CHEMICAL BONDING

Learning Outcomes

Candidates should be able to:

- (a) show understanding that all chemical bonds are electrostatic in nature and describe:
  - (i) ionic bond as the electrostatic attraction between oppositely charged ions
  - (ii) covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei
  - (iii) metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons
- (b) describe, including the use of 'dot-and-cross' diagrams,
  - (i) ionic bonding as in sodium chloride and magnesium oxide
  - (ii) covalent bonding as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxid 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
- (d) explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory
- (e) predict the shapes of, and bond angles in, molecules analogous to those specified in (d)
- (f) explain and deduce bond polarity using the concept of electronegativity
- (g) deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d));
- (h) describe the following forces of attraction (electrostatic in nature):
  - (i) intermolecular forces, based on permanent and induced dipoles, as in $CHCl_3$(l); Br_2(l) and the liquid noble gases
  - (ii) hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups
- (i) outline the importance of 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 and magnesium oxide
  - (ii) simple molecular, as in iodine
  - (iii) giant molecular, as in graphite and diamond
  - (iv) hydrogen-bonded, as in ice
  - (v) metallic, as in copper
- (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

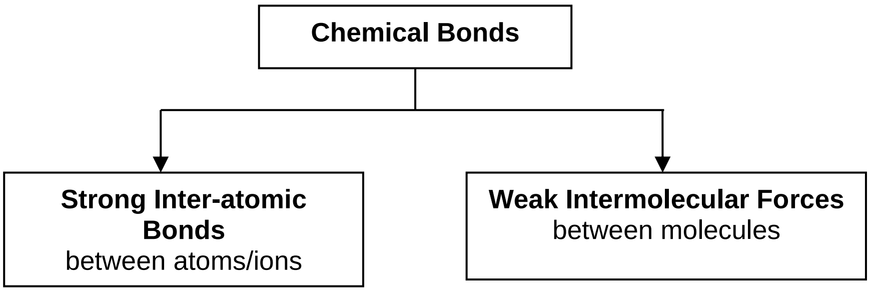
References

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

A. INTRODUCTION

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

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



- Metallic
- Ionic
- Covalent

- Instantaneous dipole - induced dipole interactions
- Permanent dipole - permanent dipole interactions
- Hydrogen bondings

Table 1: Type of chemical bonds and their approximate strengths

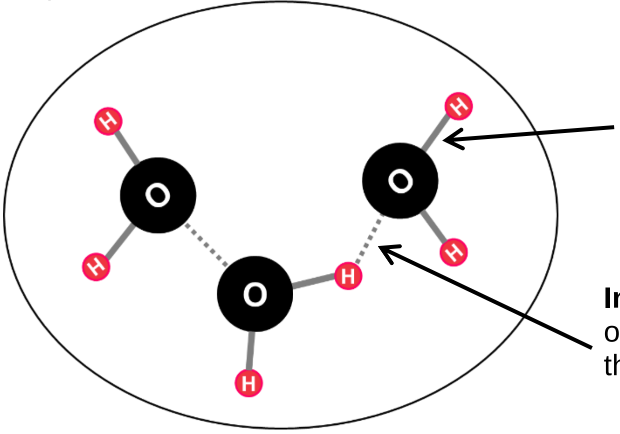
Type of bond	**Strength of bond**	**Bond Energy/ kJ mol^{-1}**
Ionic bond	Strong	120 – 450
Covalent bond	Strong	120 – 550
Metallic bond	Strong	80 – 580

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

Example: Water

Note:
Strong covalent bond between O and H atoms.

Weaker intermolecular forces between H_2O molecules.

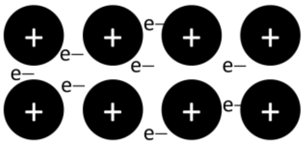
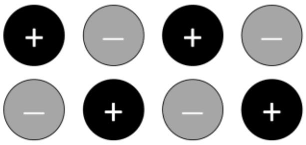
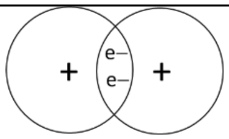
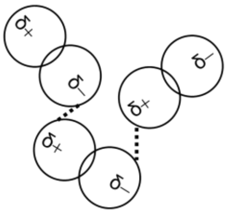
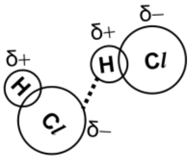
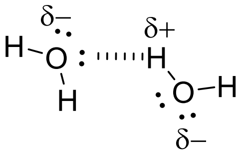
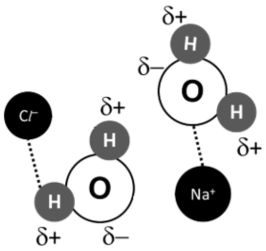


Covalent bond **between** the **O and H atoms** in a H_2O molecule

Intermolecular forces of attraction **between** the water **molecules**

Learning Objective:

- understand that all chemical bonds and forces of attraction are electrostatic in nature.

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

B. INTER–ATOMIC BONDS

Learning Objective:

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

1 METALLIC BONDS

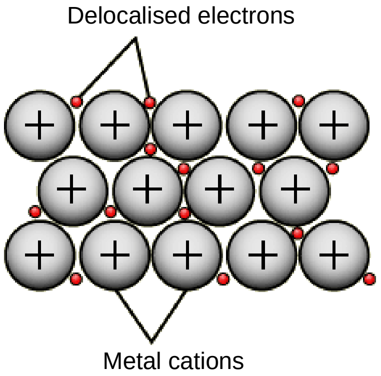
The **metallic bond** is the electrostatic forces of attraction between **metal cations** and the **sea of delocalised electrons**.

1.1 Structure and Bonding of Metals

1. Metals consist of crystalline structures of closely packed atoms with 8-12 atoms surrounding any given atom and at equal distance from it.

2. The **metallic lattice** structure comprises metal cations immersed within a sea of delocalised electrons. This is due to each metal atom contributing its loosely bound valence electrons to form a sea of delocalised electrons. The metallic cations are attracted to the sea of delocalised electrons. The sea of delocalised electrons prevents the repulsion between the cations.

3. The electrons are no longer bound to a particular metal cation but are free to move throughout the metal (delocalised electrons).



The “electron sea” model of a metallic crystal

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

1.2 Factors affecting Strength of Metallic Bonds

For Metals with different no. of delocalised electrons ➡ Metallic Bond strength $\propto$ No. of delocalised electrons

For Metals with same no. of delocalised electrons ➡ Metallic Bond strength $\propto \frac{1}{\text{ionic radius}}$

1.3 Physical Properties of Metals

❖ **High melting and boiling points**

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

❖ **Hard**

- Presence of strong and non-directional metallic bonds

❖ **Good electrical conductors**

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

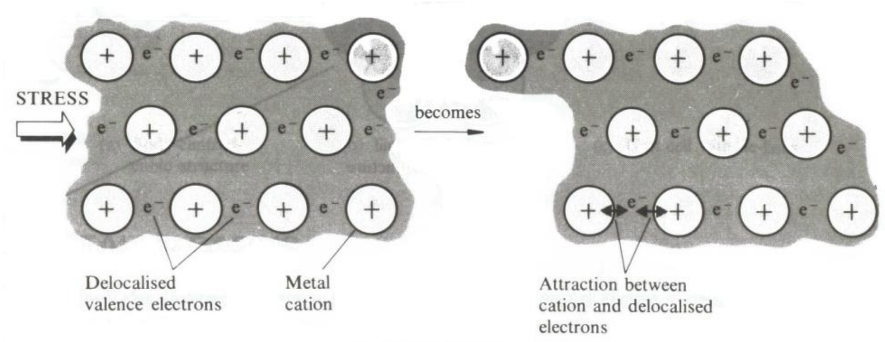
❖ **Thermal conductivity**

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

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

- When shear stress is applied, the non-directional character of metallic bonding and the mobility of the sea of delocalised electrons allow the metal ions in the structure to slide past each other, readily **accommodate any distortion in the lattice without fracturing**.

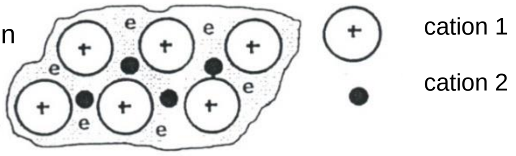
- The metal lattice does not break because the sea of delocalised electrons prevents repulsions between the cations.



❖ **Soluble in other metals** (**alloys**)

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

Alloy formation



- Alloys are harder and stronger than pure metals.
  Brass (alloy of copper with zinc) is harder and stronger than copper because the zinc ions cause a less regular copper lattice, making it more difficult for the metallic ions to slide past each other.

- Alloys have increased electrical resistance and lower conductivity. The lattice of an alloy is less regular and thus affects mobility of the electrons.

Checkpoint 1

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

Metal	Melting point / °C
Li	180
Na	98

Thinking process	**Explanation**
- *State the structure of the two substances*	Both Li and Na have ________________ structure.
- *State the number of valence electrons contributed per metal atom*	Both Li and Na contribute ___ **valence electron per atom** to form the sea of delocalised electrons.
- *Compare the ionic radius of metal cation (**ONLY** for metals with **same** no. of delocalised electrons. Skip this comparison if different no. of delocalised electrons.)*	Li$^+$ ion has a __________ ionic radius than Na$^+$ ion.
- *State which metal cation ion has greater attraction for the delocalised electrons.*	Hence Li$^+$ ions have ________ attraction for the delocalised electrons.
- *State which metal requires more energy to break the stronger metallic bonds to account for the melting point.*	________ energy is needed to break the ________ **metallic bonds in Li**, thus Li has a higher melting point.

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

Metal	Melting point / °C
Na	98
Mg	650

Learning Objective:

- describe ionic bond as the electrostatic attraction between oppositely charged ions
- use of ‘dot-and-cross’ diagrams to describe ionic bonding as in NaC*l* and MgO
- describe the ionic lattice structure of a crystalline solid as in NaC*l* and MgO
- describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

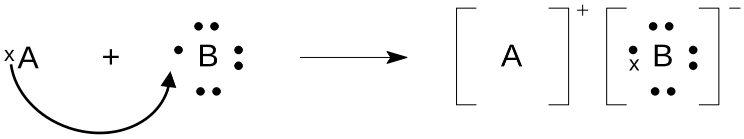
2 IONIC (ELECTROVALENT) BONDS

Inter–Atomic Bonds

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

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

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



Electron transfer

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

e.g.	Na	+	C*l*	→	Na^+	+	Cl^-
	$1s^22s^22p^6\mathbf{3s^1}$		$1s^22s^22p^63s^2\mathbf{3p^5}$		$1s^22s^22p^6$		$1s^22s^22p^63s^2\mathbf{3p^6}$

Some exceptions to the octet rule:

Atoms	Ions	Remarks
<u>Transition metals</u>		
Fe $1s^22s^22p^63s^23p^63d^64s^2$	$\mathbf{Fe^{2+}}$ $1s^22s^22p^6\underline{3s^23p^63d^6}$	Fe^{2+} ion has 14 electrons in <u>outermost shell</u>.
Mn $1s^22s^22p^63s^23p^63d^54s^2$	$\mathbf{Mn^{2+}}$ $1s^22s^22p^6\underline{3s^23p^63d^5}$	Mn^{2+} ion has 13 electrons in <u>outermost shell</u>.
Pb $[Xe]\ 4f^{14}5d^{10}6s^26p^2$	$\mathbf{Pb^{2+}}$ $[Xe]\ 4f^{14}5d^{10}\underline{6s^2}$	Pb^{2+} ion has 2 electrons in <u>outermost shell</u>.

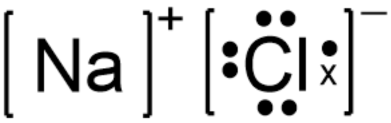
2.1 Dot-and-cross diagrams of ionic compounds

Note:
For A level dot-and-cross diagram:
1) electron shell (orbit) are **NOT** shown

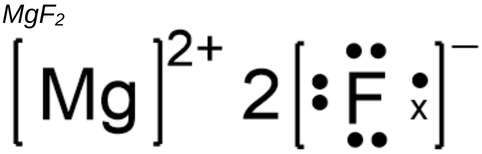
2) **<u>Only</u>** the outermost shell (valence) electrons are shown

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

NaCl



MgF_2



Checkpoint 2

Draw a dot and cross diagram for

(i) K_2O (K - Grp 1; O - Grp 16)

(ii) Al_2O_3 (Al - Grp 13; O - Grp 16)

2.2 Structure and Bonding of Ionic Compounds

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

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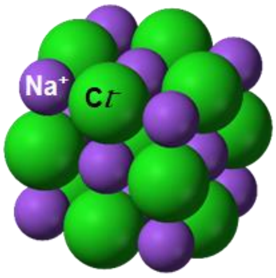
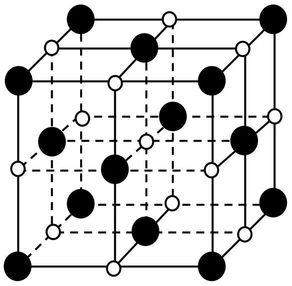




Lattice Structure of NaCl

● chloride ion
○ sodium ion

Each Na^+ ion is surrounded by 6 Cl^- ions

Each Cl^- ion is surrounded by 6 Na^+ ions

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

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

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

2.3 Factors affecting Strength of Ionic Bonds

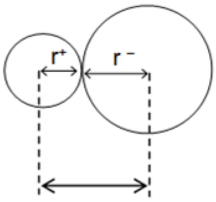
The strength of ionic bonds in ionic solids with the same crystal structure is indicated by its **lattice energy (L.E.)**.

