2022 JC1 H2 CHEMISTRY (9729)
CORE IDEA 2: STRUCTURE AND PROPERTIES
TOPIC 2: CHEMICAL BONDING

Name: ____ Civics Group: _________

Students should be able to:

- (a) show understanding that all chemical bonds are electrostatic in nature and describe:
  - (i) ionic bond as the electrostatic attraction between oppositely charged ions
  - (ii) covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei
  - (iii) metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons
- (b) describe, including the use of 'dot-and-cross' diagrams,
  - (i) ionic bonding as in sodium chloride and magnesium oxide
  - (ii) covalent bonding as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene
  - (iii) co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al_2Cl_6 molecule
- (c) describe covalent bonding in terms of orbital overlap (limited to s and p orbitals only), giving σ and π bonds (see also Section 11.1)
- (d) explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory
- (e) predict the shapes of, and bond angles in, molecules analogous to those specified in (d)
- (f) explain and deduce bond polarity using the concept of electronegativity
  [quantitative treatment of electronegativity is not required]
- (g) deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d))
- (h) describe the following forces of attraction (electrostatic in nature):
  - (i) intermolecular forces, based on permanent and induced dipoles, as in $CHCl_3(l)$, $Br_2(l)$ and the liquid noble gases
  - (ii) hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups
- (i) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water
- (j) explain the terms *bond energy* and *bond length* for covalent bonds
- (k) compare the reactivities of covalent bonds in terms of bond energy, bond length and bond polarity
- (l) describe, in simple terms, the lattice structure of crystalline solid which is:
  - (i) ionic, as in sodium chloride and magnesium oxide
  - (ii) simple molecular, as in iodine
  - (iii) giant molecular, as in graphite and diamond
  - (iv) hydrogen-bonded, as in ice
  - (v) metallic, as in copper

  [the concept of the 'unit cell' is not required]
- (m) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances
- (n) suggest the type of structure and bonding present in a substance from given information

Lecture Contents

REFERENCES

1 Chemistry (for CIE AS & A Level) by Peter Cann & Peter Hughes

2 Cambridge International AS and A Level Chemistry Revision Guide by Judith Potter and Peter Cann

3 Chemical Bonding and Molecular Geometry by Ronald Gillespie & Paul Popelier

1 Covalent Bonding

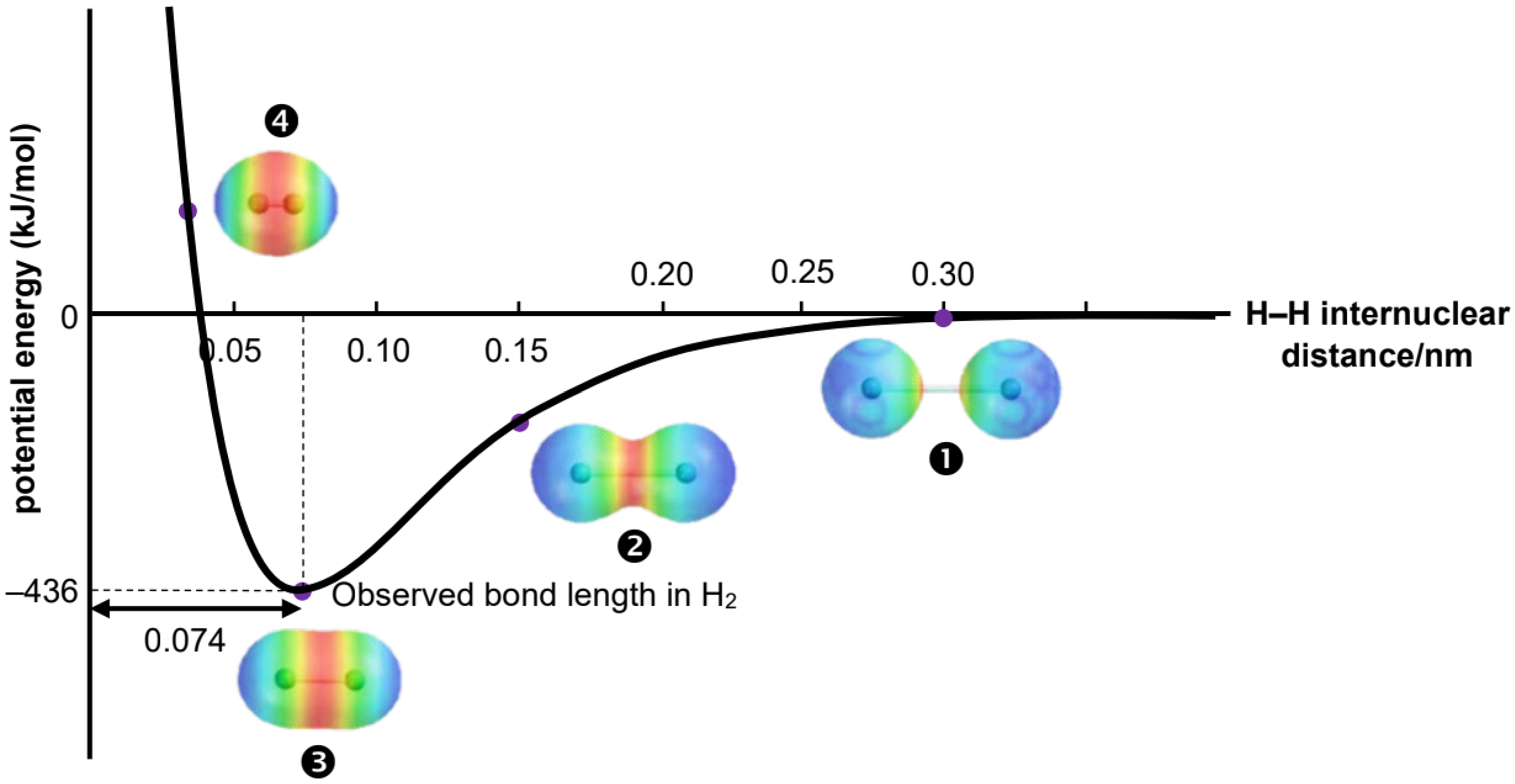
1.1 Covalent Bond Formation

LO (a) show understanding that all chemical bonds are electrostatic in nature and describe:
(ii) covalent bond as the electrostatic attraction between shared electrons and positively charged nuclei

Covalent bond is the **electrostatic forces of attraction** between **shared electrons and the positively charged nuclei.**

A covalent bond is formed when atoms (*usually* **non-metals**) **share valence electrons** through **overlap of orbitals**, leading to increased electron density between the two nuclei where the shared electrons are most likely to be found.

Using a hydrogen molecule as an example:



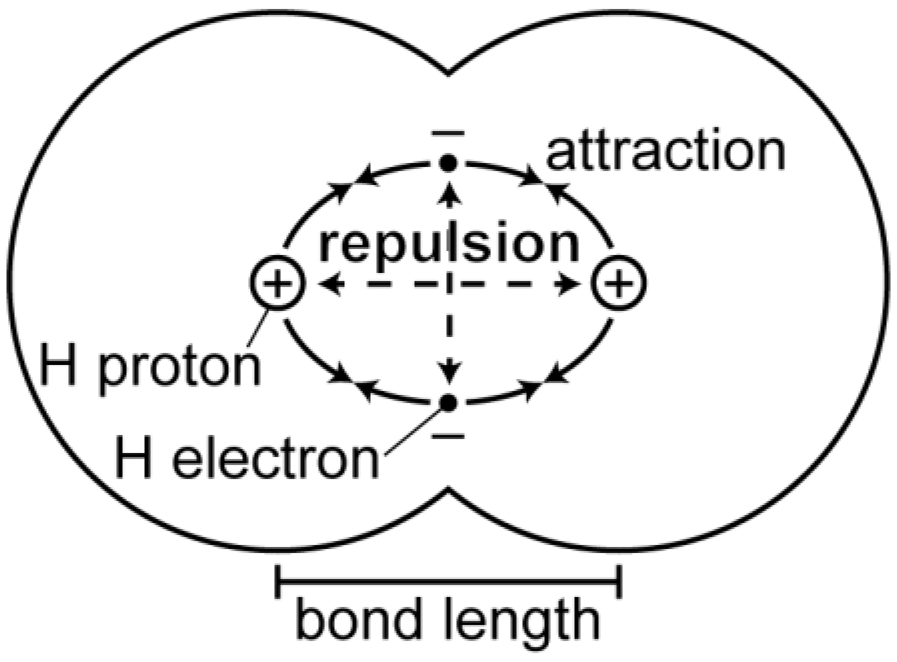
❶ As the two hydrogen atoms approach each other from a distance, the electron of one atom will repel the electron of the other atom. However, this will be compensated by the additional electrostatic force of attraction between this electron and the nucleus of the other hydrogen atom.

❷ As the hydrogen atoms get closer, the two electrons will encounter an even greater attraction to the opposite nucleus, but will also continue to repel each other.

❸ At a certain point, there is a **nett electrostatic force of attraction**, i.e. the attractions of the two electrons to the two nuclei are just balanced by the electron-electron and nucleus-nucleus repulsions. **This is when a covalent bond is formed.**

❹ If the hydrogen atoms continue to get closer, eventually when the two nuclei become very close together, they in turn will start to repel each other, since both nuclei are positively charged.

At ❸ when a covalent bond is formed, the average nucleus-nucleus distance is known as the **bond length**.



Being attracted to both the hydrogen nuclei, the two electrons spend most of their time in the region between the two nuclei. This is where the **highest electron-density** (or electron probability) occurs in a covalent bond. The two electrons are therefore *shared* between the two adjacent atoms.

