and p-block elements.
- Examples of various alloys should be covered.

4.5.1 Electron–Sea Model to Explain Metallic Bonding

The metallic lattice is considered as a regular array of positive ions (metallic atoms minus their valence electrons).

These positive ions are fixed in position in a mobile 'sea of electrons' or positive ions embedded in a plasma of electrons.

The valence electrons can move freely throughout the lattice i.e. electrons are delocalised, producing a mobile electron cloud.

The valence electrons are delocalised through the lattice and attract the positive ions electrostatically, thereby, holding the lattice together.



A metallic bond is the electrostatic attraction between a lattice of positive ions (cations) and delocalised electrons.

4.5.2 Strength of Metallic Bonding

The strength of metallic bonding is a measure of the electrostatic attraction between the delocalised electron cloud and the positive metallic cations.

The strongest metallic bonds will be formed between cations of high charge density and electrons cloud which have the highest density. This would in turn lead to a greater mutual attraction between them.

The strength of metallic bonds increases as

• the number of valence electrons per atom increases (such that the density of electron cloud increases)

Group 1 elements have only one electron in their outermost shell. Group 2 elements have two valence electrons in their outermost shell. The melting points of group 2 elements are higher than those of their preceding neighbour in the same period.

Most transition metals have very high melting points. E.g. tungsten

As a general rule, the more unpaired d–electrons a transition metal has, the more electrons are contributed to the metallic bonding.

• the nuclear charge increases and the metallic radii decreases (such that the charge density of the metallic cation increases).

Note: In general, if the metallic bonds are strong, the metal will be hard and will have a high melting point.

Example : Metallic elements in Period 3

Na (m.p. 98°C)A1(m.p. 659°C)softhard

From the example given above, aluminium has the greatest metallic bond strength and hence the highest melting point.

4.5.3 Physical Properties

The typical properties of metals are:

- High melting and boiling points
- Good conductors of heat and electricity
- High density
- Malleable and ductile

This table above the	www.www.wetter.e	محرما فامحر والمربي والمافا والمراج	
I his table shows the	properties of metals	and the explanations	of these properties.

Property	Explanation
High melting	A large amount of thermal energy is required to break the strong
point and	metallic bonds.
boiling point	
Good thermal	When heat is supplied to one end of a piece of metal, the kinetic energy
conductor	or the electrons is increased. This increase is transmitted through the
	system of delocalised electrons to other parts of the metal.
	Metals are good conductors of heat due to the movement of mobile electrons.
Electrical	Metals are good conductors of electricity in solid and molten state because
conductor in	of its mobile or delocalised electrons . When a potential difference is
molten state	structure and hence carry a current
monteri state	
Malleability (can be hammered into new	The regular arrangement of atoms allows the particles to slide past each other when an external force is exerted. Therefore, the structure can change without breaking because the delocalised electrons can still hold the displaced ions together i.e. metallic bonds still intact.
ductility (can be drawn into wires)	torce applied here
,	
	atoms in a piece of metal
	when a pair of force is applied, the layers