Lattice energy is the energy released when one mole of ionic solid is formed from its constituent gaseous ions. (To be covered in ***Chemical Energetics***)

Example: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ L.E. = – 771 kJ mol^{-1}

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

where
q_+ is charge of cation
q_- is charge of anion
r_+ is radius of cation
r_- is radius of anion



Interionic distance

Magnitude of lattice energy depends on:

1) Product of Charge of the ions:
the greater the charge of the ions, the larger the magnitude of lattice energy

2) Interionic distance:
the shorter the interionic distance, the larger the magnitude of lattice energy

Checkpoint 3

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

- *Compare the charge and size of the ions*

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

- *Compare the product of charges of ions and interionic distance*

The product of charges in MgO is ________ compared to that in $NaCl$.
The interionic distance in MgO is ________ than that of $NaCl$.

- *Compare the magnitude of lattice energy to determine the strength of the ionic bond*

Given $|L.E| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$,
Magnitude of lattice energy of MgO is ________ than that of $NaCl$.

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

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

2.4 Physical properties of ionic solids

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

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

$$AB\ (s) \xrightarrow[\text{melting}]{\Delta H_{fusion}} AB\ (l)$$

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

Boiling involves overcoming **all ionic bonds**

$$AB(l) \xrightarrow[\text{boiling}]{\Delta H_{vaporisation}} AB\ (g)$$

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

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

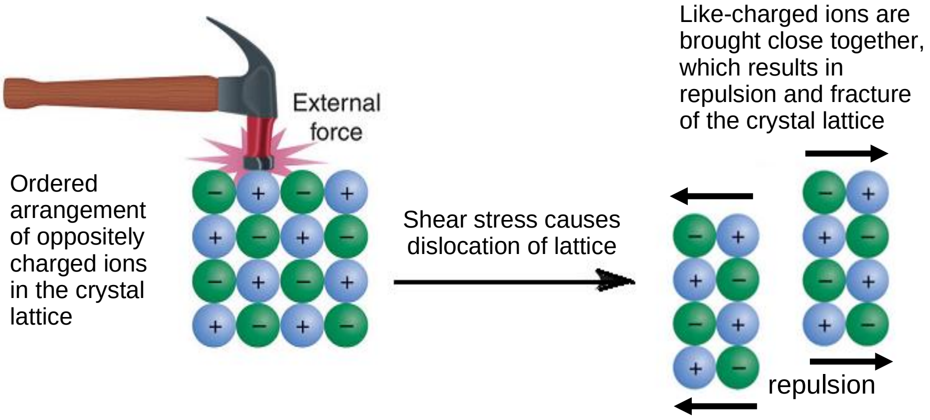
The energy needed to break down a lattice is reflected in its melting point.

Ionic Compound	Cationic Radius /nm	Anionic Radius /nm	Lattice Energy /kJ mol^{-1}	Melting Point /°C
NaC*l*	0.095	0.181	–771	808
NaBr	0.095	0.195	–743	750
MgO	0.065	0.132	–3889	2852
CaO	0.099	0.132	–3513	2614

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

b) Hard and brittle

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



An ionic lattice shatters when deformed

c) Different electrical conductivity in different physical states

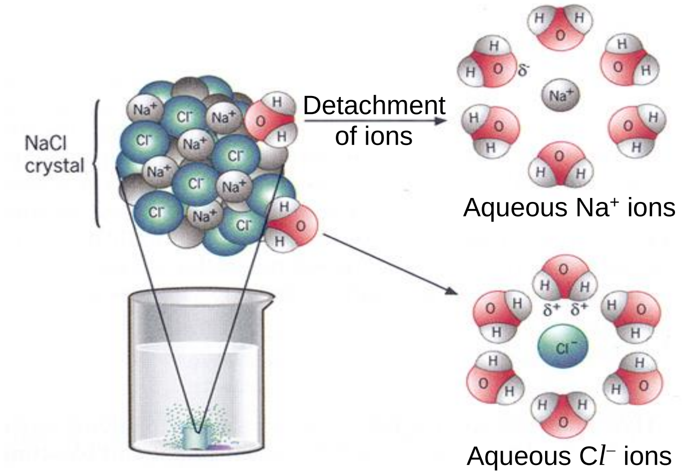
- In solid state, the ions are held in **fixed positions** by strong ionic bonds, hence unable to conduct electricity due to absence of *mobile* charge carriers.
- In molten and aqueous states, the ionic crystal lattice is **broken down.** The ions, acting as **mobile charge carriers**, are free to move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

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

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

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

d) Soluble in water and polar solvents (**usually**)



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

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

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

Checkpoint 4

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

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

❖ *State the structure of the two compounds*	
❖ *State the relevant data from the Data Booklet*	
❖ *Compare the strength of ionic bond between the two compounds*	The product of charges in NaC*l* and NaBr is the ______ since Na^+, $\mathrm{C}l^-$ and Br^- ions are all singly charged. The interionic distance in NaC*l* is ______ than that of NaBr as $\mathrm{C}l^-$ ion is ______ than Br^- ion. Given $\lvert L.E \rvert \propto \left\lvert \frac{q_+ \times q_-}{r_+ + r_-} \right\rvert$, magnitude of lattice energy of NaC*l* is ______ than NaBr.
❖ *State which compound requires more energy to break the stronger ionic bonds to account for the melting point.*	More energy is needed to break the ______ ionic bonds in NaC*l* than that of NaBr. Thus, NaC*l* has a ______ melting point than NaBr.

Learning Objective:

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

Inter–Atomic Bonds

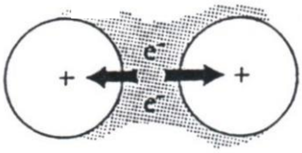
3 COVALENT BONDS

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

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

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

$$A^{\times} \quad + \quad {\bullet}B \quad \longrightarrow \quad A\overset{\times}{\bullet}B$$



Electron sharing in a covalent bond

3.1 Theories on Covalent Bond Formation

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

a. Lewis Theory (1916)

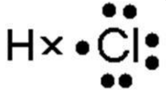
In 1916, Gilbert N. Lewis, American chemist, stated that two atoms may achieve noble gas configuration, not only by transfer of electrons from one atom to another, but also by sharing one or more pairs of valence electrons. This idea was a compilation of knowledge on bonding that existed then.

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

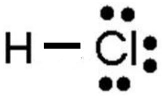
The 2 types of electron pair exhibited in the Lewis structure are:

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

Dot-and-cross diagram



Lewis Structure



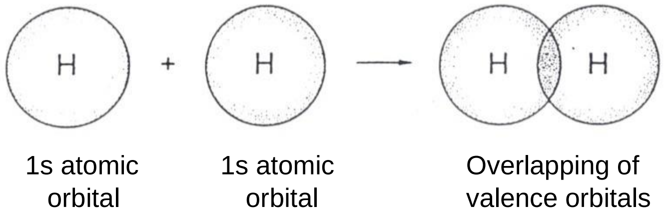
Note:
Within a HC*l* molecule, there are:

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

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

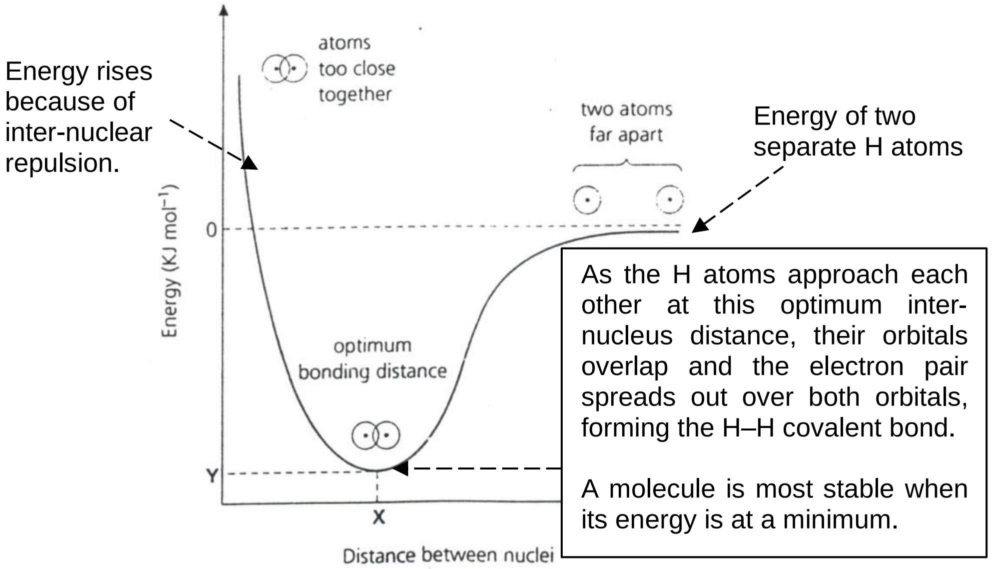
With the advent of quantum mechanics, Walter Heitler and Fritz London in 1927 devised the valence bond theory of bonding.

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



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

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



Energy rises because of inter-nuclear repulsion.

Energy of two separate H atoms

As the H atoms approach each other at this optimum inter-nucleus distance, their orbitals overlap and the electron pair spreads out over both orbitals, forming the H–H covalent bond.

A molecule is most stable when its energy is at a minimum.

Potential energy vs distance between nuclei

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

Learning Objective:

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

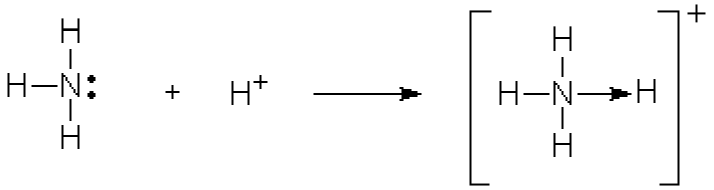
3.2 Co-ordinate Bond (Dative covalent bond)

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

- If **both electrons** in a covalent bond come from **only one of the atoms**, the bond is called a **co-ordinate bond /dative covalent bond**.

- Dative bond is formed when a filled valence orbital of an atom overlaps with a vacant valence orbital of another atom, i.e. an atom (donor) donates **a lone pair of electrons** to another atom (acceptor) which has **a empty low-lying orbital (energetically accessible orbital)** to **accommodate** the electrons.

  E.g. Ammonium ion, NH_4^+
  NH_3 has a lone pair on N which is donated to the empty low-lying orbital of the H^+ ion, forming a dative bond.



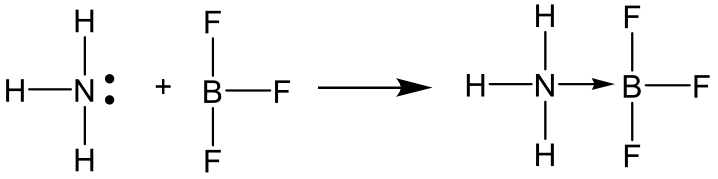
- The dative bond is denoted by an arrow ⟶. The direction of the arrow is drawn from the donor atom to the acceptor atom.

- The **<u>bonding electron pair</u> comes from <u>only one</u> atom**.

Other examples:

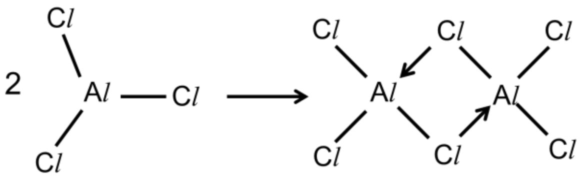
(i) $BF_3.NH_3$

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



(ii) Al_2Cl_6 (A*l* forms covalent bond with C*l*. See section B 4.2)

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



Learning Objective:

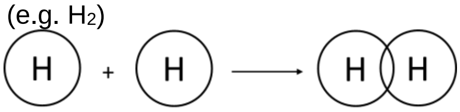
- describe covalent bonding in terms of orbital overlap (limited to s and p orbitals only), giving σ and π bonds

3.3 Types of Covalent Bonds

a. Sigma (σ) Bond

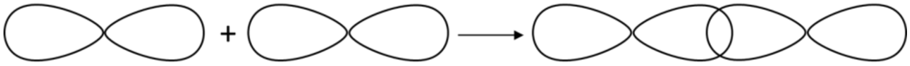
- σ bond is formed by **head-on (collinear) overlap** of two atomic orbitals.
- Electron density is concentrated between the nuclei of the bonding atoms.
- There can only be **ONE** sigma bond between two atoms as there is no way for another head-on overlap of the atomic orbitals to take place.

- Examples of sigma bond:
  - s – s overlap (e.g. H_2)



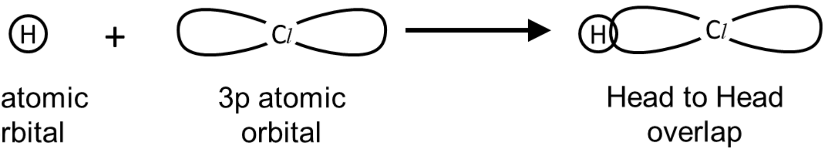
1s atomic orbitals head-to-head overlap

  - p–p overlap (e.g. F_2)



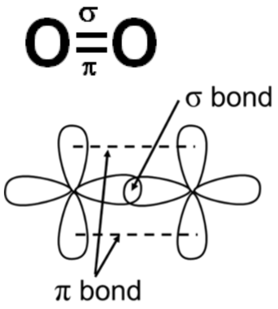
2p atomic orbitals head-to-head overlap

  - s–p overlap (e.g. HC*l*)



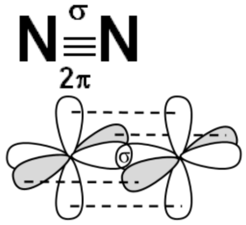
Note:
A **double bond** consists of a σ bond and a π bond.