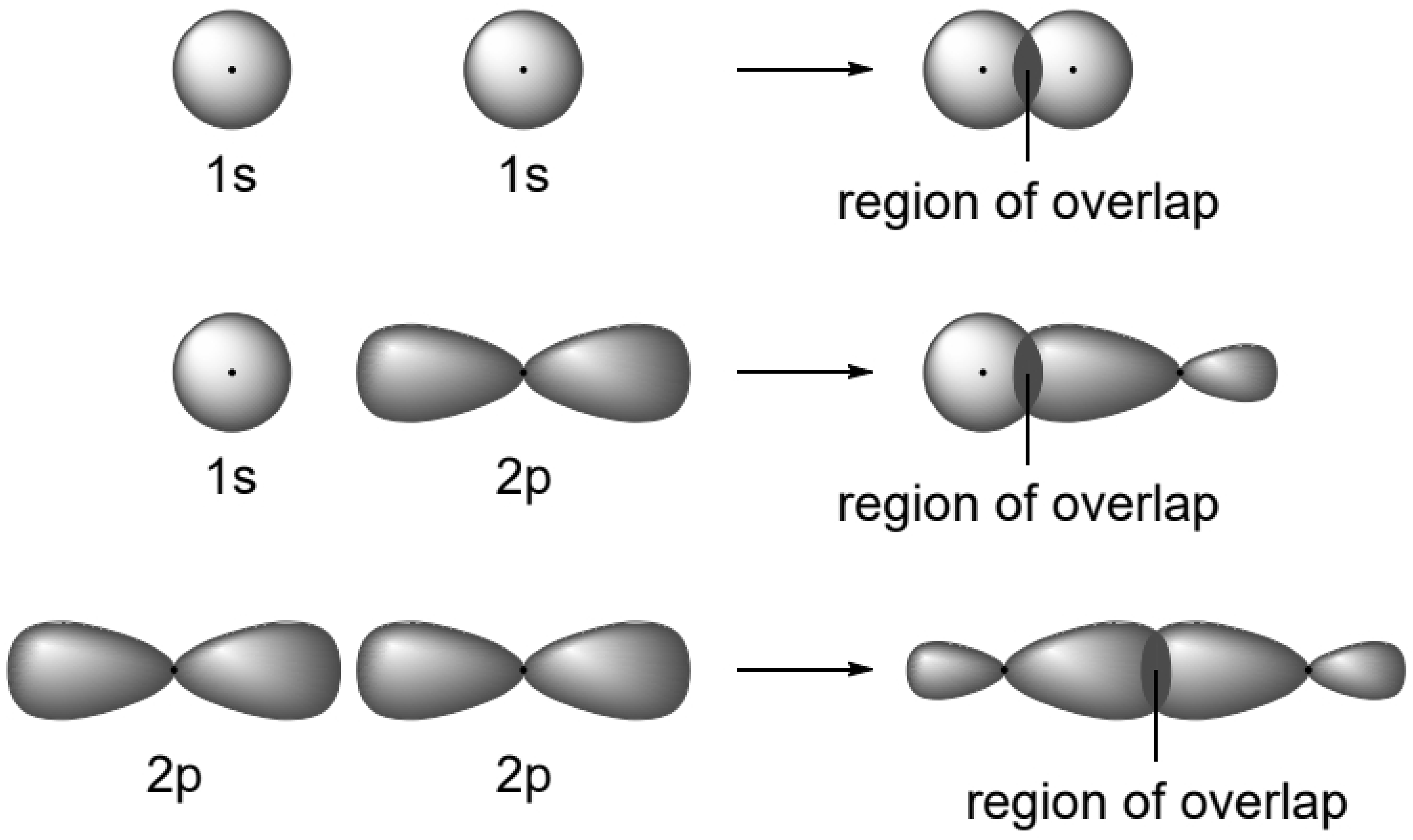
Similar to the idea of *atomic orbitals*, the region of space ***within*** a molecule where a particular electron is found is known as a **molecular orbital**.

1.2 The Overlap of Orbitals: Sigma Bonds and Pi Bonds

LO (c) Describe covalent bonding in terms of orbital overlap (limited to s and p orbitals only), giving σ and π bonds.

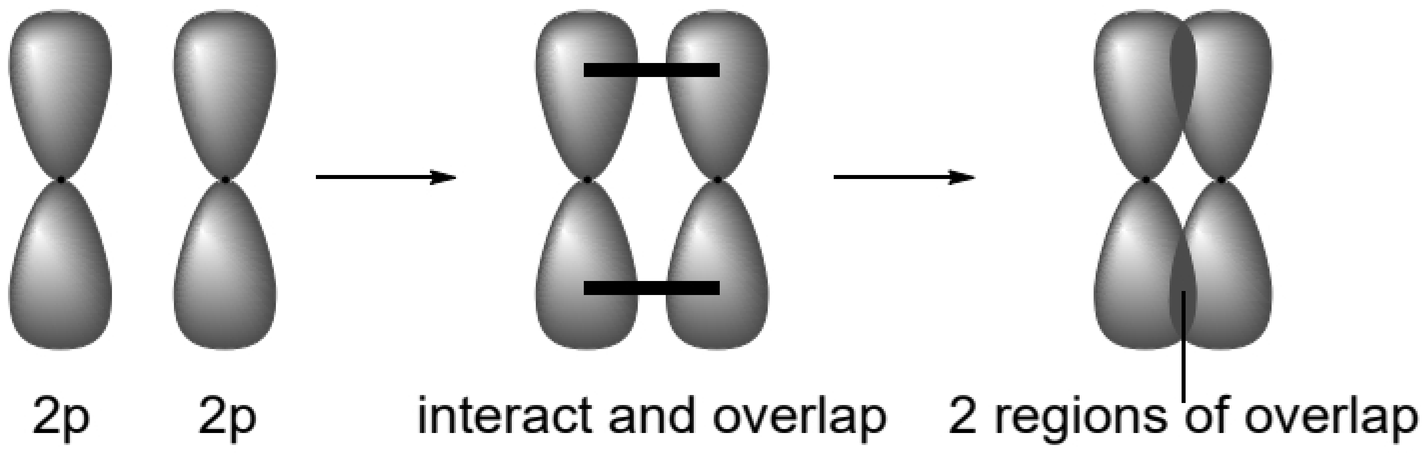
1.2.1 Sigma (σ) Bonds

A single bond is formed when a pair of electrons is shared between two atoms. If this bond is formed due to the **head-on overlap of an orbital of each atom** (this can involve s orbitals, p orbitals, or a mixture of the two as shown in the diagram below), then this bond is referred to as a **sigma (σ) bond**.



1.2.2 Pi (π) Bonds

It is also possible to form a bond due to the **sideways overlap of a p orbital on each atom**. Such a bond is referred to as a **pi (π) bond**.



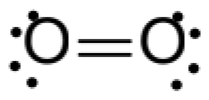
In a π bond, there is **less effective overlap of orbitals**. Hence, **a π bond is weaker than a σ bond**.

This sideways overlap of two p orbitals is always preceded by the head-on overlap of two other orbitals on the same atoms *i.e.* **π bonds can only form after a σ bond is formed**.

1.3 Types of Covalent Bonds

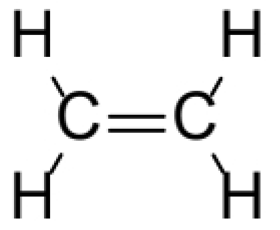
1.3.1 Multiple Bonding – Double and Triple Bond

Atoms can share more than one electron pair with their neighbours. Sharing two electron pairs produces a **double bond**, *e.g.* in the oxygen molecule, O_2, and sharing three electron pairs produces a **triple bond**, *e.g.* in the nitrogen molecule, N_2.



:N≡N:

Carbon can also form multiple bonds, *e.g.* in ethene, C_2H_4, and ethyne, C_2H_2.



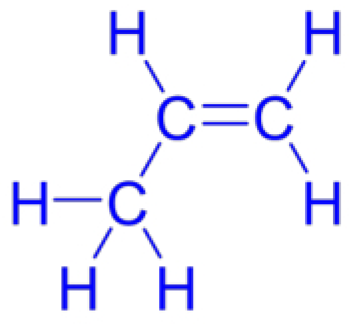
H–C≡C–H

A **double bond** consists of a **σ bond and a π bond** between the same two atoms.
A **triple bond** consists of a **σ bond and two π bonds** between the same two atoms.

A **single** bond corresponds to	**1** σ bond
A **double** bond corresponds to	**1** σ bond and **1** π bond
A **triple** bond corresponds to	**1** σ bond and **2** π bonds

Example 1A

State the number of σ bonds and π bonds in propene, $CH_3CH{=}CH_2$.



1.3.2 Dative Bonding/Co-ordinate Bonding

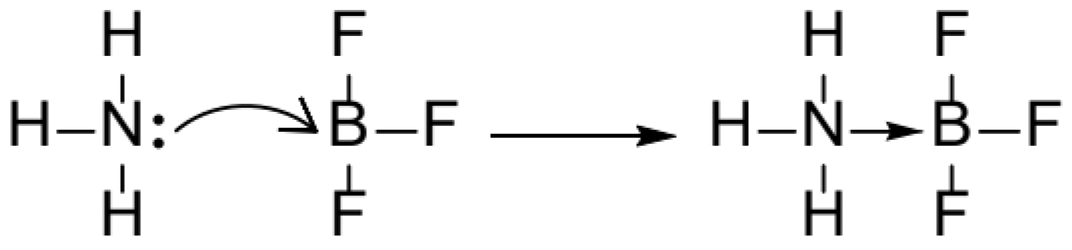
Usually, a covalent bond consists of each atom contributing one electron for sharing. It is also possible for just one of the atoms involved to provide **both** bonding electrons to form a covalent bond.

The **donor atom** provides two electrons (from a **lone pair of electrons***)* to an **acceptor atom**. The acceptor must contain an **empty valence orbital**. This kind of bonding is called **dative bonding** or **co-ordinate bonding**. Dative bonds are represented by arrows "→" showing which way the lone pair is donated.

The dative bond, once formed, is not different from any other covalent bond i.e. has the same bond strength as a normal covalent bond.

<u>Example 1</u>

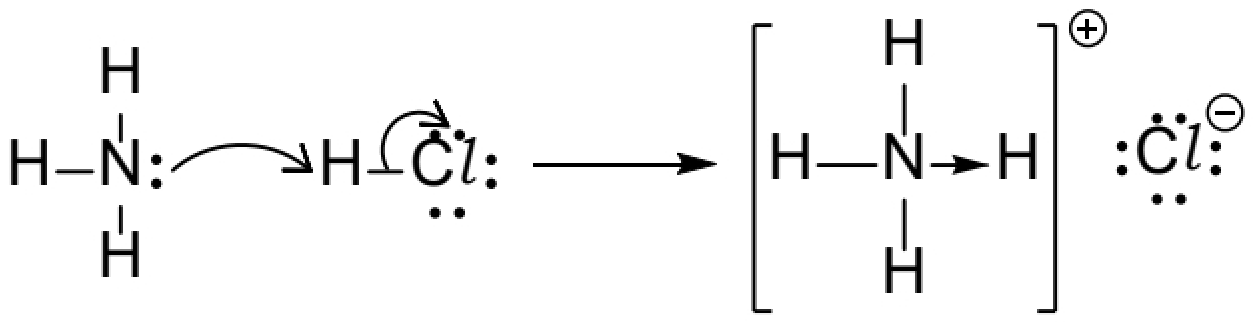
When gaseous ammonia and gaseous boron trifluoride react together, a white solid is formed, with the formula NH_3BF_3. The nitrogen atom in ammonia has a lone pair, and the boron atom in boron trifluoride has an empty 2p orbital.



<u>Example 2</u>

When gaseous ammonia and gaseous hydrogen chloride react, the white solid ammonium chloride is formed. The lone pair of electrons on the nitrogen atom of ammonia has formed a dative bond with the hydrogen atom of the hydrogen chloride molecule.

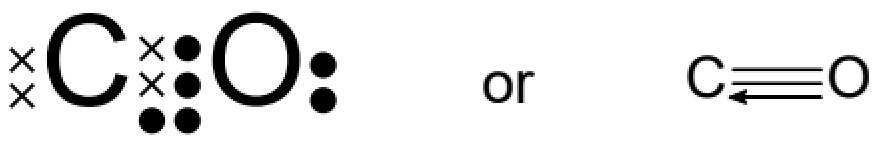
At the same time, the H–C*l* bond breaks and the electrons in the H–C*l* bond form a fourth lone pair on the chlorine atom, giving rise to a chloride ion.