E.g. Oxygen, O_2:



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

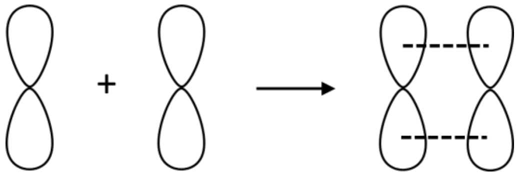
E.g. Nitrogen, N_2



--- represents π bond

b. Pi (π) Bond

- **π bond** is formed by **side-way (collaterally) overlap** of **two p atomic orbitals**.



p atomic orbitals side-way overlap

*Sigma (**σ**) versus Pi (π) bonds*

- The strength of a covalent bond is determined by the degree of orbital overlap. Since the overlap of the orbitals is greater in sigma bond formation, **a sigma bond is stronger than a pi bond.**

- A pi bond is formed **only after** a sigma bond is first formed.
  - Therefore, π bonds are present only in multiple bonds (such as double bond or triple bond).

Learning Objective:

- explain the terms *bond energy* and *bond length* for covalent bonds

3.4 Covalent Bond Strength and Bond Length

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

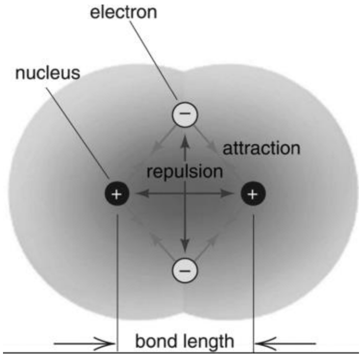
The strength of the covalent bond is determined by the **degree of orbital overlap** between the two bonded atoms. It can be inferred from its **bond dissociation energy (bond energy)**.

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

The distance between the nuclei of the two bonding atoms in a covalent bond is known as the **bond length**. Thus, bond length is the result of a balance between:

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

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



The strength of covalent bonds is affected by several factors:

a) Bond Order
b) Effectiveness of Orbital Overlap
c) Bond Polarities

a) Bond Order – the number of covalent bonds formed between the 2 atoms

- Strength of triple bond > double bond > single bond
- The **higher the bond order**, the **greater the no. of orbitals overlapped**, hence **increase in electron density** between the bonding atoms, **greater attraction** between the bonding nuclei and the shared electrons, and **stronger** covalent bond.

Bond	Bond energy (kJ/mol)
C – C	350
C = C	610
C ≡ C	840

Note:
Why is Bond energy of C=C not 2 × bond energy of C−C?

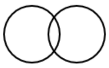
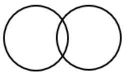
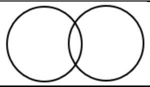
The bonds in C=C consists of a σ bond and a π bond.
π bond is weaker than a σ bond since the orbital overlap is less effective .

b) Effectiveness of Orbital Overlap

- In general, **more effective orbital overlap** results in a **stronger bond**
- **Larger orbitals are more diffuse.** When the larger orbitals overlap with each other, there is **less effective orbital overlap** (lower percentage of electron density between the nuclei). Hence the **covalent bond is weaker**.

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

The **F−F bond length is so short** that the lone pairs of electrons on the fluorine atoms **repel** each other and **weakens** the **F−F bond**

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

c) Bond Polarity

Polar covalent bond occurs due to a difference in electronegativities between 2 bonding atoms. Partial charges (δ+ and δ-) arise on the two bonded atoms.

- The presence of partial charges increases the attraction between bonding atoms, on top of the existing covalent bond.
- This increases the strength of the covalent bond.

Note:
C−C and C−F have similar effectiveness of orbital overlap since electron cloud of C and F are similar in size.

Bond	Bond energy (kJ mol^{-1})
C–C (non-polar)	350
C–F (polar)	485

"**Electronegativity**" was a concept studied by many chemists including Avogadro long ago, but was introduced as a term only in 1811. However, the scale to measure electronegativity was not established until 1932 when Linus Pauling proposed an electronegativity scale as a development of valence bond theory.

Electronegativity cannot be directly measured and must be calculated. Although there may be small differences in the numerical values of the electronegativity based on the different calculation methods, all methods show the same periodic trends between elements. The most commonly used method of calculation for the dimensionless quantity, commonly referred to as the **Pauling scale** (χ_r), on a relative scale running from around 0.7 to 3.98 (hydrogen = 2.20).

Pauling Electronegativity Values for the Elements

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

Learning Objective:

- describe the simple molecular lattice structure of a crystalline solid as in I_2
- describe the giant molecular lattice structure of a crystalline solid as in graphite and diamond
- use of 'dot-and-cross' diagrams to describe covalent bonding as in H_2, O_2, N_2, Cl_2, HCl, CO_2, CH_4 and C_2H_4

3.5 Physical Properties of Covalent Compounds

- The physical properties of covalent compounds are dependent on the structures of covalent substances:

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

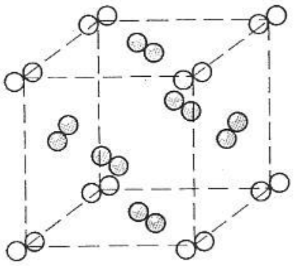
- Covalent compounds consist of simple discrete molecules

- Strong covalent bonds exist between the atoms while weak intermolecular forces of attractions are present between the molecules

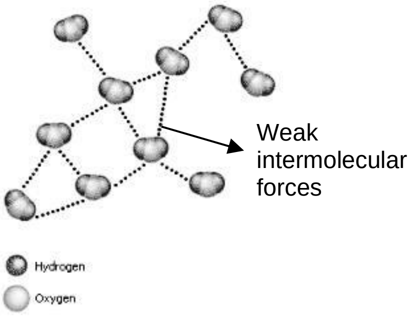
- **Low melting point and boiling points** (exist as gases, liquids or low-melting solids)
  - Small amount of energy is needed to overcome the weak intermolecular forces between the molecules
  - Covalent bonds remain intact

- Usually **soluble in non-polar organic solvents** such as CCl_4
  - Polar covalent molecules have greater solubility in polar solvent such as H_2O

- Non-electrical conductor due to absence of mobile charge carriers
  - Some covalent molecules can ionise in water and may conduct electricity in aqueous state such as HCl (aq)



Iodine in solid state

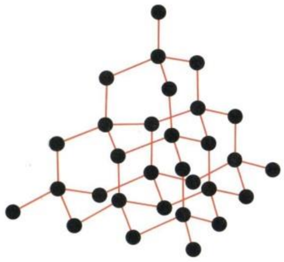


Water

b. ***Giant Molecular Lattice Structure*** ***(e.g. Diamond, graphite, Si, SiO_2)***

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

I. Diamond and its properties



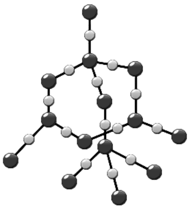
Each carbon atom is bonded to **4 carbon atoms** with strong covalent bonds in tetrahedral arrangement throughout the lattice.

The C atom is sp^3 hybridized.

- **Very high melting point** - Large amount of energy is required to break the strong covalent bonds throughout the lattice.
- **Non- electrical conductor** - Absence of mobile charged carriers
- **Hard** - Atoms are held rigidly by the strong covalent bonds throughout the covalent lattice.
- **Insoluble in all solvents** - Solvent molecules cannot penetrate the covalent lattice because of the strong covalent bonds between atoms and thus it cannot dissolve in solvents.

Note:
Si solid has the same lattice structure as diamond.

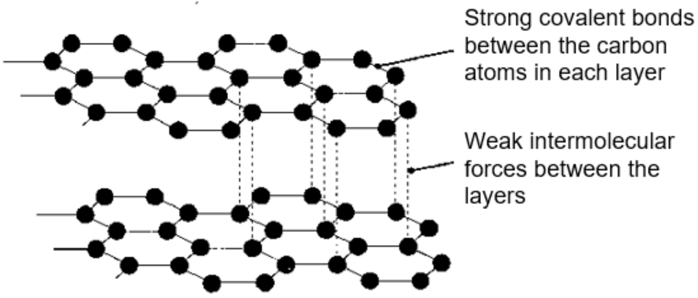
SiO_2 has a structure that is similar to diamond



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

This gives a Si:O ratio of 1:2 and thus a formula of SiO_2.

II. Graphite and its properties



In each layer, each carbon atom bonded to **3 carbon atoms** by strong covalent bonds to form a planar network of hexagons.

The C atom is sp^2 hybridised and leaving an unhybridised p orbital perpendicular to the plane of the hexagons.

The p-orbitals overlap sideways to form a delocalised π electron cloud along the layer.

- **Very high melting point** - Large amount of energy is required to break the strong covalent bonds between the carbon atoms within the layers.
- **Good electrical conductor** - Conducts electricity in the plane of the layers due to presence of delocalised electrons along the layer.
- **Slippery and lubricating properties** - Due to the weak intermolecular forces of attractions between layers, the layers can slide over one another easily.
- **Insoluble in all solvents** - Solvent molecules cannot penetrate the covalent lattice because of the strong covalent bonds between atoms and thus it cannot dissolve in solvents.

3.6 Dot-and-Cross Diagrams for covalent molecules

Note:
Dots and crosses are the only symbols used to represent the electrons.

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

Such representation is used to account for the number of electrons in the molecules and hence determine the number of electron pairs present.

General guidelines for drawing dot-and-cross diagrams

Draw the arrangement of the atoms.

- For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds).
- Arrange the terminal atoms symmetrically around the central atom.
- **FOR IONS:** Add "[ ]" and write the overall charge on the top right corner outside the bracket.

Determine types and number of covalent bonds using valence electron comparison.

1. Write out the atoms in a row/column with the central atom as the first element
2. Fill in the no. of valence electrons for each element
    - ***For Anion:***
      Add one valence electron for every negative charge to the most electronegative atom. Assign the electrons evenly if there are more than 1 of the most electronegative atom (e.g. SO_4^{2-})
    - ***For Cation:***
      Remove one valence electron for every positive charge from the least electronegative atom.
3. Distribute the valence electrons on the central atom to the terminal atom such that all elements achieve noble gas configuration. Remaining valence electrons will be lone pairs/lone electron on the central atom.

Complete the dot-and-cross diagram.

- Draw the covalent bonds using dot-and-cross based on the type of covalent bonds present.
    - 1 shared pair of e^- indicates a single bond.
    - 2 shared pairs of e^- indicates a double bond
- Fill in any remaining valence electrons as lone pairs around the central atom.

Check the no. of electrons at the central atom.

- Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it). Replace a double bond with a dative bond if it exceeds octet.
- If it is not possible to have an octet, leave the species in the configuration as close to octet as possible.

Done!

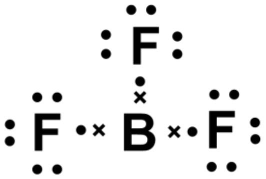
Exceptions to the octet rule

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

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

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

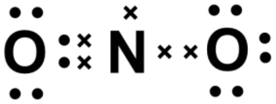
(4 electrons around Be after bonding)



(6 electrons around B after bonding)

(II) ***Species with Odd Number of Valence Electrons***

If the total number of valence electrons is odd, there will be 1 unpaired electron. This occurs most often when the central atom is nitrogen.



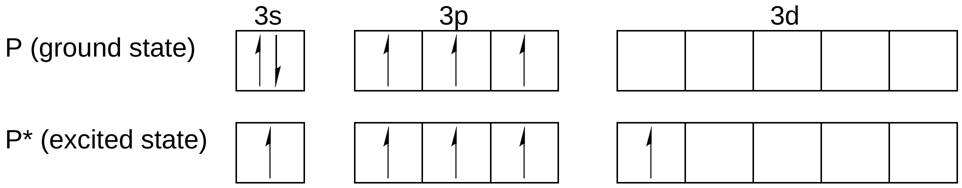
(7 electrons around N after bonding)

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

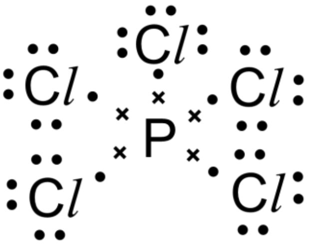
Elements from ***<u>Period 3 and beyond</u>*** can expand octet due to the availability of the energetically accessible d orbitals (within the same valence principal quantum shell) to accommodate additional electrons from the bonded atoms.

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

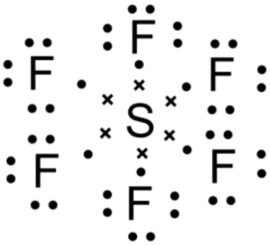
Note:
P (ground state) can form 3 covalent bonds but P* (excited state) can form 5 bonds.



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



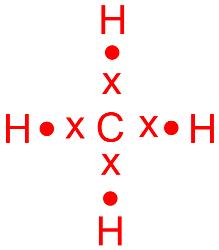
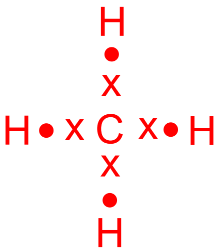
(10 electrons around P after bonding)



(12 electrons around S after bonding)

Example: Methane CH_4

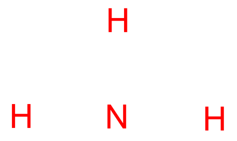
<table>
<tr>
<td><i>A</i></td>
<td>Draw the arrangement of the atoms.</td>
<td>• For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds).
• Arrange the terminal atoms symmetrically around the central atom.</td>
<td>C can form the most bonds compared to H.
C is the central atom.
H
H C H
H</td>
</tr>
<tr>
<td>B</td>
<td>Determine <u>types</u> and <u>number</u> of covalent bonds using valence electron comparison.</td>
<td>1. Write out the atoms in a row/column with the central atom as the first element</td>
<td>
<table>
<tr><th>Element</th><th>C</th><th>H</th><th>H</th><th>H</th><th>H</th></tr>
<tr><td>No. of valence e⁻</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>e⁻ distribution</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>
</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Fill in the no. of valence electrons for each element</td>
<td>
<table>
<tr><td>Element</td><td>C</td><td>H</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e⁻</td><td>4</td><td>1</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>e⁻ distribution</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>
</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Distribute the valence electrons on the central atom to the terminal atom such that all elements achieve noble gas configuration.

Remaining valence electrons will be lone pairs/lone electron on the central atom.</td>
<td>
<table>
<tr><td>Element</td><td>C</td><td>H</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e⁻</td><td>④</td><td>1</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>e⁻ distribution</td><td>0</td><td>1</td><td>1</td><td>1</td><td>1</td></tr>
</table>
</td>
</tr>
<tr>
<td>C</td>
<td>Complete the dot-and-cross diagram.</td>
<td>• Draw the covalent bonds using dot-and-cross based on the type of covalent bonds present.
  ○ 1 shared pair of e– indicates single bond.</td>
<td>Since C share 1 e⁻ with each H, C forms single bond with each H.
 </td>
</tr>
<tr>
<td>D</td>
<td>Check the no. of electrons at the central atom.</td>
<td>• Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it).</td>
<td>
C is from period 2 and has met octet rule.
This is the answer.</td>
</tr>
</table>

Example: Ammonia (NH_3)

<table>
<tr>
<td>A</td>
<td>Draw the arrangement of the atoms.</td>
<td>

For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds).
Arrange the terminal atoms symmetrically around the central atom.

</td>
<td>N can form the most bonds compared to H.
N is the central atom.


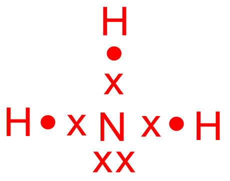
</td>
</tr>
<tr>
<td>B</td>
<td>Determine <u>types</u> and <u>number</u> of covalent bonds using valence electron comparison.</td>
<td>
1. Write out the atoms in a row/column with the central atom as the first element

2. Fill in the no. of valence electrons for each element

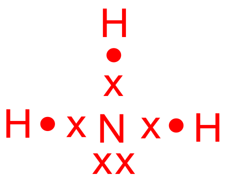
3. Distribute the valence electrons on the central atom to the terminal atom such that all elements achieve noble gas configuration.

Remaining valence electrons will be lone pairs/lone electron on the central atom.
</td>
<td>
<table>
<tr><td>Element</td><td>N</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e⁻</td><td></td><td></td><td></td><td></td></tr>
<tr><td>e⁻ distribution</td><td></td><td></td><td></td><td></td></tr>
</table>
<table>
<tr><td>Element</td><td>N</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e⁻</td><td>5</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>e⁻ distribution</td><td></td><td></td><td></td><td></td></tr>
</table>
<table>
<tr><td>Element</td><td>N</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e⁻</td><td>5</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>e⁻ distribution</td><td>2</td><td>1</td><td>1</td><td>1</td></tr>
</table>
</td>
</tr>
<tr>
<td>C</td>
<td>Complete the dot-and-cross diagram.</td>
<td>

Draw the covalent bonds using dot-and-cross based on the type of covalent bonds present.
1 shared pair of e– indicates single bond.
Fill in any remaining valence electrons as lone pairs on the central atom.

</td>
<td>Since N share 1 e⁻ with each H, N forms single bond with each H. The 2 electrons left on N as lone pairs.

</td>
</tr>
<tr>
<td>D</td>
<td>Check the no. of electrons at the central atom.</td>
<td>

Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it).

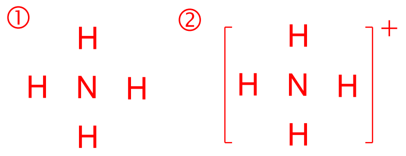
</td>
<td>

N is from period 2 and has met octet rule. This is the answer.
</td>
</tr>
</table>

Example: Ammonium ion (NH_4^+)

<table>
<tr>
<td>A</td>
<td>Draw the arrangement of the atoms.</td>
<td>

For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds).
Arrange the terminal atoms symmetrically around the central atom.
FOR IONS: Add “[ ]” and write the overall charge on the top right corner outside the bracket.

</td>
<td>
N can form the most bonds compared to H.
N is the central atom.



</td>
</tr>
<tr>
<td>B</td>
<td>Determine <u>types</u> and <u>number</u> of covalent bonds using valence electron comparison.</td>
<td>
1. Write out the atoms in a row/column with the central atom as the first element

2. Fill in the no. of valence electrons for each element
For Cation: Remove one valence electron for every positive charge from the least electronegative atom.

3. Distribute the valence electrons on the central atom to the terminal atom such that all elements achieve noble gas configuration.

Remaining valence electrons will be lone pairs/lone electron on the central atom.
</td>
<td>
<table>
<tr><td>Element</td><td>N</td><td>H</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e^-</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>e^- distribution</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

<table>
<tr><td>Element</td><td>N</td><td>H</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e^-</td><td>5</td><td>0</td><td>1</td><td>1</td><td>1</td></tr>
<tr><td>e^- distribution</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

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<tr><td>Element</td><td>N</td><td>H</td><td>H</td><td>H</td><td>H</td></tr>
<tr><td>No. of valence e^-</td><td>5</td><td>0</td><td>1</td><td>1</td><td>1</td></tr>
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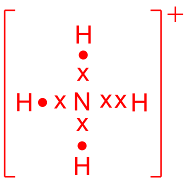
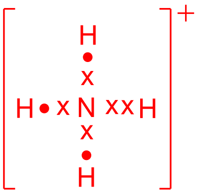
<td>Complete the dot-and-cross diagram.</td>
<td>

Draw the covalent bonds using dot-and-cross based on the type of covalent bonds present.
1 shared pair of e– indicates single bond.
Fill in any remaining valence electrons as lone pairs on the central atom.

</td>
<td>
N shared 1 e^- with 3 of the H, N forms single bond with each of these H.
N shared 2 e^- with 1 of the H, N form dative bond with this H.


</td>
</tr>
<tr>
<td>D</td>
<td>Check the no. of electrons at the central atom.</td>
<td>

Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it).

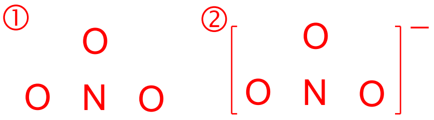
</td>
<td>


N is from period 2 and has met octet rule.
This is the answer.
</td>
</tr>
</table>

Example: Nitrate ion (NO_3^-)

<table>
<tr>
<td>A</td>
<td>Draw the arrangement of the atoms.</td>
<td>

For compounds of chemical formula AB_n, identify the central atom (usually the atom which can form the most number of covalent bonds).
Arrange the terminal atoms symmetrically around the central atom.
FOR IONS: Add “[ ]” and write the overall charge on the top right corner outside the bracket.

</td>
<td>
N can form the most bonds compared to O.
N is the central atom.


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<tr>
<td>B</td>
<td>Determine <u>types</u> and <u>number</u> of covalent bonds using valence electron comparison.</td>
<td>
1. Write out the atoms in a row/column with the central atom as the first element

2. Fill in the no. of valence electrons for each element
For Anion: Add one valence electron for every negative charge to the most electronegative atom.

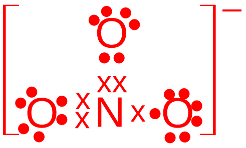
3. Distribute the valence electrons on the central atom to the terminal atom such that all elements achieve noble gas configuration.

Remaining valence electrons will be lone pairs/lone electron on the central atom.
</td>
<td>
<table>
<tr><td>Element</td><td>N</td><td>O</td><td>O</td><td>O</td></tr>
<tr><td>No. of valence e⁻</td><td></td><td></td><td></td><td></td></tr>
<tr><td>e⁻ distribution</td><td></td><td></td><td></td><td></td></tr>
</table>
<table>
<tr><td>Element</td><td>N</td><td>O</td><td>O</td><td>O</td></tr>
<tr><td>No. of valence e⁻</td><td>5</td><td>6</td><td>6</td><td>7</td></tr>
<tr><td>e⁻ distribution</td><td></td><td></td><td></td><td></td></tr>
</table>
<table>
<tr><td>Element</td><td>N</td><td>O</td><td>O</td><td>O</td></tr>
<tr><td>No. of valence e⁻</td><td>5</td><td>6</td><td>6</td><td>7</td></tr>
<tr><td>e⁻ distribution</td><td>0</td><td>2</td><td>2</td><td>1</td></tr>
</table>
</td>
</tr>
<tr>
<td>C</td>
<td>Complete the dot-and-cross diagram.</td>
<td>

Draw the covalent bonds using dot-and-cross based on the type of covalent bonds present.

1 shared pair of e– indicates single bond.
2 shared pair of e– indicates double bond.

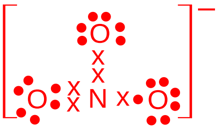
Fill in any remaining valence electrons as lone pairs on the central atom.

</td>
<td>
N share 1 e⁻ with one of the O, N forms single bond with that O.
N share 2 e⁻ with the other 2 O, N forms double bonds with the 2 O.


</td>
</tr>
<tr>
<td>D</td>
<td>Check the no. of electrons at the central atom.</td>
<td>

Central atom from Period 2 cannot exceed octet rule (i.e. cannot have more than 8 electrons around it).

Replace a double bond with a dative bond if it exceeds octet.

</td>
<td>


N has 8 e⁻ After replacing double bond with a dative bond.
This is the answer.
</td>
</tr>
</table>

Checkpoint 5

Draw dot-and-cross diagrams of the following molecules or polyatomic ions:

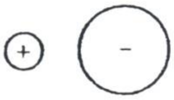
CCl_4	**$BeCl_2$**
NO_2	**NO_2^+**
$AlCl_4^-$	**ICl_4^-**
CO_3^{2-}	

4 INTERMEDIATE BOND TYPES

There are compounds that might be expected to be ionic which have properties more typical of covalent compounds. For example,

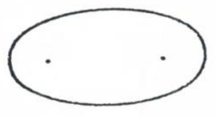
- some salts sublime at low temperatures, e.g., aluminium chloride, $AlCl_3$.
- there are covalent compounds that dissolve readily in water to produce ionic solutions, e.g. HCl gas and NH_3, ammonia.

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



Ionic model

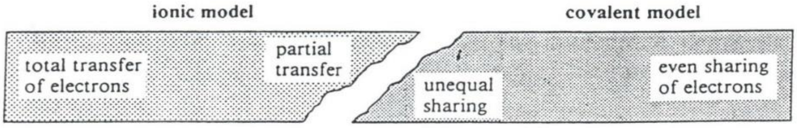
vs



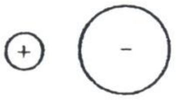
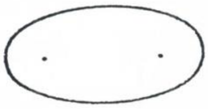
Covalent model

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

4.1 Transition of ionic or covalent to intermediate bonds



Note:
Whether a compound is covalent or ionic depends on which model it follows.

Model 1	Model 2	Model 3	Model 4
 Pure ionic bond	 Polarised ionic bond	 Polar covalent bond	 Pure (Non-polar) covalent bond
Ions exist as discrete, point charges with **<u>NO</u>** electron density between them.	The cation attracts and distorts the electron cloud of the anion. This is called **polarisation**. The electron density is drawn into the region between the two nuclei, resulting in **partial sharing** of electrons.	Electron density is **<u>NOT</u>** symmetrically distributed in a bond between different atoms. The more electronegative atom has a greater share of the shared electron density.	Electron density is symmetrically distributed in a bond between identical atoms.
This **DOES NOT** occur, in reality, for any ionic compound.	Ionic compounds with cation and anion. Anion has a distorted electron cloud. E.g. $MgCl_2$, NaBr,	Compounds exist as polar molecules as there is a **permanent separation of partial charges**. E.g. HF, H_2O	Compounds with atoms of the same elements bonded to each other. E.g. Br_2, C
<u>Ionic Compounds</u>		**<u>Covalent Compounds</u>**	

The degree of sharing of electrons in an ionic bond depends on the **extent of distortion** of the **electron cloud** of anion.

This means a compound formed from a metal and non-metal may have a simple molecular structure, instead of an ionic lattice!

The **nature of bonding in compounds** can only be inferred from their physical properties such as **melting and boiling points** and solubility in polar or non-polar solvents.

4.2 Polarisation of Ionic Bond

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

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

(b) Size of the Anion
- Polarisability of anion
  - The ability of the electron cloud of the anion to be distorted.
  - A large anion (large electron cloud) is easily polarised.
  - The electron cloud is more distant from its nucleus, easier to be attracted and distorted by the cation.