All four N–H bonds are exactly the same. It is not possible to tell which one is a dative bond.

<u>Example 3</u>

Carbon monoxide has an interesting structure. One of the bonds in the triple bond between carbon and oxygen is a dative bond.



1.4 Electronegativity

LO (f) Explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is **not** required.]

Electronegativity refers to the ability of an atom to **attract the shared pair(s) of electrons** in a **covalent bond**.

Electronegativity depends on the nuclear charge and the distance of the outer electrons from the nucleus.

In 1960, Linus Pauling developed a relative index of the ability of an atom to attract electrons, referenced to an **arbitrary** value of 2.1 for hydrogen. Numerical values of electronegativity on this scale range from fluorine, with a value of 4.0, to an alkali metal such as caesium, with a value of 0.7. The larger the number, the more electronegative (electron attracting) the atom is.

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
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	lanthanoids	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 2.4
Fr 0.7	Ra 0.9	actinoids	Rf –	Db –	Sg –	Bh –	Hs –	Mt –	Ds –	Rg –	Cn –		Fl –		Lv –		

lanthanoids	La 1.1	Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.2	Eu 1.1	Gd 1.2	Tb 1.1	Dy 1.2	Ho 1.2	Er 1.2	Tm 1.3	Yb 1.1	Lu 1.1
actinoids	Ac 1.1	Th 1.3	Pa 1.5	U 1.4	Np 1.4	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr –

In general, electronegativity:

- **Increases across the period**, *e.g.* F is more electronegative than O which is more electronegative than N
- **Decreases down the group**, *e.g.* Br is less electronegative than Cl

(Useful tip: Remember that **F is the most electronegative element**!)

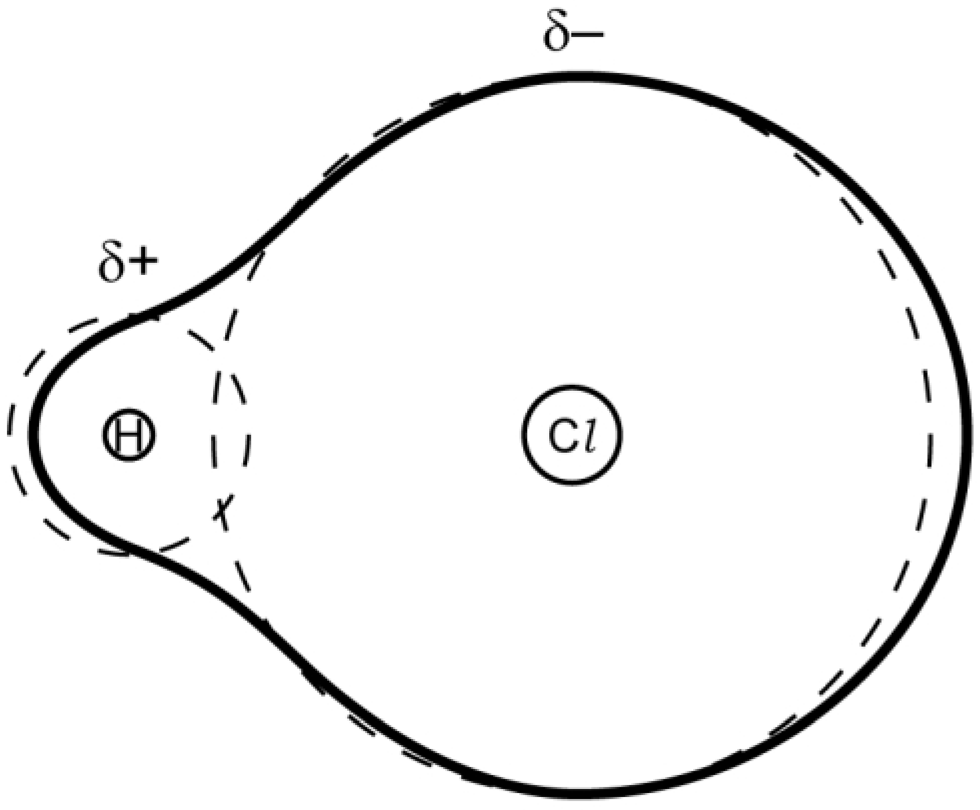
1.5 Properties of Covalent Bonds

LO (f) Explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is **not** required.]
(j) Explain the terms bond energy and bond length for covalent bonds.
(k) Compare the reactivities of covalent bonds in terms of bond energy, bond length and bond polarity.

1.5.1 Bond Polarity

A **polar covalent bond** is formed if the two atoms involved have **different electronegativities**, resulting in bonding electrons being **unequally shared** between the two atoms. The difference in electronegativities cause a **permanent separation of partial charges** (**dipoles**) between the two atoms.

For example, in hydrogen chloride, HCl, the more electronegative chlorine atom draws electron density towards itself, resulting in the formation of dipoles.



δ+ : partial positive charge
(*i.e.* less electronegative / more electropositive)
δ– : partial negative charge
(*i.e.* more electronegative / less electropositive)

We sometimes represent the polar HC*l* molecule in this way: $\underset{\longmapsto}{\overset{\delta+}{\mathrm{H}}—\overset{\delta-}{\mathrm{C}l}}$

The 'cross-and-arrow' symbol ($\longmapsto$) shown above is used to show the direction in which the electrons are attracted more strongly i.e. towards the more electronegative atom, where the length of the arrow corresponds to the degree of charge separation, or dipole.

The strength of a dipole is measured by its **dipole moment**, μ, which is the product of the separated electric charge, δ+ or δ–, and the distance between them. The debye unit, D (named after the chemist Peter Debye), has the dimensions of coulomb-metre ($1\ \mathrm{C{\cdot}m} = 2.9979 \times 10^{29}\ \mathrm{D}$).

The **bigger the difference** in the electronegativities of the atoms, the **larger the dipole moment**, and the **more polar** the covalent bond.

1.5.2 Bond Strength

The strength of a covalent bond is measured by its **bond energy**. The **stronger** the covalent bond, the **higher** the bond energy.

> Bond energy is the **amount of energy** required to break **one mole of covalent bonds** in the **gaseous state**.
>
> *e.g.* $C\ell_2(g) \rightarrow 2C\ell(g)$

Energy is **released** during bond **formation** (i.e. this is an **exothermic** reaction)
Energy is **absorbed** during bond **breaking** (i.e. this is an **endothermic** reaction)

The strength of covalent bonds is generally dependent on the following factors:

- **bond order** i.e. number of covalent bonds formed between two atoms
- **effectiveness of overlap of orbitals**
- **bond polarity**

(i) Bond order

As bond order **increases**, the **number of bonding electrons within the inter-nuclei region increases**. Hence, the **electrostatic forces of attraction for these electrons increases**.

bond order	types of bond
1	**single**
2	**double**
3	**triple**

Bond strength **increases**

<u>Example:</u> Strength of covalent bond: C–C < C=C < C≡C

	C–C	C=C	C≡C
bond energy / kJ mol^{-1}	350	610	840
bond length / nm	0.154	0.134	0.120

(ii) Effectiveness of orbital overlap

Generally, **larger orbitals are more diffused**, which results in **less effective orbital overlap**. Hence, bonds formed by **larger atoms** will tend to have **lower bond strength**.

<u>Example:</u> Trend of bond energies of some Group 17 elements

	bond energy / kJ mol^{-1}
Cℓ–Cℓ	244
Br–Br	193
I–I	151

(iii) Bond polarity (i.e. unequal sharing of electrons in a covalent bond)
In a polar bond, there are **additional attractive forces between the δ+ and δ–** that **strengthens the covalent bond**, leading to **higher bond strength**.

The **more polar** the bond, the **stronger** the bond. This factor of bond polarity only comes into play when bonds have **comparable** bond order and effectiveness of orbital overlap.

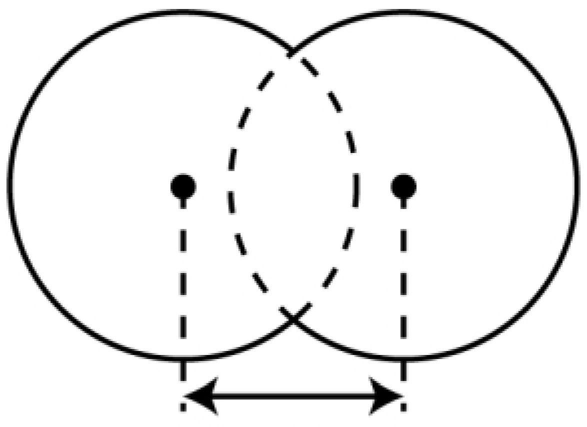
Example:

	bond energy / kJ mol^{-1}	bond length / nm
C≡O	1070	0.113
N≡N	994	0.110

CO and N_2 have similar bond lengths. However, the C≡O bond is polar while the N≡N is not, leading to the C≡O bond having higher bond strength.

1.5.3 Bond Length

Bond length is the **average distance** between the **nuclei of atoms**.



bond length

The **longer** the bond, the **weaker** the covalent bond. For example, the H–F bond energy is 562 kJ mol^{-1} while the H–C*l* bond energy is 431 kJ mol^{-1}, indicating that the H–F bond is stronger. This is due to fluorine having a smaller atomic radius, leading to H–F bond having a shorter bond length than H–C*l*.

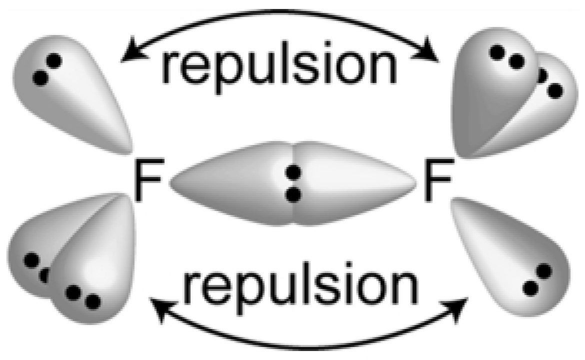
In summary, when
(1) **bond order increases** or
(2) **effectiveness of orbital overlap increases** or
(3) **polarity of bond increases**,
bond length decreases and **bond strength increases**.

Example 1B

As F is smaller than C*l*, we would expect that F–F should have more effective overlap of orbitals and hence a stronger bond. However, based on the bond energy values, C*l*–C*l* is in fact a stronger bond. Suggest why this is so.

	bond energy / kJ mol^{-1}	atomic radius / nm
F–F	158	0.072
C*l*–C*l*	244	0.099

As the F atom is very small, the F–F bond length is ____________________. This results in the ____________________ on F being in ________________ with those of the other F atom. Thus, ______________ occurs which ______________ the covalent bond. This phenomenon happens in small molecules such as F_2 and O_2.