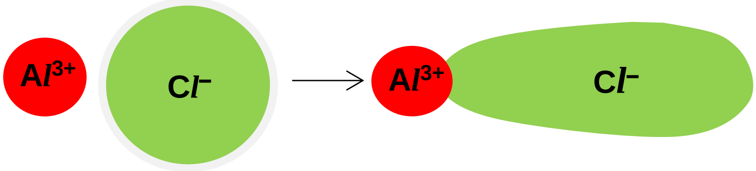
The **greater** the polarisation, the **greater** the ***covalent character*** in the ionic bond

Learning Objective:
- suggest the type of structure and bonding present in a substance from given information

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

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

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



The high charge to size ratio of Al^{3+} ion will cause significant distortion (polarisation) of the neighbouring anion electron cloud. Electron density of Cl^- ion is partially shared with Al^{3+}. With large anions such as Cl^-, in which polarisation occurs more extensively, the distortion can be so great that the bonding is best described as covalent (due to sharing of electron cloud).

Hence, $AlCl_3$ has a simple molecular structure consisting of simple discrete molecules.

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

Al and Be compounds with non–metal larger than Cl, the compound will be predominantly covalent as well. Examples $AlBr_3$ is covalent but AlF_3 is ionic.

C. INTERMOLECULAR FORCES OF ATTRACTION

There are three types of intermolecular forces.

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

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

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

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

The type of intermolecular forces present between the molecules depends on its polarity.
In order to determine the polarity of molecules, we must first determine the geometry of molecules.

Learning Objective:

- 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
- predict the shapes of, and bond angles in, molecules analogous to those specified above

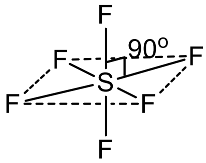
1 MOLECULAR GEOMETRY AND POLARITY

1.1 Determining Geometry of Molecules

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

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

e.g. SF_6



Bond angle = 90°

Shape = Octahedral

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

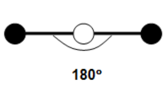
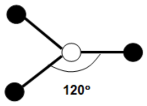
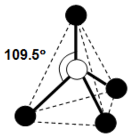
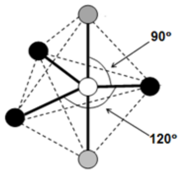
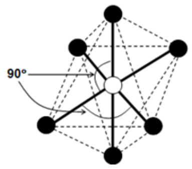
We can predict the geometry of the molecules based on **Valence Shell Electron Pair Repulsion (VSEPR) theory**.

a. General principle of VSEPR

1. Determine the number of electron regions around the central atom.
   Each lone pair e$^-$ OR lone e$^-$ → One electron region
   Each single bond or dative bond → One electron region
   Each double bond or triple bond → One electron region
   E.g. There are 2 electron regions around C in O=C=O.

2. Electron regions (bond pairs and lone pairs) around the central atom arrange themselves to be as far apart as possible to **minimise mutual repulsion** and dictate its shape.

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

2 e$^-$ regions	3 e$^-$ regions	4 e$^-$ regions	5 e$^-$ regions	6 e$^-$ regions
				
Linear	**trigonal planar**	**Tetrahedral**	**trigonal bipyramidal**	**Octahedral**

3. Lone pair electrons influence the geometry of the molecule. Lone pair electrons are closer to the nucleus. They take up more space of the central atom and exercise greater repulsion than bond pairs. Thus,

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

b. Determining the Shapes of Molecules/Polyatomic Ions based on Electron Regions

The dot-and-cross diagram can tell us how many electron regions surrounds the central atom. We can then use this data to study the geometry around this central atom.

- The position of the **electron regions** around the central would determine the **Electron Pair Geometry**.
- The position of the **atoms** around the central atom would determine the **Molecular Geometry**.

The **<u>number of lone pairs and bond pairs</u>** determines the shape of molecules (molecular geometry).

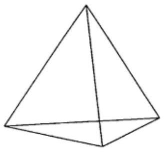
To Determine Shapes of Molecules/Polyatomic ions

1. Draw the **dot-and-cross diagram** of the molecule or polyatomic ion.
2. Count the **total number of electron regions** around the central atom.
   lone pair e$^-$/ lone e$^-$
   single bond/ double bond/ triple bond } Each counts as 1 electron region
3. Determine the **arrangement of the electron regions** around the central atom (electron pair geometry).
4. Determine the **shape/molecular geometry** around the central atom.

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

Note:
Presence of each lone pair electrons causes the bond angle to decrease by approximately 2.5 ° from the theoretical bond angle in the electron pair geometry.
E.g.
3 e⁻ regions → 120 °
2b.p. + 1l.p. → 117.5 °

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



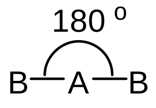
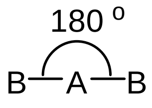
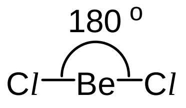
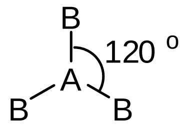
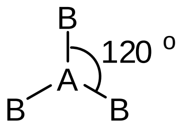
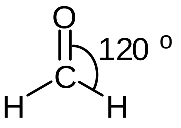
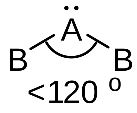
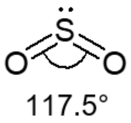
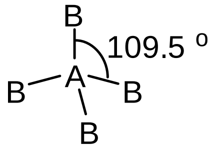
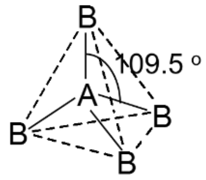
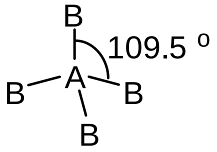
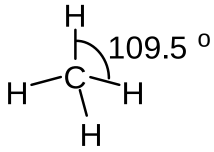
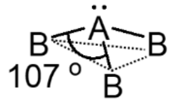
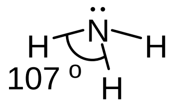
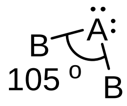
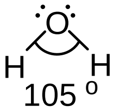
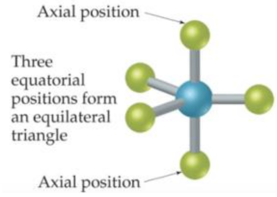
No. of electron regions	Electron Pair Geometry	No. of bond pairs	No. of lone pairs	Molecular Geometry / Shape	Example
2	 Linear	2	0	 Linear	 $BeCl_2$
3	 Trigonal planar	3	0	 Trigonal planar	 HCHO
		2	1	 Bent	 SO_2
4	  Tetrahedral	4	0	 Tetrahedral	 CH_4
		3	1	 Trigonal pyramidal	 NH_3
		2	2	 Bent	 H_2O

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

Note:
For trigonal bipyramidal e^- pair geometry, there are 2 types of positions for the outer atoms.



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

lone pair e^- preferentially occupy the **equatorial position** as this minimises the repulsion between the e^- regions (only close to 2 other e^- regions)
[Axial position is close to 3 other e^- regions]

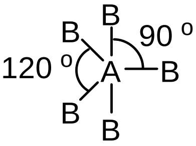
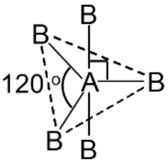
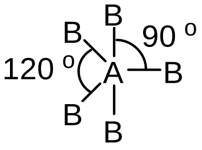
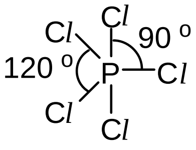
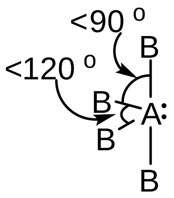
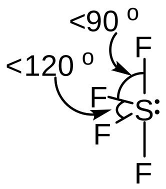
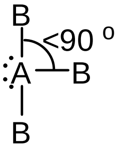
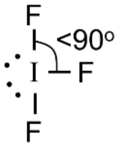
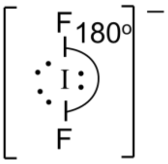
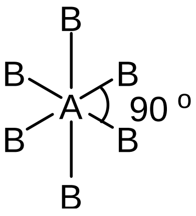
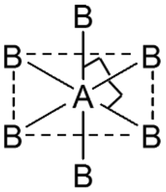
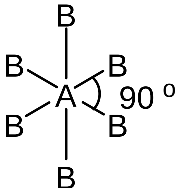
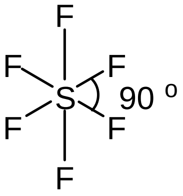
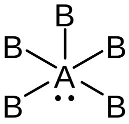
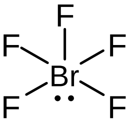
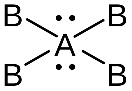
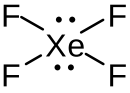
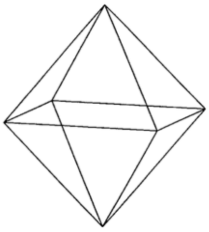
No. of electron regions	Electron Pair Geometry	No. of bond pairs	No. of lone pairs	Molecular Geometry/ Shape	Example
5	  Trigonal bipyramidal	5	0	 Trigonal bipyramidal	 PCl_5
		4	1	 Unsymmetrical tetrahedron (seesaw)	 SF_4
		3	2	 T-shaped	 IF_3
		2	3	 Linear	 IF_2^-
6	  Octahedral	6	0	 Octahedral	 SF_6
		5	1	 Square pyramidal	 BrF_5
		4	2	 Square planar	 XeF_4

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

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



Learning Objective:

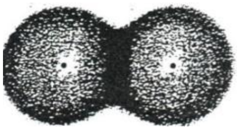
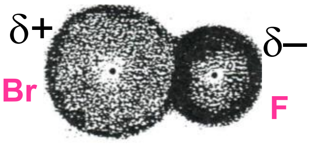
- explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is **not** required]
- deduce the polarity of a molecule using bond polarity and its molecular shape

1.2 Polarity of Molecules

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

(a) What makes a Covalent Bond Polar?

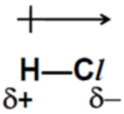
Polarity is the state of having poles, or in this context, separation of charges (positive and negative pole). This polarity of a covalent bond is determined by the electronegativity difference between the bonding atoms.

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

Take Note:

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

e.g.



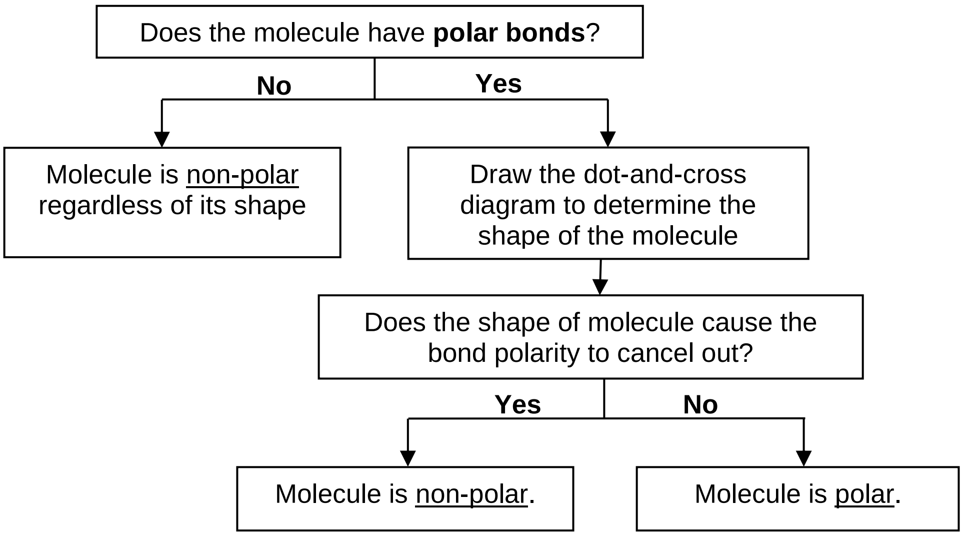
$$\overset{+\!\!\!\longrightarrow}{\underset{\delta+\quad\delta-}{H—Cl}}$$

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

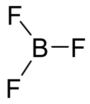
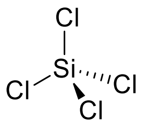
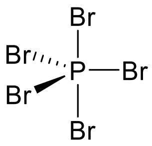
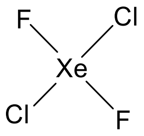
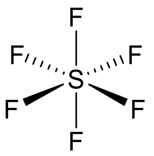
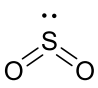
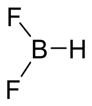
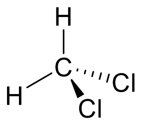
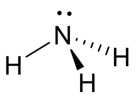
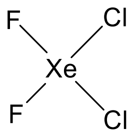
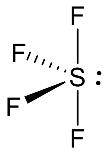
Note:
C-H bond is non-polar!

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

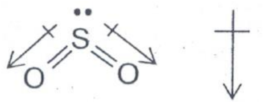
1) **bond polarity** of all the bonds in the molecule and
2) **shape** of the molecule.



Examples of Polar and Non-Polar Molecules

NON–POLAR Molecules	(1) it contains **no polar bonds** (e.g. Br_2, CH_4) **or** (2) individual bond dipoles cancel each other completely with zero net dipole moment (For molecule with polar bonds. e.g. CO_2, BF_3) $O=C=O$      *[**Note:** Highly symmetrical molecules with same terminal atoms are usually non-polar.]*
POLAR molecules	(1) it contains polar bond(s) **AND** (2) the individual dipole moments do not cancel out each other, giving rise to a **net dipole** moment      

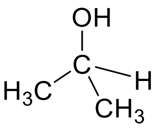
Note:
SO_2 has a net dipole moment as shown



net dipole moment

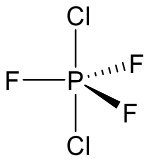
Checkpoint 6

1. Which molecules are polar?



Hexane (C_6H_{14})

Ammonia (NH_3)



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

(i) PBr_3

(ii) CF_4

(iii) $CHBr_3$

(iv) $AlCl_3$

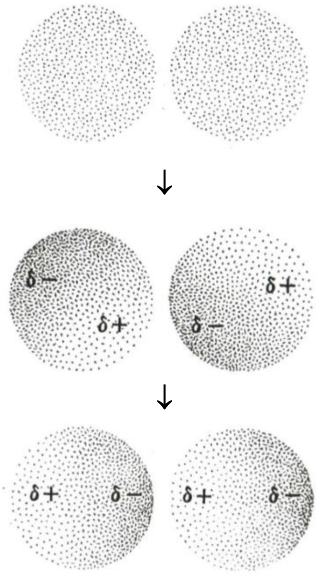
Learning Objective:

- describe instantaneous dipole-induced dipole interactions, as in Br_2(l) and the liquid noble gases
- describe permanent dipole-permanent dipole interactions, as in CH_3Cl(l)
- describe hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups

2 INSTANTANEOUS DIPOLE−INDUCED DIPOLE INTERACTIONS

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

How is instantaneous dipole-induced dipole interaction formed?



Consider a collection of He atoms. Average distribution of electron charge about each nucleus is spherically symmetrical.

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

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

The “cycle” repeats.

The dipoles are temporary but the **net attraction** which they produce is **permanent**.

Note:
The attraction between non-polar molecules can be explained similarly

<u>Factors affecting strength of instantaneous dipole-induced dipole (id-id) interactions</u>

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

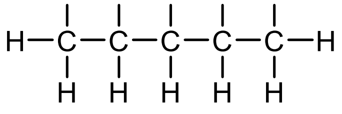
A covalent molecule with a larger M_r would have a larger electron cloud.

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

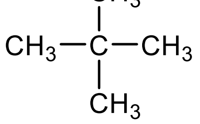
In general, if a molecule is larger,

- there is a larger number of electrons
- the larger electron cloud is **more easily distorted**
- dipoles are **more** easily induced
- **more energy** is required to overcome **stronger** id-id interactions
- boiling/melting point is higher

(2) **Surface area of contact between molecules**
- straight chain molecules vs branched chain isomers of organic molecules.



pentane (b.p. 36 °C)



2,2-dimethylpropane (b.p. 10 °C)

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

Checkpoint 7

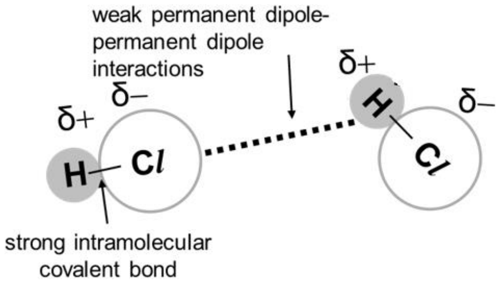
Rank the following molecules in the order of increasing strength of instantaneous dipole – induced dipole interaction.

CH_3CH_3, BF_3, I_2

3 PERMANENT DIPOLE-PERMANENT DIPOLE INTERACTIONS

Intermolecular Forces

This is the predominant intermolecular forces between **polar molecules** with permanent dipoles.

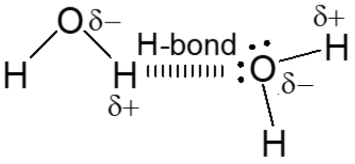


Permanent dipole-permanent dipole (pd-pd) interactions are **stronger** than instantaneous dipole-induced dipole (id-id) for molecules of similar size.

4 HYDROGEN BONDING

Intermolecular Forces

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



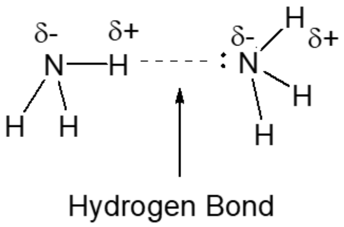
Note:
In a diagram showing hydrogen bonding between molecules, you must indicate

(i) partial charges: (δ+) on protonic H, and (δ–) on F, O or N that the protonic H is bonded to.

(ii) a lone pair on F, O or N on a neigbouring molecule. (δ–) on F, O or N and (δ+) on the atom bonded to it

(iii) a dotted line labelled as hydrogen bond.

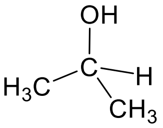
Conditions required for Hydrogen Bonding:

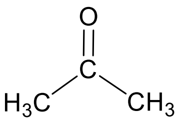


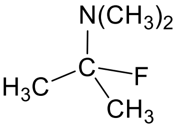
(1) Protonic H in F–H, N–H and O–H covalent bonds
(2) Lone pairs on a highly electronegative atom (N, O, F) in a neighbouring molecule.

Checkpoint 8

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







CH_3CH_2SH

Factors that affect strength of Hydrogen bonding

(1) Extensiveness of Hydrogen bonding (H−bonds)

Different molecules can form different number of H-bonds.

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

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

Example:

	HF	**H_2O**	**NH_3**
No. of protonic H	1	2	3
No. of lone pairs	3	2	1
Average no. of H-bonds per molecule	1	2	1

(2) Polarity of H–Y bond (Y = F, O or N)

More polar H–Y bond ⇒ Stronger H-bond formed
Electronegativity decreases from F > O > N
⇒ Polarity of H–Y bond decreases from $^{\delta+}$H–F$^{\delta-}$ > $^{\delta+}$H–O$^{\delta-}$ > $^{\delta+}$H–N$^{\delta-}$
⇒ Strength of hydrogen bonding should decrease from **H–F > H–O > H–N**.

Worked Example 1

Account for the observed boiling points of the following compounds.

compound	**HF**	**H_2O**	**NH_3**
boiling point / °C	20	100	−33

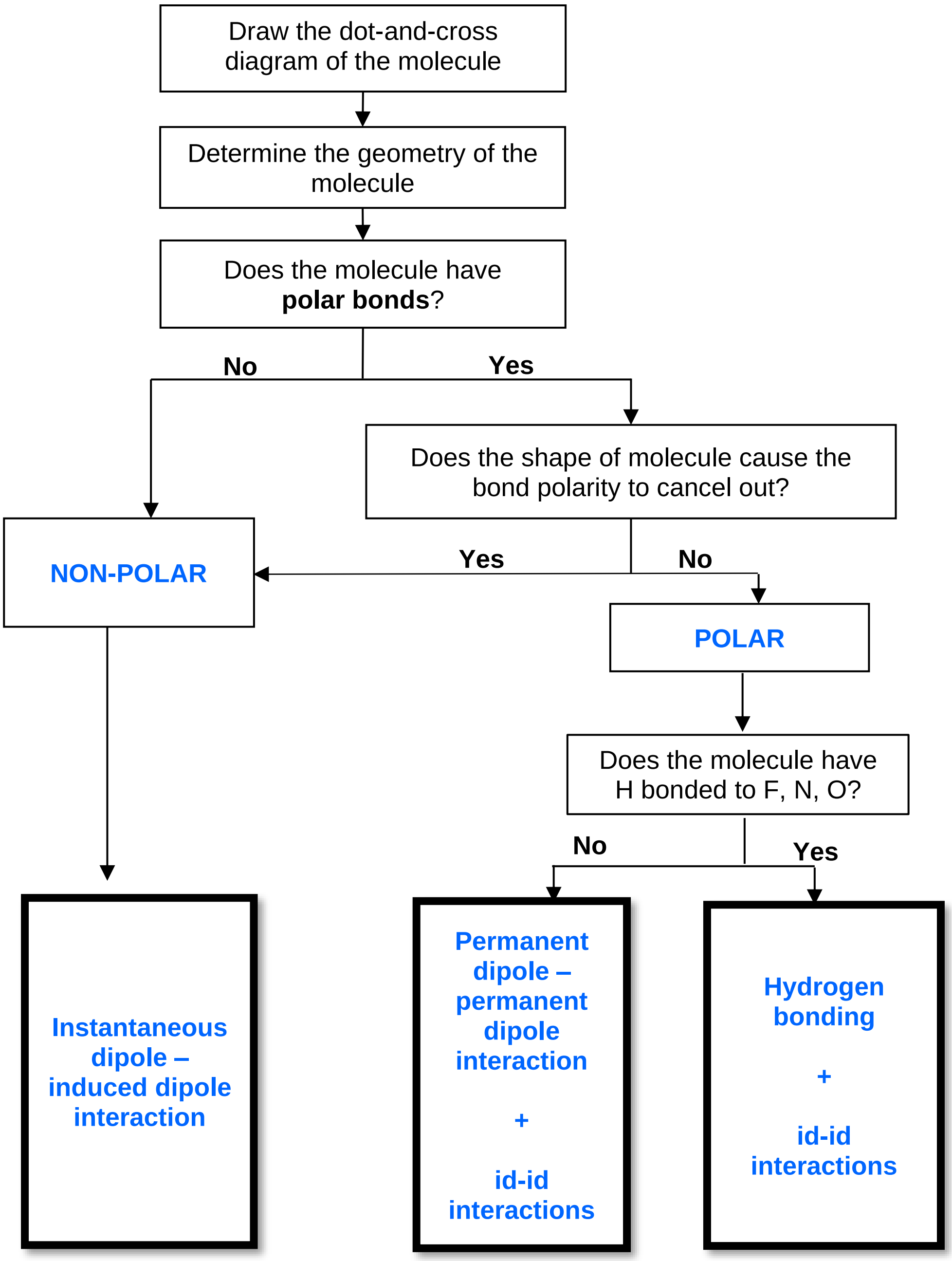
All three compounds are polar covalent molecules with intermolecular forces of hydrogen bonding. Their electron cloud sizes are comparable.

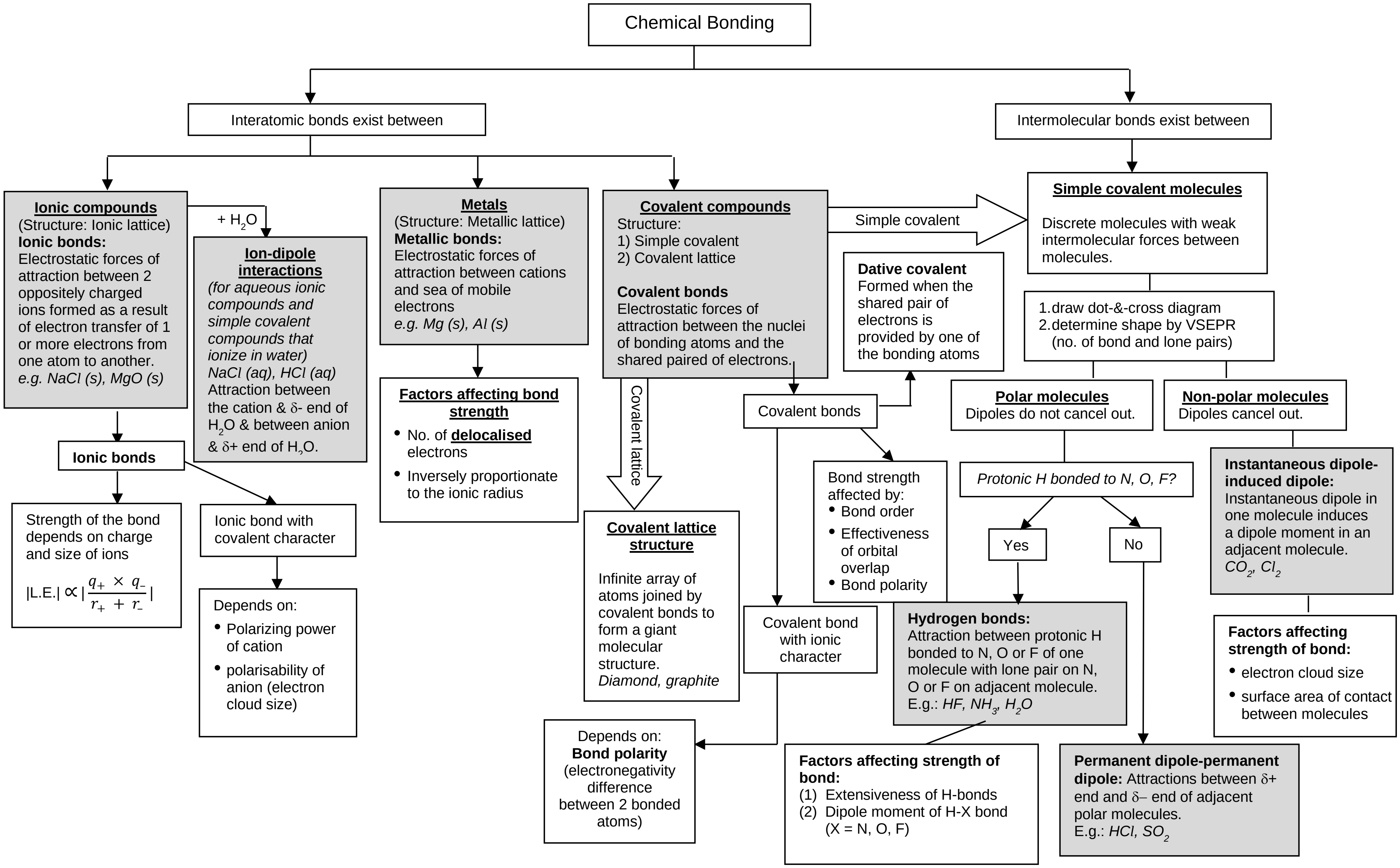
H_2O can form more extensive hydrogen bonding (average 2 H-bonds per molecule) than NH_3 and HF (average 1 H-bonds per molecule).
More energy is required to overcome the more extensive hydrogen bonding between the H_2O molecules.
Hence H_2O has the highest boiling points.