Checkpoint

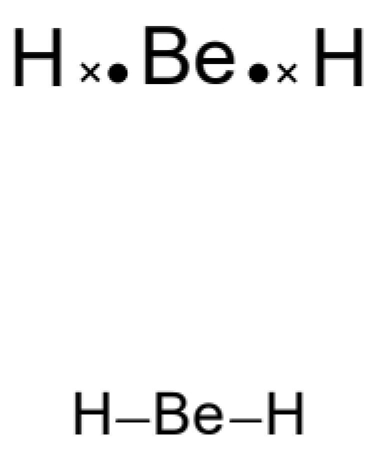
- ☐ I know that all chemical bonds are basically electrostatic forces of attraction.
- ☐ I know the definition of a covalent bond.
- ☐ I know how sigma and pi bonds are formed, and how they lead to the formation of single, double and triple bonds.
- ☐ I know what dative bonding is, identify when it is formed, and how to represent it.
- ☐ I am able to identify if a bond is polar or non-polar.
- ☐ I am able to use the 3 factors (bond order, effectiveness of orbital overlap or bond polarity) to explain differences in bond strength/bond energy.

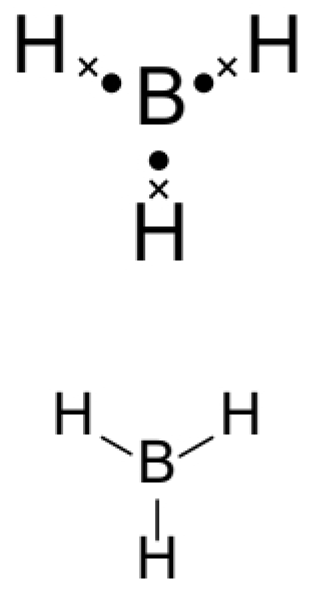
1.6 Representing Covalent Bonds: Dot-And-Cross Diagrams

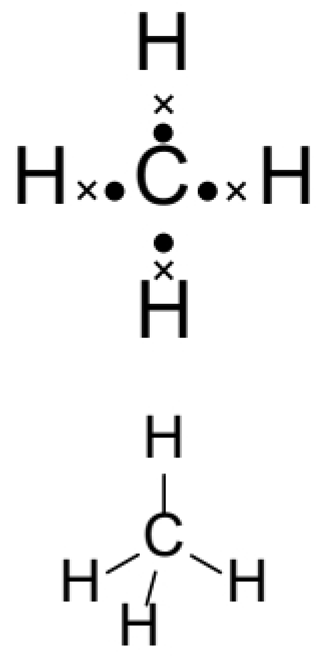
LO (b) Describe, including the use of 'dot-and-cross' diagrams:
- (ii) covalent bonding, as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene
- (iii) co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al_2Cl_6 molecule.

When an atom bonds with others, normally only electrons in the **valence shell** are involved. When looking at bonding in *simple terms*, we can ignore the distinction between the various types of orbitals (s, p, d, *etc.*) in a shell and consider all electrons in the valence shell as a group.

If an atom has more than one electron in its valence shell, it can form more than one covalent bond with other atoms. For example, the beryllium atom ($1s^2\ 2s^2$) has a pair of 2s electrons. When forming a compound such as beryllium hydride, BeH_2, these electrons can unpair themselves and form two bonds with two hydrogen atoms:







The boron atom ($1s^2\ 2s^2\ 2p^1$) can form three bonds as exemplified by boron hydride, BH_3, while the carbon atom ($1s^2\ 2s^2\ 2p^2$) with four electrons in its valence shell can form four bonds as in methane, CH_4, shown above.

Often, for clarity, bonding diagrams show only the electrons in the valence shell, omitting the inner shells.

How to draw dot-and-cross diagrams for species containing covalent bonds

Step 1: Identify the **central atom** in the **chemical formula**. The central atom is *usually* the atom with the **lowest electronegativity (except H)**.

Step 2: Determine the **number of valence electrons (by group number)** for each atom.

For an **anion**, **add electron(s)** to the **more** **electronegative** atom (F, O, C*l*, N).
For a **cation**, **remove electron(s)** from the **less** **electronegative** atom.

Step 3: Determine the **type of bond formed** (single, double, triple or dative) between the central atom and its neighbouring atoms through sharing of valence electrons to achieve **noble gas electronic configurations**. Use **dots** and **crosses** on **alternate atoms**.

Step 4: Arrange the **remaining valence electrons (not involved in bonding) in pairs**. These electrons are known as **lone pairs of electrons** (non-bonding electrons).

Step 5: Check that each atom achieves a **stable noble gas configuration** (*ideal case*, but sometimes, the central atom does not achieve this). **Elements from period 3 onwards can expand octet** i.e. have more than 8 electrons around the atom (see Note on next page for the reason why). If the central atom cannot expand octet, consider changing a double bond to a dative bond.

Note:

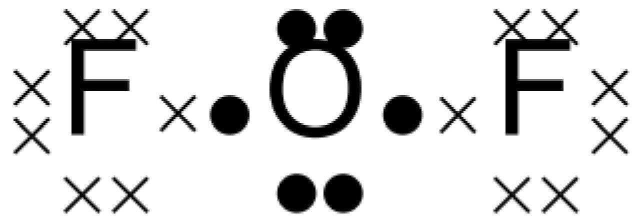
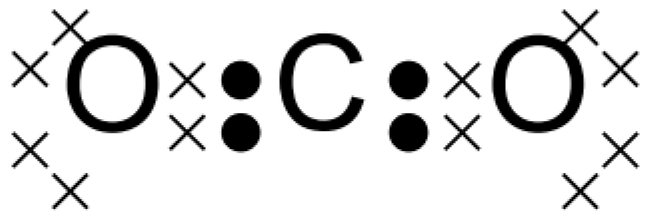
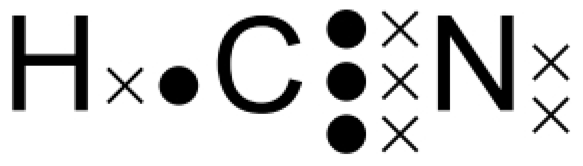
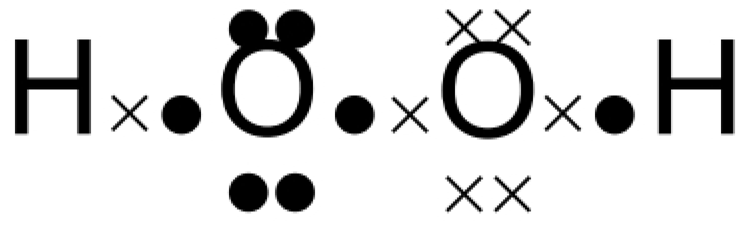
- Octet Rule (which was taught in secondary school) is based on empirical observation and it applies **strictly** to the **period 2 elements** (*e.g.* C, N, O, F) due to the availability of 2s and 2p orbitals in the valence shell.

- Unlike elements in the second row of the Periodic Table, those in the third and subsequent rows can use their **d orbitals** in bonding, in addition to their s and p orbitals. Hence, they can **expand octet due to their vacant and energetically accessible d orbitals**. As a result, they are able to form more than four covalent bonds to other atoms (*e.g.* PCl_5, SF_6).

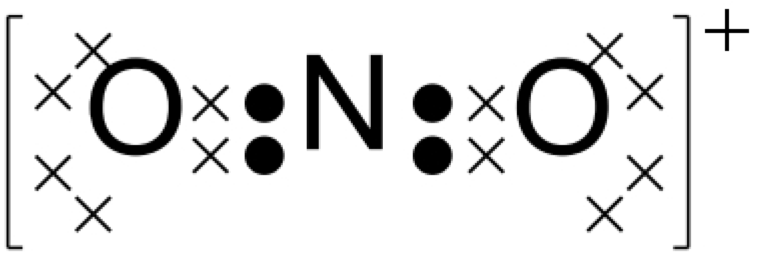
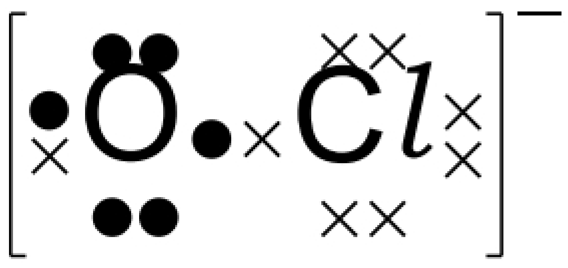
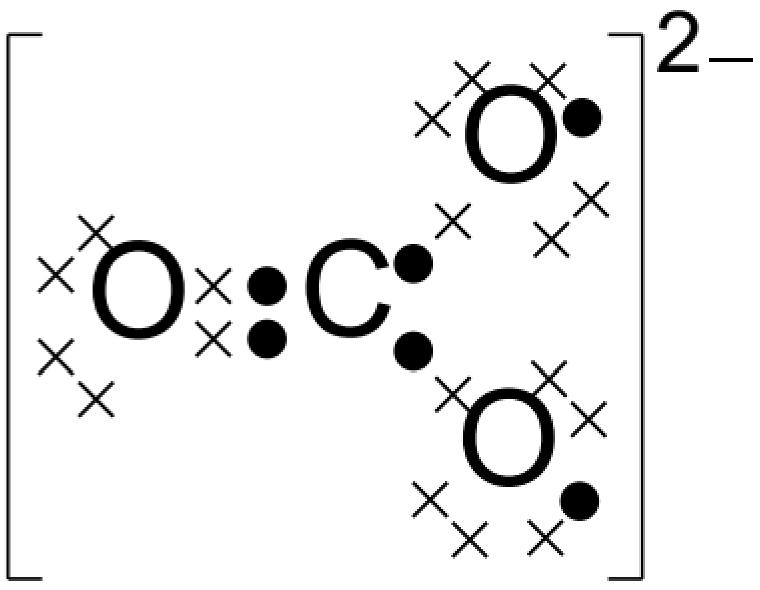
- For *many* elements, the number of bonds they can form in a molecule is fixed and is termed the **covalency** of the element. For example, oxygen has a covalency of 2, and carbon has a covalency of 4.

- Elements in Groups 15 to 17 in the third and subsequent rows of the Periodic Table (Period 3 and higher) can display more than one covalency. For example, phosphorus has a covalency of 3 or 5, and chlorine has a covalency of 1, 3 or 5.