Both HF and NH_3 forms an average of one hydrogen bonding per molecule. H−F bond is more polar than H−N bond, thus the hydrogen bonding between HF molecules are stronger than those between NH_3 molecules.
Hence, HF has a higher boiling point than NH_3.

5 STEPS TO DETERMINE THE TYPE OF INTERMOLECULAR FORCES

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





Chemical Bonding

Interatomic bonds exist between

Ionic compounds
(Structure: Ionic lattice)
Ionic bonds: Electrostatic forces of attraction between 2 oppositely charged ions formed as a result of electron transfer of 1 or more electrons from one atom to another.
e.g. NaCl (s), MgO (s)

+ H_2O

Ion-dipole interactions
(for aqueous ionic compounds and simple covalent compounds that ionize in water)
NaCl (aq), HCl (aq)
Attraction between the cation & δ- end of H_2O & between anion & δ+ end of H_2O.

Ionic bonds

Strength of the bond depends on charge and size of ions

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

Ionic bond with covalent character

Depends on:
- Polarizing power of cation
- polarisability of anion (electron cloud size)

Metals
(Structure: Metallic lattice)
Metallic bonds: Electrostatic forces of attraction between cations and sea of mobile electrons
e.g. Mg (s), Al (s)

Factors affecting bond strength
- No. of **delocalised** electrons
- Inversely proportionate to the ionic radius

Covalent compounds
Structure:
1) Simple covalent
2) Covalent lattice

Covalent bonds
Electrostatic forces of attraction between the nuclei of bonding atoms and the shared paired of electrons.

Covalent lattice

Covalent lattice structure
Infinite array of atoms joined by covalent bonds to form a giant molecular structure.
Diamond, graphite

Covalent bonds

Dative covalent
Formed when the shared pair of electrons is provided by one of the bonding atoms

Bond strength affected by:
- Bond order
- Effectiveness of orbital overlap
- Bond polarity

Covalent bond with ionic character

Depends on:
Bond polarity
(electronegativity difference between 2 bonded atoms)

Simple covalent

Intermolecular bonds exist between

Simple covalent molecules
Discrete molecules with weak intermolecular forces between molecules.

1. draw dot-&-cross diagram
2. determine shape by VSEPR (no. of bond and lone pairs)

Polar molecules
Dipoles do not cancel out.

Protonic H bonded to N, O, F?

Yes

Hydrogen bonds:
Attraction between protonic H bonded to N, O or F of one molecule with lone pair on N, O or F on adjacent molecule.
E.g.: *HF, NH_3, H_2O*

Factors affecting strength of bond:
(1) Extensiveness of H-bonds
(2) Dipole moment of H-X bond (X = N, O, F)

No

Permanent dipole-permanent dipole: Attractions between δ+ end and δ– end of adjacent polar molecules.
E.g.: *HCl, SO_2*

Non-polar molecules
Dipoles cancel out.

Instantaneous dipole-induced dipole:
Instantaneous dipole in one molecule induces a dipole moment in an adjacent molecule.
CO_2, Cl_2

Factors affecting strength of bond:
- electron cloud size
- surface area of contact between molecules

Learning Objective:

- suggest the type of structure and bonding present in a substance from given information

D. APPLICATION: BOILING/MELTING POINT AND SOLUBILITY

In the previous sections, we learnt about the different types of chemical bonds which could exist in a substance.

However, which chemical bond exactly is present between two particles in a substance?

There are no instruments nor any visual methods we can use to see the sharing of electrons or intermolecular forces, simply because electrostatic force are invisible. We can only know which interaction exists based on the physical properties such as boiling and melting point.

1 BOILING/ MELTING POINT (BP/MP)

Physical properties such as boiling and melting points are observable or measurable traits of a substance.

Boiling and melting involves the breaking of chemical bonds between particles. For example, hydrogen bonds need to be broken for water to melt or boil and ionic bonds need to be broken for NaC*l* to melt into molten state.

The relationship between boiling/melting point and bond strength is as such:

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

Most of the time the BP/MP trends fit what we understand about a species and the factors affecting the different chemical bonds. However, there are exceptions where trends are different from what we expect, in such cases we decide simply based on the data that were given.

Expected Trend 1: Factors affect the different types of Inter-atomic bonding

Metallic Bonding	*Sodium* • 1 valence e^- for delocalisation	*vs*	*Aluminium* • 3 valence e^- for delocalisation
Expected BP/MP Trend			

Ionic Bonding	*NaCl*	*vs*	*NaBr* • Br^- ________ ionic radius • ________ lattice energy
Expected BP/MP Trend			

Covalent Bonding	*SiO_2*	*vs*	*GeO_2* *(same structure as SiO_2)* • Ge ________ atomic radius • ______ effective orbital overlap
Expected BP/MP Trend			

Expected Trend 2: Inter-atomic bonding vs Intermolecular forces

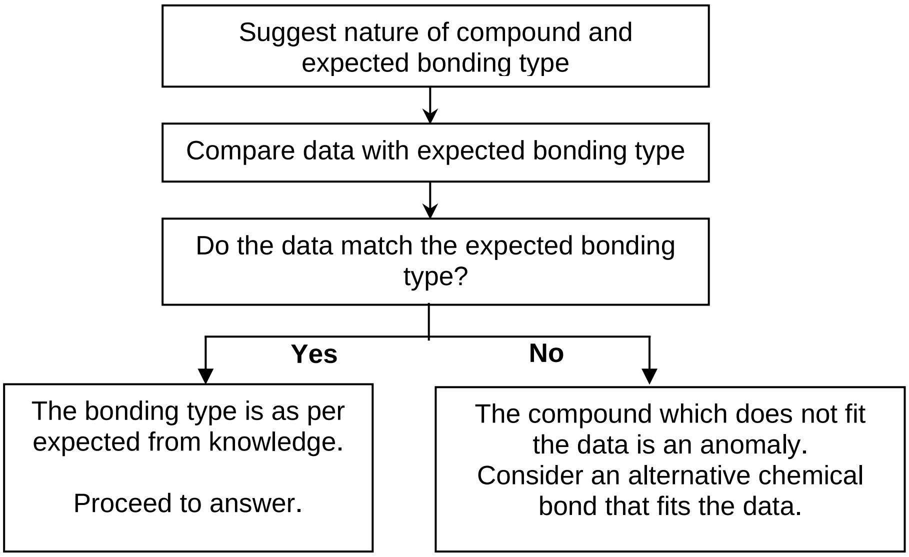
	Bonds being Broken **Inter-atomic bond (e.g. ionic bonding)**	*vs*	*Bonds being Broken* **Intermolecular forces (e.g. id-id)**
Expected BP/MP Trend			

Expected Trend 3: Intermolecular forces

	Bonds being Broken **Instantaneous dipole – induced dipole**	*vs*	*Bonds being Broken* **Permanent dipole – permanent dipole**	*vs*	*Bonds being Broken* **Hydrogen Bonding**
Expected BP/MP Trend					

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

<u>General Approach to thinking through BP/MP trend questions</u>



Suggest nature of compound and expected bonding type

Compare data with expected bonding type

Do the data match the expected bonding type?

The bonding type is as per expected from knowledge.

Proceed to answer.

The compound which does not fit the data is an anomaly. Consider an alternative chemical bond that fits the data.

How to structure your answer such Boiling/Melting point question?

Answering format for questions involving comparison of melting/boiling point

(i) **State** the structure of the compound
(ii) State the type of bonds to be broken during melting/boiling
(iii) **Compare** the strength of the bonds *(or factors affecting bond strength if bonds are similar)*
(iv) **Link to energy** *(i.e. more energy is required to break which type of bond)*
(v) **Conclude** with melting/boiling point.

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

Worked Example 2

Explain the trend in the melting points of $NaCl$ (801 ^oC) and $AlCl_3$ (193 ^oC).

State the structure of the compound - *Do the data fit the expected trend?*	$NaCl$ have ionic lattice structure, while $AlCl_3$ has simple molecular structure.
State the type of bonds / IMF to be broken during melting/boiling	$NaCl$: strong ionic bonds between the ions. $AlCl_3$: instantaneous dipole – induced dipole interaction between the molecules.
Link to energy	Most energy is required to overcome.
Compare the strength of the bonds - *Compare the strength of the 2 chemical bonds.*	the strong ionic bond in $NaCl$ than the weak instantaneous dipole – induced dipole interaction between $AlCl_3$ molecules.
Conclude with melting/boiling point.	Therefore, $NaCl$ have the higher melting point than $AlCl_3$.

Worked Example 3

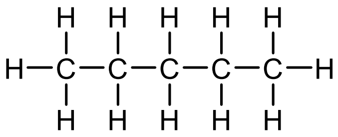
Explain the trend in the boiling points of the following halogens:

Boiling point of Cl_2 (–35 ^oC) < Br_2 (59 ^oC) < I_2 (184 ^oC)

State the structure of the compound - *What is the polarity of these molecules?*	All 3 covalent compounds have simple molecular structures and are non-polar.
State the type of bonds / IMF to be broken during melting/boiling	instantaneous dipole – induced dipole interaction (id–id)
Compare the strength of the bonds / IMF - *Compare the size of electron cloud among these halogens.* - *Compare and explain the strength of intermolecular forces among these halogens*	Electrons cloud size: $I_2 > Br_2 > Cl_2$ Electron cloud size in I_2 is the largest, so dipoles are most easily induced in I_2, followed by Br_2, then Cl_2. Hence, the instantaneous dipole – induced dipole interaction between I_2 molecules are the strongest, followed by Br_2, then Cl_2.
Link to energy	Most energy is required to overcome the strongest instantaneous dipole – induced dipole interactions in I_2.
Conclude with melting/boiling point.	Therefore, I_2 have the highest boiling point and Cl_2 have the lowest boiling point.

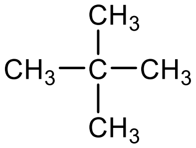
Worked Example 4

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



$CH_3CH_2CH_2CH_2CH_3$

Pentane (b.p. = 36 °C)



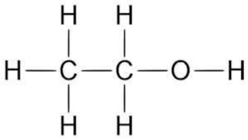
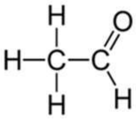
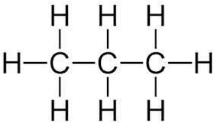
$C(CH_3)_4$

2,2-dimethylpropane
(b.p. = 10 °C)

State the structure of the compound • *What is the polarity of these molecules?*	Both covalent compounds have simple molecular structures and are non-polar.
State the type of bonds / IMF to be broken during melting/boiling	instantaneous dipole – induced dipole interaction (id–id)
Compare the strength of the bonds / IMF • *Compare the size of electron cloud between these 2 isomers.* • *Compare and explain the difference between the 2 isomers.* • *Use this to explain the difference in strength of IMF.*	Similar electrons cloud size. Due to a greater surface area of contact between straight chain pentane molecules than between branched 2,2-dimethylpropane molecules, dipoles are more easily induced in pentane molecules. Hence, a stronger id–id between straight chain pentane molecules than the branched isomer.
Link to energy	More energy is required to overcome the stronger id-id between pentane molecules than 2,2-dimethylpropane.
Conclude with melting/boiling point.	Hence, pentane has a higher boiling point than 2,2-dimethylpropane.

Worked Example 5

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

Compound	**Structure**	**M_r**	**Boiling point / °C**
Ethanol	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$	46	78
Ethanal		44	21
Propane	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	44	–42

State the structure of the compound - *What is the polarity of these molecules?*	All 3 covalent compounds have simple molecular structure with similar M_r / electron cloud size. However, ethanol and ethanal are polar while propane is non–polar.
State the type of bonds / IMF to be broken during melting/boiling	Ethanol: Hydrogen Bonding (H–Bond) Ethanal: Permanent dipole – permanent dipole (pd–pd) Propane: instantaneous dipole – induced dipole (id–id)
Compare the strength of the bonds / IMF - *Compare the strength of the 3 IMF.*	Hydrogen bonding between ethanol molecules are strongest among the 3 intermolecular forces. The permanent dipole–permanent dipole interaction between ethanal is stronger than instantaneous dipole–induced dipole interaction between propane molecules.
Link to energy	Most energy is required to overcome the strongest hydrogen bonding between ethanol molecules, while the least is required for overcoming the instantaneous dipole–induced dipole interaction between propane molecules.
Conclude with melting/boiling point.	Therefore, ethanol has the highest and propane has the lowest boiling point.

Note:
H_2O can form hydrogen bonding. But discussing H-bonding does not explain the trend. Hence we look at id-id.
(*M*r of molecules is significantly different)

Worked Example 6

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

State the structure of the compound • *What is the polarity of these molecules?*	Both covalent compounds have simple molecular structures. I_2 is non-polar while H_2O is polar.
State the type of bonds / IMF to be broken during melting/boiling • *Is the observation expected?* • *Why is there a difference?*	Both have instantaneous dipole – induced dipole interaction (id–id). H_2O has hydrogen bonding a well.
Compare the strength of the bonds / IMF • *Compare the size of electron cloud between these 2 molecules to address the anomaly.* • *Compare the strength of IMF.*	I_2 has a significantly larger election cloud than H_2O, which is more easily distorted compared to H_2O. The instantaneous dipole–induced dipole interaction between I_2 molecules is stronger than that between H_2O molecules.
Link to energy	There is sufficient energy at room temperature to overcome the id-id and H-bonds between H_2O molecule but not the id-id between I_2 molecules.
Conclude with melting/boiling point.	Hence, H_2O is liquid at room temperature but I_2 is a solid.

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

Worked Example 7

Explain the difference in boiling point of HCl (−85 °C), HBr (−67 °C) and HI (−35 °C).

State the structure of the compound • *What is the polarity of these molecules?*	All 3 covalent compounds have simple molecular structures and are polar.
State the type of bonds / IMF to be broken during melting/boiling • *Is the observation expected?*	All 3 have instantaneous dipole–induced dipole interaction (id-id) and permanent dipole-permanent dipole interactions (pd-pd).
Compare the strength of the bonds / IMF • *Compare the size of electron cloud between the compounds to address the anomaly.* • *Compare and explain the difference in strength of IMF among the 3 molecules.*	The electron cloud size of the 3 molecules is significantly different. HI has the largest election cloud and hence most easily distorted followed by HBr, then HC*l*. The instantaneous dipole–induced dipole interaction between HI molecules is strongest followed by HBr, then HC*l*.
Link to energy	Most energy is required to overcome the strongest IMF between HI molecules, while the least is required for HC*l* molecules.
Conclude with melting/boiling point.	Hence, HI has the highest boiling point and HC*l* the lowest.

2 SOLUBILITY OF COMPOUNDS IN SOLVENTS

Generally, a solute will dissolve in a solvent if :

energy released in the formation of solute-solvent interactions ≥ energy taken in to break the solute-solute and solvent-solvent interactions

2.1 Solubility of SIMPLE COVALENT Compounds

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

(i) solute-solute interaction
(ii) solvent-solvent interaction
(iii) solute-solvent interaction

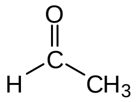
To predict solubility, consider the following:

Answering format for questions involving comparison of solubility:

A. Polarity and structure of molecule
B. Solute-Solute/Solvent-Solvent interactions to be broken
C. Solute-Solvent interactions to be formed
D. If energy is released in (C) ≥ energy used in (B), solute will dissolve.
If energy is released in (C) < energy used in (B), solute cannot dissolve.

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

Worked Example 8

Predict the solubility of ethanal,  in

(a) $CHCl_3$ (b) water

(a) Energy released in the formation permanent dipole−permanent dipole interaction between ethanal and $CHCl_3$ is sufficient to overcome the permanent dipole−permanent dipole interaction between ethanal molecules and between $CHCl_3$ molecules.
Therefore, ethanal is soluble in $CHCl_3$.

(b) Energy released in the formation of hydrogen bonding between ethanal and water is sufficient to overcome the permanent dipole−permanent dipole interaction between ethanal molecules and hydrogen bonding between H_2O molecules.
Therefore, ethanal is soluble in water.

Checkpoint 9

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

(a) Solvent: Hexane

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

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

(b) Solvent: Water

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

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

2.2 Solubility of ionic compounds

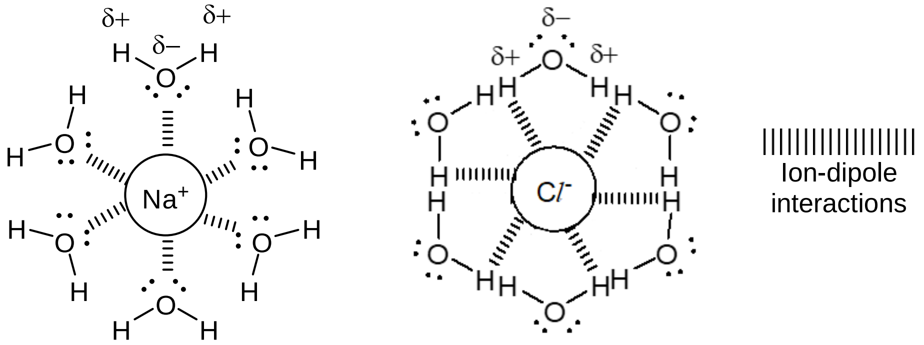
When ionic compounds dissolve in a polar solvent, it will form **ion-dipole interactions**.

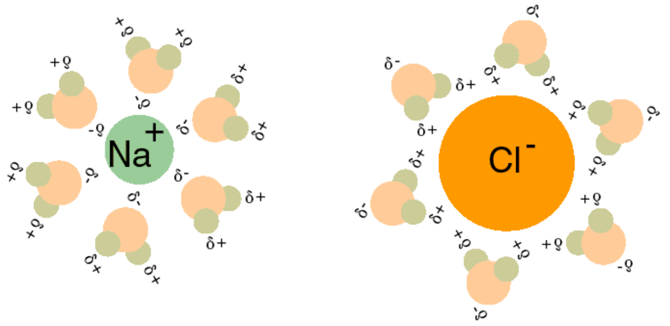
Example: NaCl dissolving in water

$$\mathrm{NaC}l\ (s) + aq \rightarrow \mathrm{Na^+}\ (aq) + \mathrm{C}l^-\ (aq)$$

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

The diagram below shows ion-dipole interactions between water and $\mathrm{Na^+}$ & $\mathrm{C}l^-$ ions. E.g. $\mathrm{Na^+}$ interacts with $\delta-$ on O of H_2O and $\mathrm{C}l^-$ interacts with $\delta+$ on H of H_2O.





Molecular acid undergoing dissociation in water
Some covalent molecules can dissociate in water to form ions.

$$\mathrm{HC}l\ (g) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + \mathrm{C}l^-\ (aq)$$

The dissociated ions formed from the reaction of $\mathrm{HC}l$ with water form ion-dipole interactions with water molecules.

Energy released in the formation of ion-dipole interactions between H^+ and $\mathrm{C}l^-$ ions and water molecules is sufficient to overcome the hydrogen bond between water molecules and covalent bond between H and $\mathrm{C}l$ atoms, hence $\mathrm{HC}l$ is soluble in water.

E OTHER APPLICATIONS

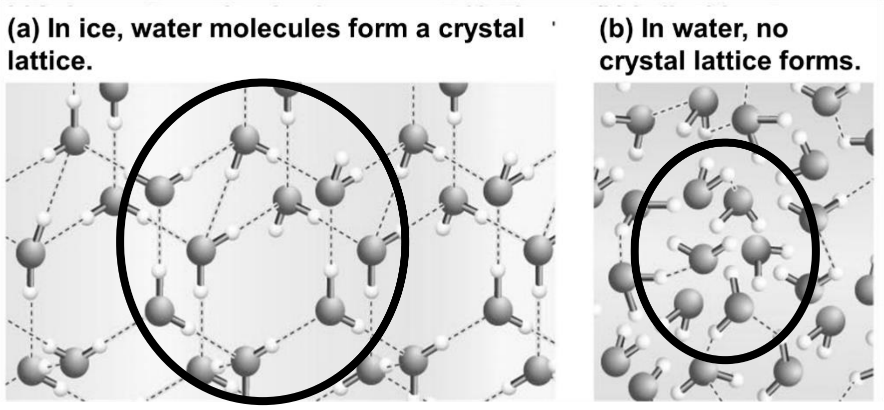
Learning Objective:

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

1 The Structure & Properties of Ice

Most liquids become denser when they change into their solid forms, however, ice floats on water!

Using the picture below, explain this phenomenon.



- *What is the anomaly in the observation?*

  Since most liquid becomes denser when they change into solid, ice (being solid state of water) should also be denser and sink in water. But this is not observed.

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

  Water: H_2O molecules experience hydrogen bonds that constantly break and re-form as the molecules move around.

  Average no. of hydrogen bonds formed per molecule < theoretical max of four

  Ice: As water freezes, H_2O molecules become fixed in place, and each H_2O molecule participates in four hydrogen bonds (permanent).

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

  Molecules in ice are arranged further apart in fixed position in an open structure, whereas molecules in water are randomly arranged but closer to each other.

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

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

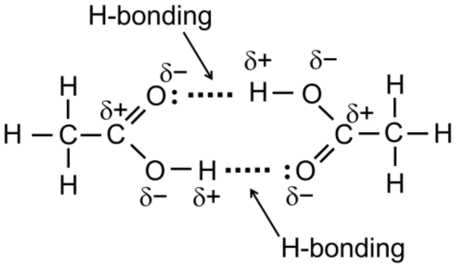
2 Dimerisation of ethanoic acid, CH_3COOH (via Hydrogen bonding)

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

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

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

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



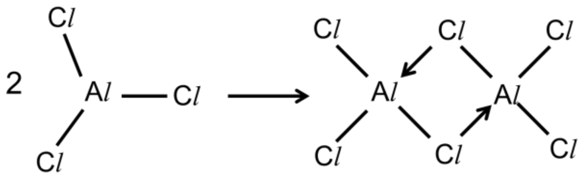
- *Why not in aqueous state?*
  - CH_3COOH is capable of forming hydrogen bond with water.
  - CH_3COOH dissociates partially in water to form CH_3COO^- and H_3O^+.

  Hence, in both cases, dimerization does not occur.

3 Dimerisation of $AlCl_3$ (via dative bonding)

Molecules of $AlCl_3$ can dimerise to give Al_2Cl_6.

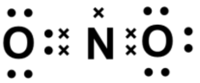
In each molecule of $AlCl_3$,
- the Al atom only has 6 electrons in its valance shell after bonding. It has an empty low-lying 3p orbital that is able to accept 2 additional electrons.
- the Cl atom has lone pair electrons that can be donated.



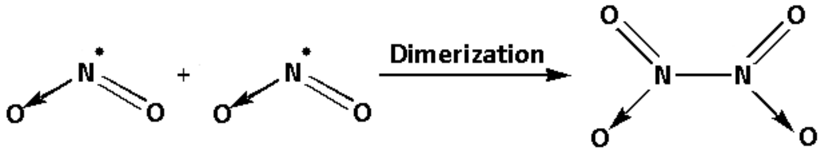
4 Dimerisation of NO_2 (via covalent bond)

Molecules of NO_2 can dimerise to give N_2O_4.

In each molecule of NO_2,
- the N atom only has 7 electrons in its valance shell after bonding.



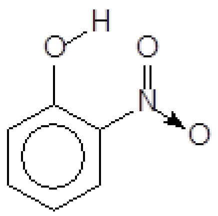
The NO_2 molecule can share the single electron on the N atom with the N atom of another NO_2 molecule and form a new sigma bond.



5 Intramolecular Hydrogen Bonding

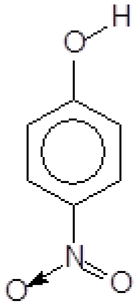
Even though 2-nitrophenol and 4-nitrophenol are isomers (similar electron cloud size), their boiling points are significantly different.

2-nitrophenol



Boiling point = 214 °C

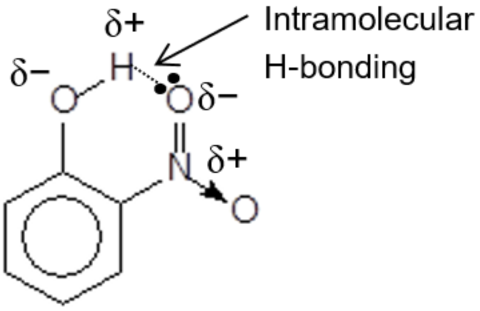
4-nitrophenol



Boiling point = 259 °C

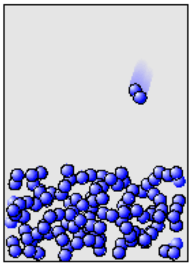
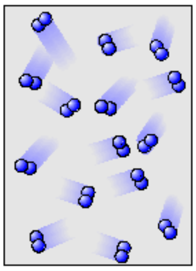
The lower boiling point of 2-nitrophenol is due to intramolecular hydrogen bonding that occurs in 2-nitrophenol but not in 4-nitrophenol.

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



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

6 Liquefaction of gases

Physical State	Liquid	Gas
Order of Packing of Particles	 Loose clusters of particles	 No order; far apart

Many gases can be put into a liquid state at normal atmospheric pressure by simple cooling (low temperature). High pressure can also cause gases to change into liquid state.

Gases with stronger intermolecular forces can be liquified more readily when exposed to low temperature/high pressure.

	Success Criteria	√
	I am able to:	
(a)	explain the physical properties of (i) metal (ii) ionic compound (iii) covalent compound with simple molecular structure (iv) covalent compound with giant molecular structure (diamond and graphite)	
(b)	explain the factors affecting strength (i) metallic bond (ii) ionic bond (iii) covalent bond	
(c)	draw the ‘dot-and-cross’ diagram for (i) ionic compound (ii) covalent molecules (iii) polyatomic ions	
(d)	describe the formation of (i) sigma (σ) bond (ii) pi (π) bond (iii) dative bond (co-ordinate bond)	
(e)	understand that element from Period 3 and beyond can form compounds with more than 8 valence electrons in its valence shell	
(f)	suggest the type of structure and bonding present in a substance from given information e.g. $AlCl_3$ exists as simple molecular structure	
(g)	explain and predict the shape and bond angle of covalent molecule using VSEPR theory	
(h)	determine the polarity of a molecule based on bond polarity and shape of molecule	
(i)	determine the type of intermolecular forces for covalent molecules	
(j)	explain the factors affecting strength of intermolecular forces (i) instantaneous dipole-induced dipole (ii) hydrogen bonding	
(k)	describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances (e.g. m.p/b.p, solubility)	
(l)	outline the importance of hydrogen bonding to the physical properties of substances, including ice and water	
(m)	Use knowledge of chemical bonding to explain observations such as dimerization and intramolecular hydrogen bonding	