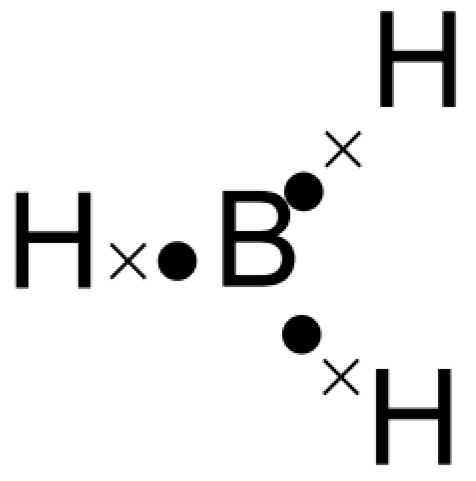
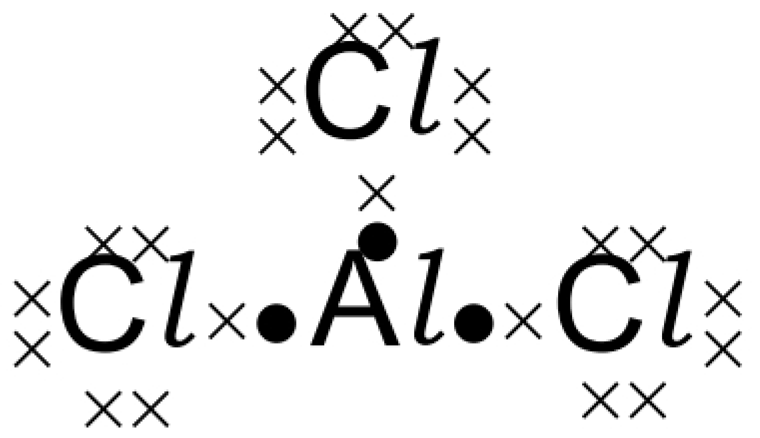
1.6.1 Dot-And-Cross for Molecules

	Valence Electrons / Bond Types	Dot-and-Cross Diagram
1) F_2**O**	F (Gp 17): 7 valence electrons O (Gp 16): 6 valence electrons ⇒ forms **single** bond with each F	
2) **C**O_2	C (Gp 14): 4 valence electrons O (Gp 16): 6 valence electrons ⇒ forms **double** bond with C	
3) H**C**N	C (Gp 14) : 4 valence electrons H: 1 valence electron ⇒ forms **single** bond with C N (Gp 15): 5 valence electrons ⇒ forms **triple** bond with C	
4) H_2**O_2**	***Note: TWO O central atoms** O (Gp 16): 6 valence electrons ⇒ forms **single** bond with O and H H: 1 valence electron ⇒ forms **single** bond with O	

1.6.2 Dot-And-Cross Diagrams for Cations / Anions

	Valence Electrons / Bond Types	Dot-and-Cross Diagram
5) **<u>N</u>**O_2^+	**Electronegativity: N < O** **Charge = +1 (remove 1 electron from N)** N (Gp 15): 5 – 1 = 4 valence electrons O (Gp 16): 6 valence electrons ⇒ forms **double** bond with N	
6) **<u>O</u>**Cl^-	**Electronegativity: O > C*l*** **Charge = –1 (add 1 electron to O)** O (Gp 16): 6 + 1 = 7 valence electrons C*l* (Gp 17): 7 valence electrons ⇒ forms **single** bond with O	
7) **<u>C</u>**O_3^{2-}	**Electronegativity: O > C** **Charge = –2 (shared by 2 O atoms, add 1 electron to each O)** C (Gp 14): 4 valence electrons 2 O (Gp 16) <u>each</u>: 6 + 1 = 7 valence electrons <u>each</u> ⇒ forms **single** bond with C 1 O: 6 valence electrons ⇒ forms **double** bond with C	

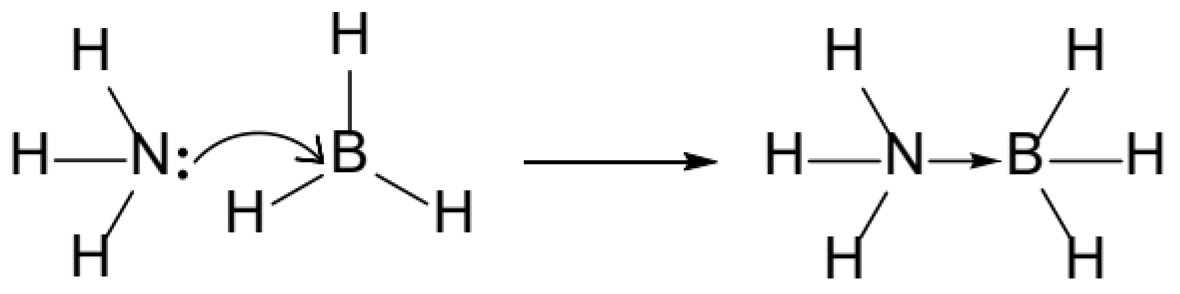
1.6.3 Dot-And-Cross Diagrams for Electron Deficient (with Incomplete Octet) Molecules

		Dot-and-Cross Diagram
8) **Be**Cl_2	Central atom from Group 2 and 13 (*e.g.* Be, B, A*l*) may have less than 8 valence electrons due to them having fewer valence electrons.	
9) **B**H_3		
10) **A*l***Cl_3		

Electron deficient molecules may achieve a noble gas electronic configuration through **addition reactions**, resulting in the formation of **dative bonds**.

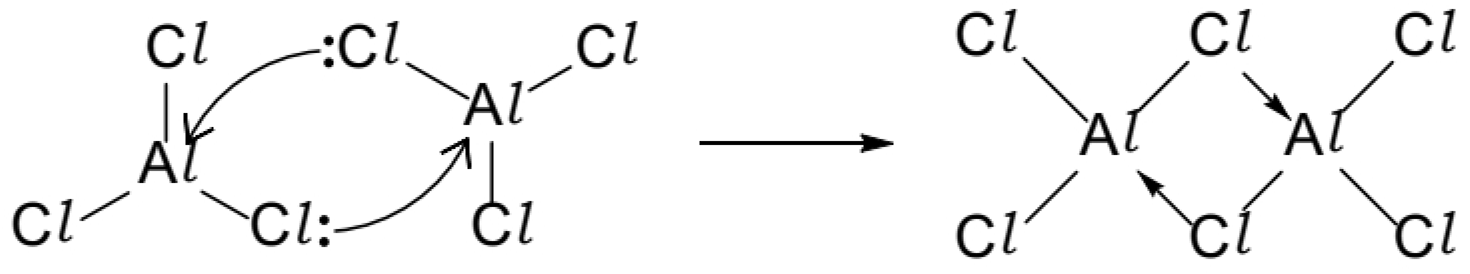
For example:

- Reaction between ammonia and boron hydride



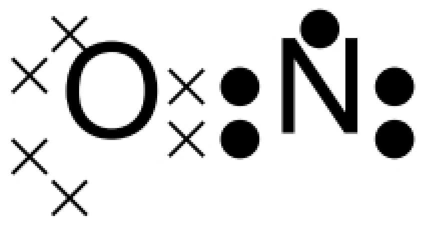
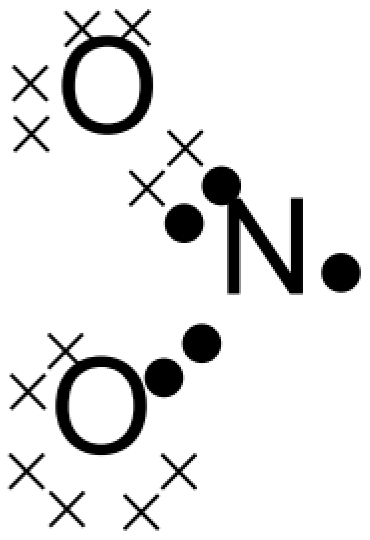
- Dimerisation of aluminium chloride

  The electron-deficient aluminium chloride may achieve a noble gas electronic configuration through the formation of a dimer.

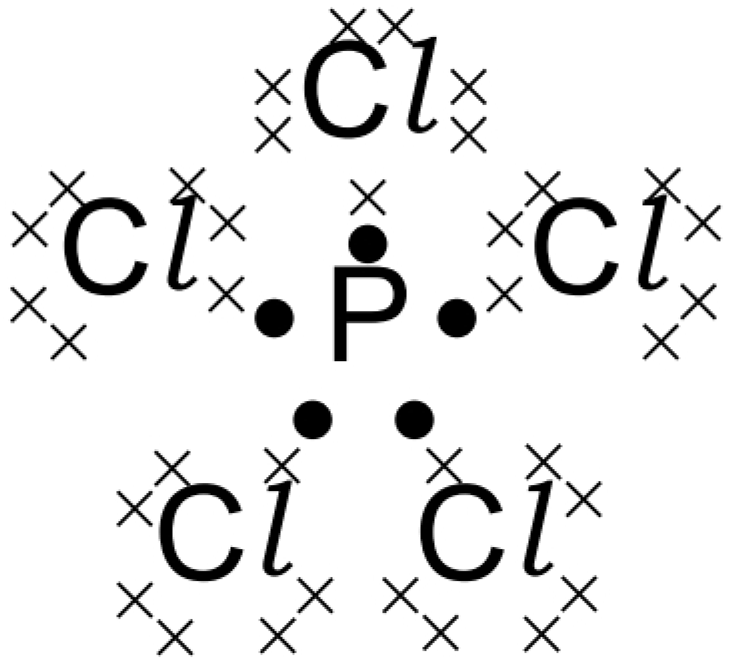
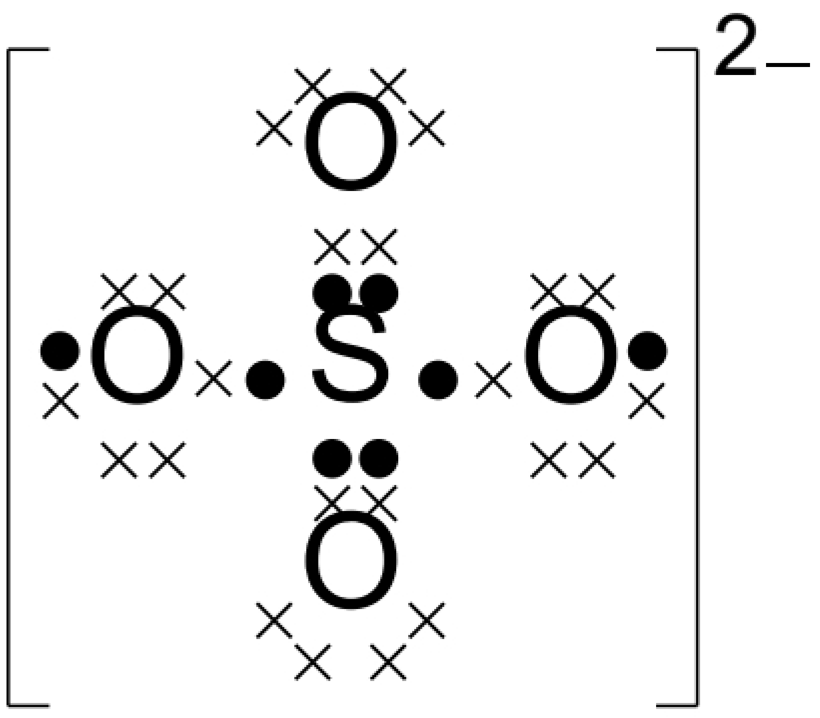


1.6.4 Dot-And-Cross Diagrams for Species with Odd Number (Unpaired) Valence Electrons

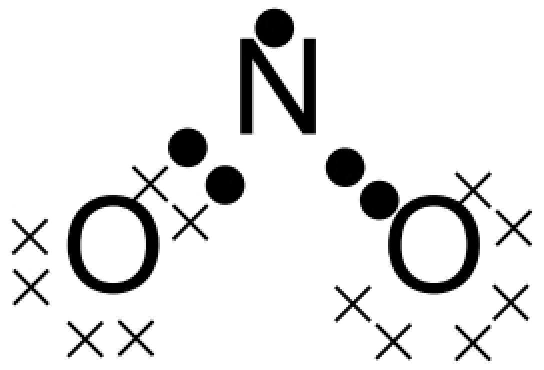
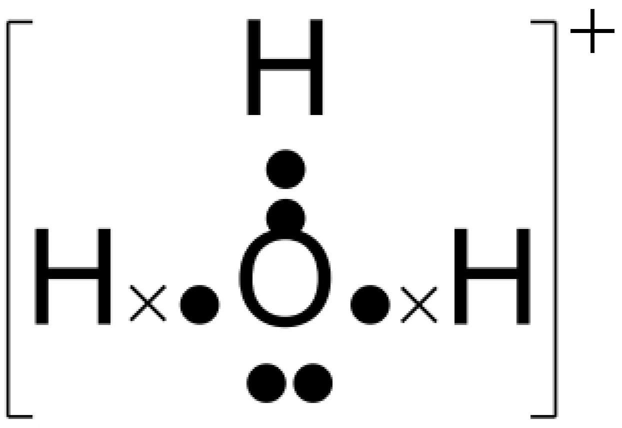
Note: Central atom may have **fewer than 8** valence electrons.

		Dot-and-Cross Diagram
11) **<u>N</u>O**	Central atom may have **odd number of valence electrons**. **Substances with an unpaired electron are called radicals** and are usually very reactive. Radicals may achieve a noble gas electronic configuration through the formation of a dimer. *e.g.* $2NO_2 \rightarrow N_2O_4$	
12) **<u>N</u>**O_2		

1.6.5 Dot-And-Cross Diagrams for Expansion of Octet Structures

		Dot-and-Cross Diagram
13) **<u>P</u>**C*l*$_5$	Only elements from **period 3 onwards** have **<u>vacant and energetically accessible</u>** d **<u>orbitals</u>** to **expand beyond octet structure** (i.e. having more than eight valence electrons).	
14) **<u>S</u>**O_4^{2-}		

1.6.6 Dot-And-Cross Diagrams Showing Dative Covalent Bonds

	Valence Electrons/ Bond Types	**Dot-and-Cross Diagram**
15) **N**O_2	N (Gp 15): 5 valence electrons O (Gp 16): 6 valence electrons 1 O forms **double** bond with N 1 O forms **dative** bond with N	
16) H_3**O**$^+$	O (Gp 16): 6 valence electrons **Electronegativity: H < O** **Charge = +1 (remove 1 electron from H)** 1 H: 1 – 1 = 0 ⇒ **forms dative bond with O** Remaining 2 H: 1 valence electron ⇒ each forms **single** bond with O	

Self Check 1B

Draw the dot-and-cross diagrams for the following substances:

(a) BF_3

(b) Cl_2O

(c) SO_3

(d) O_3

(e) H_2F^+

(f) AlH_4^-

(g) ICl_4^-

Checkpoint

☐ I know the steps to drawing dot-and-cross diagrams.

☐ I am able to draw dot-and cross-diagrams for molecules and polyatomic ions, knowing when they can have with odd electrons, incomplete octet, expanded octet and dative bonds.

2 Shape and Polarity

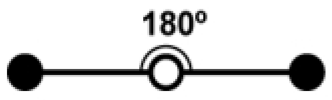
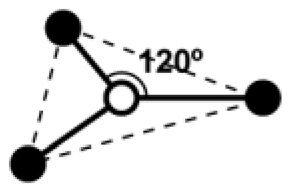
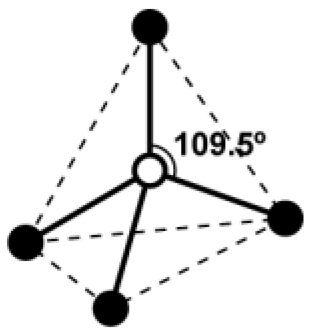
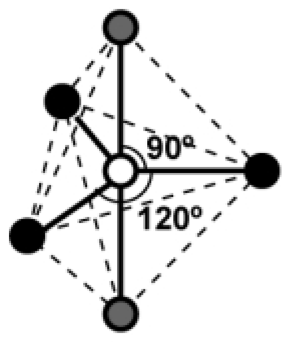
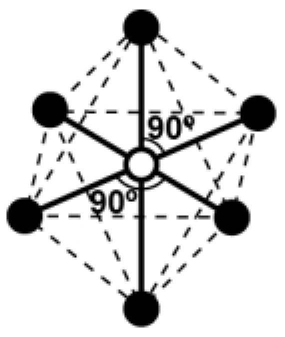
In a polyatomic species, the valence electron pairs of each atom, both bond pairs and lone pairs, repel one another to be as far as possible from each other. Hence, covalent molecules and polyatomic ions possess a definite, unique, three-dimensional shape which is determined by the angles between the bonds within them.

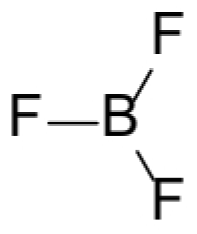
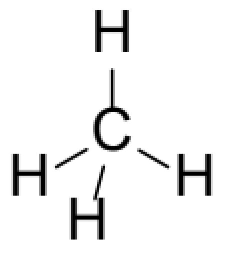
LO (d) Explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory.
(e) Predict the shapes of, and bond angles in, molecules analogous to those specified in (d)

2.1 The Valence Shell Electron Pair Repulsion (VSEPR) Theory

The Valence Shell Electron Pair Repulsion (VSEPR) theory is used to predict the shape of a molecule or ion. The two general principles of VSEPR theory are:

<u>Principle 1</u> **Electron pairs** (bond pairs and lone pairs) around a central atom are arranged **as far apart as possible** so as to **minimise repulsion**.

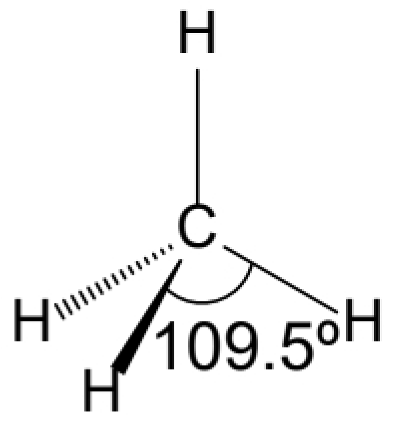
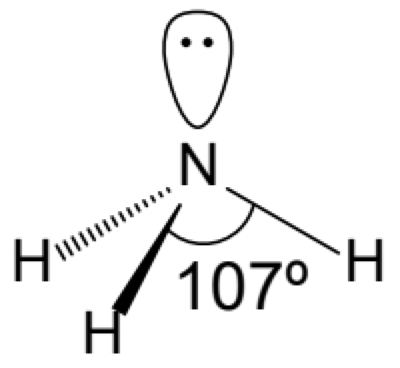
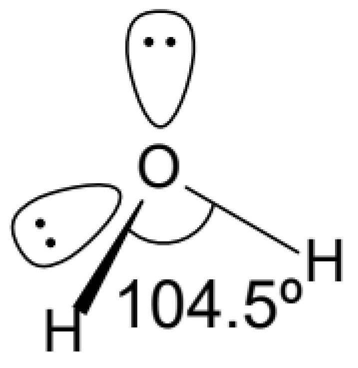
no. of electron pairs	shape	electron pairs are directed to…
2		opposite sides of each other
3		corners of an equilateral triangle
4		corners of a tetrahedr<u>on</u>
5		corners of a trigonal bipyramid
6		corners of an octahedr<u>on</u>

no. of electron pairs	2	3	4
example	O=C=O		
bond angle	180°	120°	109.5°

Principle 2 **lone pair–lone pair repulsion > lone pair–bond pair repulsion > bond pair–bond pair repulsion**

Orbitals containing lone pairs are closer to the nucleus than those containing bond pairs. Thus, they take up more space around the central atom and occupy a larger volume. Hence, lone pairs repel the other electron pairs that surround the atom more strongly.

Due to the **difference in extent of repulsion**, **bond angle** between the bond pairs **decreases** when there are more lone pairs.

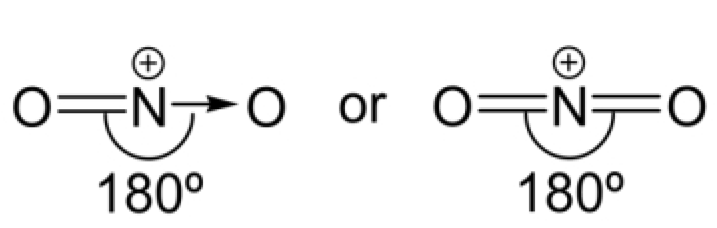
Example	**CH_4**	**NH_3**	**H_2O**
no. of electron pairs	4	4	4
no. of bond pairs	4	3	2
no. of lone pairs	0	1	2
type and extent of repulsion	bond pair–bond pair	lone pair–bond pair > bond pair–bond pair	lone pair–lone pair > lone pair–bond pair > bond pair–bond pair
bond angle	109.5°	107°	104.5°
shape	 *tetrahedral*	 *trigonal pyramidal*	 *bent*

Determining shape and bond angle:

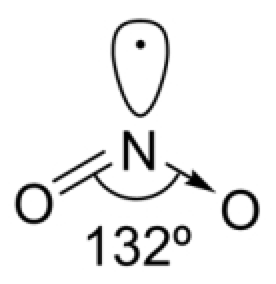
The starting point for working out a molecular shape is the dot-and-cross diagram. From there, determine the number of lone pairs and bond pairs. Refer to the table on the next page for the various shapes and bond angles.

Useful info to take note of:

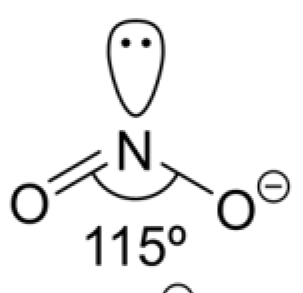
- A dative bond is a covalent bond. Hence, it is counted as a bond pair.
- Single unpaired electrons generally occupy less space compared to an electron pair, whether bond pair or lone pair, and will be less effective in diminishing the basic angle as **<u>lone pair–bond pair repulsion is greater than lone electron–bond pair repulsion</u>**:



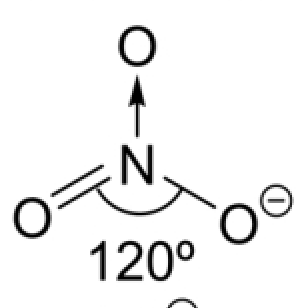
$NO_2^{\oplus}$



NO_2

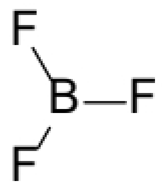
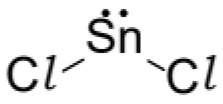
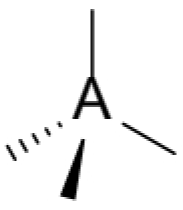
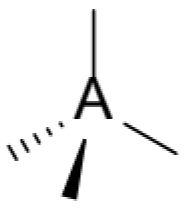
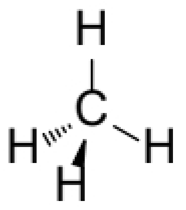
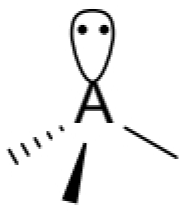
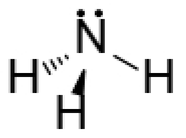
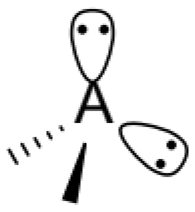
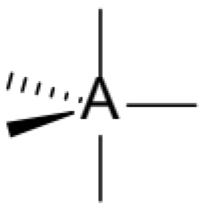
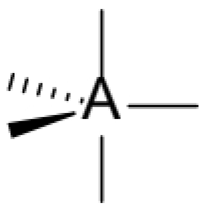
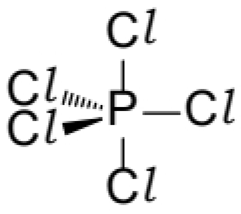
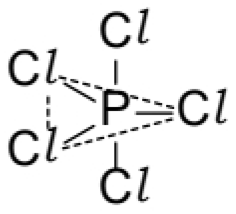
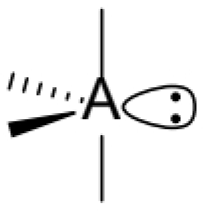
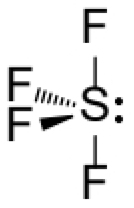
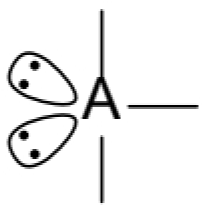
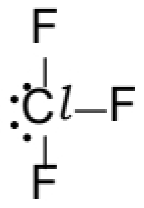
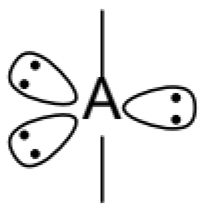
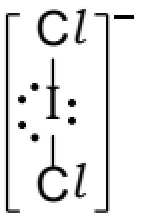
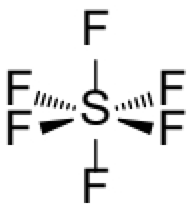
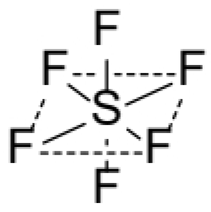
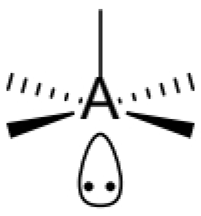
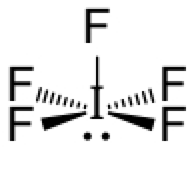
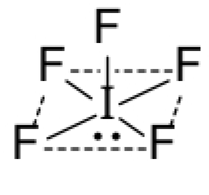
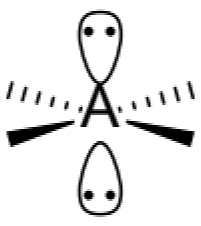
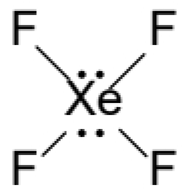


$NO_2^{\ominus}$



$NO_3^{\ominus}$

- Multiple bonds contain both σ and π bonds. But for the purpose of VSEPR, they are assumed to occupy a region of electron density.
  Consider the carbon in CO_2 (O=C=O):
  The central C atom is doubly bonded to each of the O atoms and is surrounded by just **two electron regions**. It is therefore predicted to be linear.

no. of electron pairs	electron-pair geometry	no. of bond pairs	no. of lone pairs	molecular geometry (actual shape)	examples	bond angle
2	**linear** —A—	2	0	linear —A—	CO_2 O=C=O	180º
3	**trigonal planar** 	3	0	trigonal planar 	BF_3 	120º
		2	1	bent 	$SnCl_2$ 	<120º (*e.g.* 119º)
4	**tetrahedral** 	4	0	tetrahedral 	CH_4 	109.5º
		3	1	trigonal pyramidal 	NH_3 	107º
		2	2	bent 	H_2O 	104.5º
5	**trigonal bipyramidal** 	5	0	trigonal bipyramidal 	PCl_5  or 	120º (equatorial) 90°(axial)
		4	1	see-saw / distorted tetrahedral 	SF_4 	<120º (equatorial) <90°(axial)
		3	2	T-shaped 	ClF_3 	<90º
		2	3	linear 	$[ICl_2]^-$ 	180º
6	**octahedral** 	6	0	octahedral 	SF_6  or 	90º (equatorial & axial)
		5	1	square pyramidal 	IF_5  or 	<90º (equatorial & axial)
		4	2	square planar 	XeF_4  or 	90º

Note: Use wedge and dash notation to represent tetrahedral, trigonal pyramidal and see-saw. Indicate the plane clearly with dotted lines for trigonal bipyramidal, octahedral and square pyramidal.

Example 2A

1. Draw the structure of the following compounds and predict their shapes and bond angles.
(a) PCl_4^+ (b) IF_4^+ (c) ICl_4^-

2. Which one of the following pairs do the molecules have similar shapes?

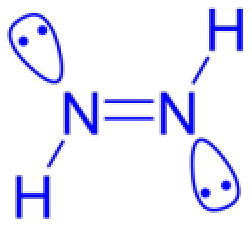
A $BeCl_2$ and H_2O

B BF_3 and NH_3

C $AlCl_3$ and BCl_3

D CO_2 and SO_2

3. Predict the shape and bond angle about the nitrogen atoms in di-imine, HN=NH.



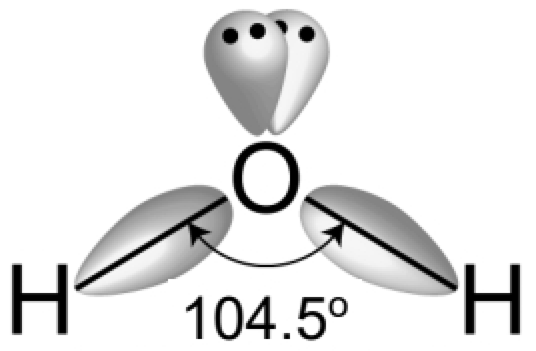
About each N atom, there are ______________________________.

To minimise repulsion, these three electron pairs are directed to the corners of an equilateral triangle.

Since ____, bond angle of H–N=H is ______________________________ and di-imine is __________ about N.

Special Cases: While bond angle typically is determined by the number of lone pair and bond pairs around the central atom, the additional factor that can affect the bond angles of molecules is the **electronegativity of the central atom or the terminal atoms**.

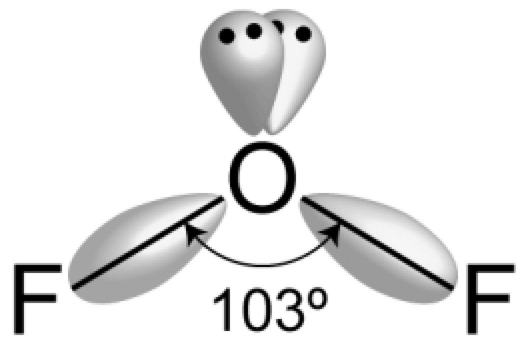
The **repulsion between the neighbouring electron pairs is decreased when the central atom has a lower electronegativity or when the terminal atoms have greater electronegativity**. In both cases, the electron density around the central atom decreases, leading to lesser repulsion between the bonding electron pairs.



(stronger repulsion)

Both H_2O and OF_2 have two bond pairs and two lone pairs, but OF_2 has a smaller bond angle than H_2O. Why?

- In OF_2, the more electronegative terminal F atoms draw electron density away from the central O atom.
- The two bond pair of electrons are further away from the nucleus of the central O atom.
- Thus, the two bond pair of electrons experience less repulsion between them as compared to the bond pair of electrons in H_2O, resulting in a smaller bond angle in OF_2.

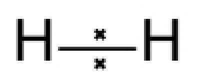


(weaker repulsion)

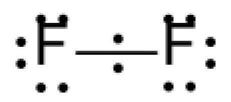
2.2 Polarity of Molecules

LO (g) Deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in **(d)**).

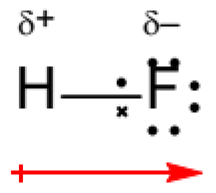
Each of the polar bonds in a molecule has its own dipole associated with it.



non-polar



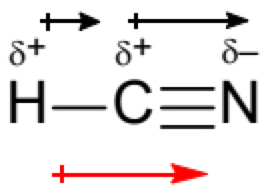
non-polar



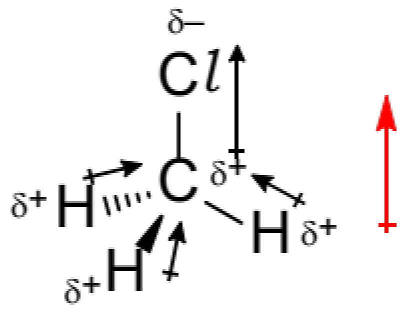
polar

The **net dipole moment** of the **molecule** depends on its **shape**. Depending on the relative angles between the bonds, the individual bond dipoles can:

either ***reinforce* each other**



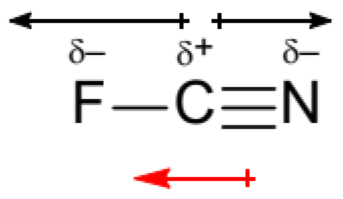
Net dipole in direction towards N



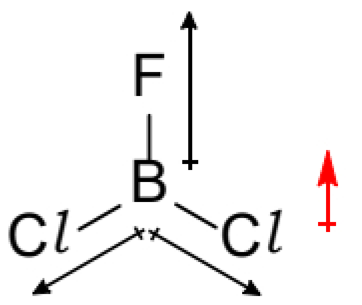
Net dipole in direction towards C*l*

- If the bond dipoles reinforce each other, molecules with very large dipoles can be formed.

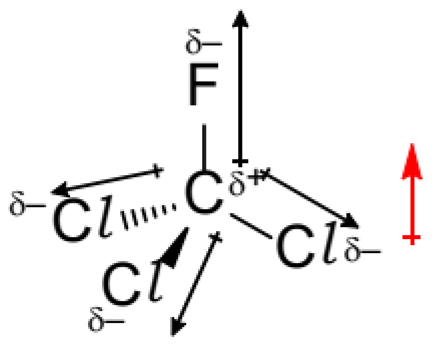
or ***cancel*** **each other**



Net dipole in direction towards F

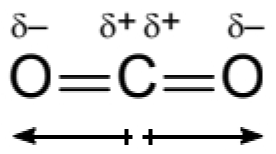


Net dipole in direction towards F



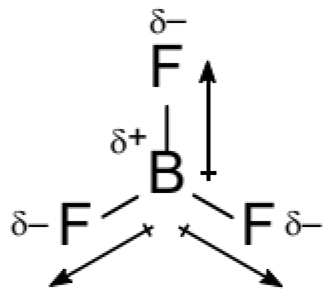
Net dipole in direction towards F

If cancellation is complete, the resulting molecule will have **no net dipole moment**, and so the molecule will be **non-polar**.



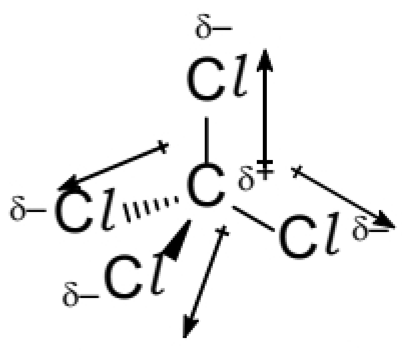
C=O bonds are polar, but molecule is non-polar

CO_2



B–F bonds are polar, but molecule is non-polar

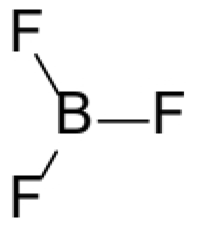
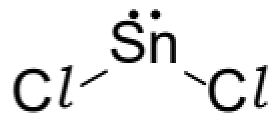
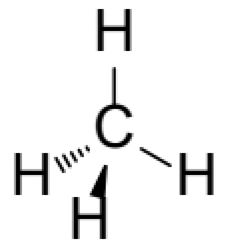
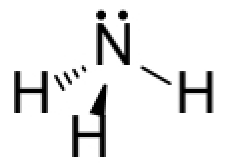
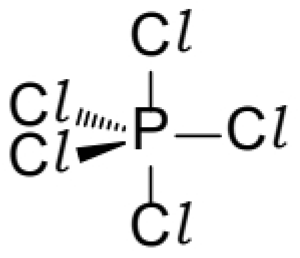
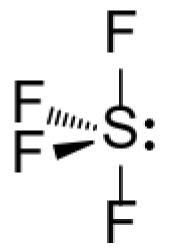
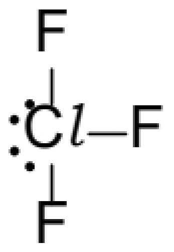
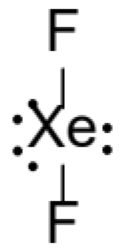
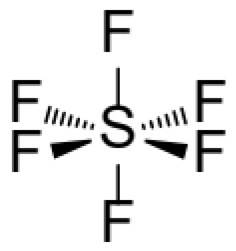
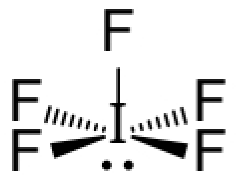
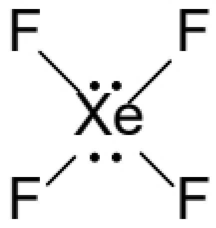
BF_3



C–C*l* bonds are polar, but molecule is non-polar

CC*l*$_4$

Other examples (with the same terminal atoms):

structure	shape	(bond) dipole moments…	polarity
O=C=O	linear	cancel off	non-polar
	trigonal planar	cancel off	non-polar
	bent	**do not** cancel off	polar
	tetrahedral	cancel off	non-polar
	trigonal pyramidal	**do not** cancel off	polar
	bent	**do not** cancel off	polar
	trigonal bipyramidal	cancel off	non-polar
	See-saw (distorted tetrahedral)	**do not** cancel off	polar
	T-shaped	**do not** cancel off	polar
	linear	cancel off	non-polar
	octahedral	cancel off	non-polar
	square pyramidal	**do not** cancel off	polar
	square planar	cancel off	non-polar

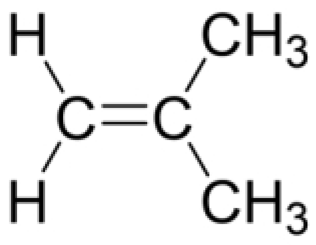
To determine if a molecule is **polar** or **non-polar**

- determine the actual shape of the molecule
- consider the electronegativity of the various atoms present in the molecule
- determine the net dipole moment by resolving the individual dipole moments

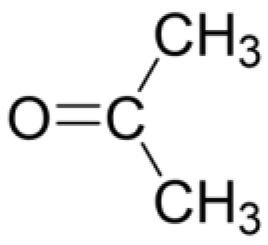
Example 2B

1. Which molecule has the largest dipole?

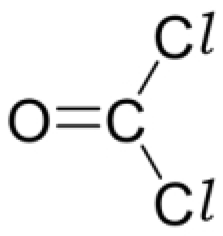
A



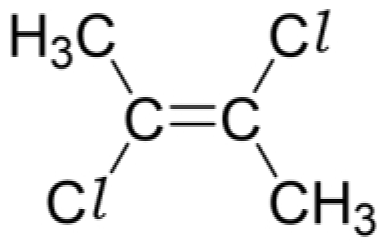
B



C



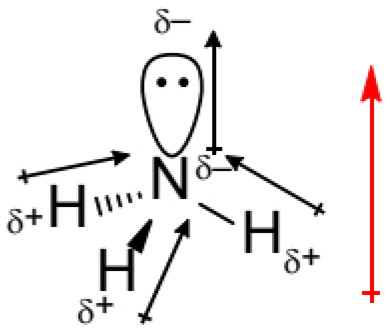
D

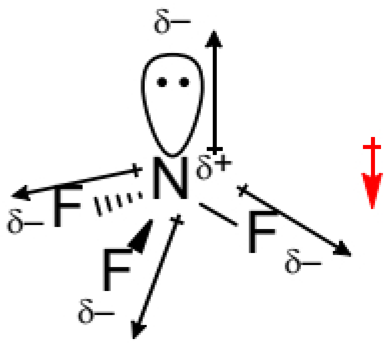


Comparing the Polarities of NH_3 and NF_3 *(for enrichment)*
Despite the differences in electronegativities between N and H, and between N and F, being similar, NH_3 has a much higher dipole moment compared to NF_3.

This is because dipoles are induced not just in polar bonds, but also in lone pairs of electrons. The lone pair of electrons is an area of negative charge, so it forms the δ– end of a dipole which points away from the positively charged nucleus of the atom.

In NH_3, the dipole due to the lone pair helps reinforce the dipoles from the N–H bonds, resulting in a highly polar molecule. However, in the case of NF_3, this dipole partially offsets the dipole due to the N–F bonds, resulting in a smaller resultant dipole.





Checkpoint

☐ I am able to predict the shape of the molecule and its bond angle.

☐ I am able to represent and represent the shape of molecules and polyatomic ions clearly, using dash and wedge where necessary, and drawing the bonds at appropriate angles to each other.

☐ I am able to able to predict if a molecule is polar or non-polar.

3 Intermolecular Forces of Attraction

The covalently bonded molecules we have looked at so far have **simple molecular structures**.

Substances made up of such molecules are often gases or liquids at room temperature. This is because, although the **intramolecular** covalent bonding *within* each molecule is very strong, the **intermolecular attractions** *between* one molecule and another are comparatively weak.

There are three main categories of intermolecular attraction:

- **instantaneous dipole–induced dipole interactions**
- **permanent dipole–permanent dipole interactions**
- **hydrogen bonding**

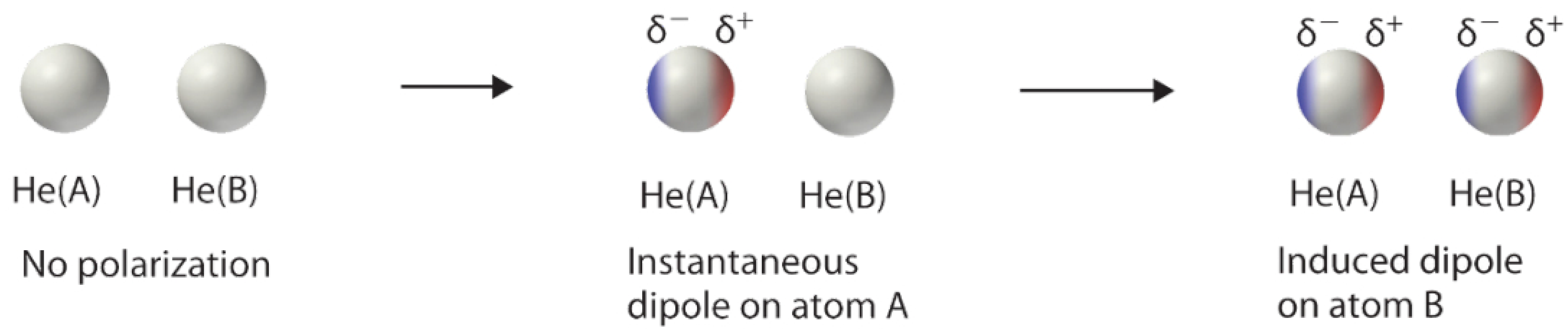
LO (h) Describe the following forces of attraction (electrostatic in nature):
  (i) intermolecular forces, based on permanent and induced dipoles, as in $CHCl_3(l)$; $Br_2(l)$ and the liquid noble gases
  (ii) hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups

3.1 Instantaneous Dipole–Induced Dipole Interactions

Temporary fluctuations in the electron distributions within atoms and non-polar molecules could result in the formation of short-lived **instantaneous dipole moments**, which produce attractive forces between otherwise non-polar substances. These attractive interactions are weak and fall off rapidly with increasing distance.

Consider a pair of adjacent He atoms:

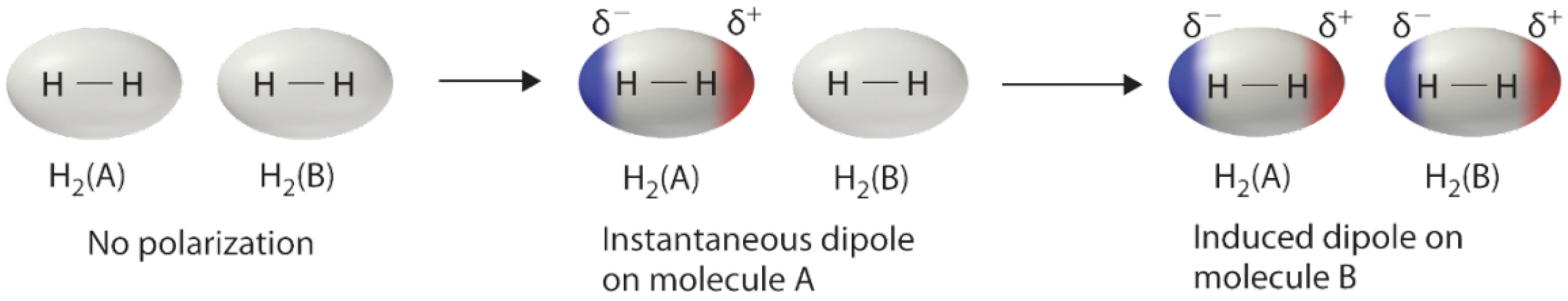
- On average, the two electrons in each He atom are uniformly distributed within the nucleus. However, because the electrons are in constant motion, their distribution in one atom is likely to be *asymmetrical* at any given instant, resulting in an **instantaneous dipole moment** that lasts in the order of 10^{-16} seconds:



- As shown above, the instantaneous dipole on one atom can interact with the electrons in an adjacent atom, pulling them towards the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the **temporary** formation of a dipole, called an **induced dipole**, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another.

- An instant later, the first atom might change its dipole through another movement of electrons within it, so the original dipole attraction might be destroyed. This changed dipole will induce new dipoles in another neighbouring atom, however, and so new intermolecular attractions will be formed.

Similar interactions are formed between molecules such as hydrogen gas.

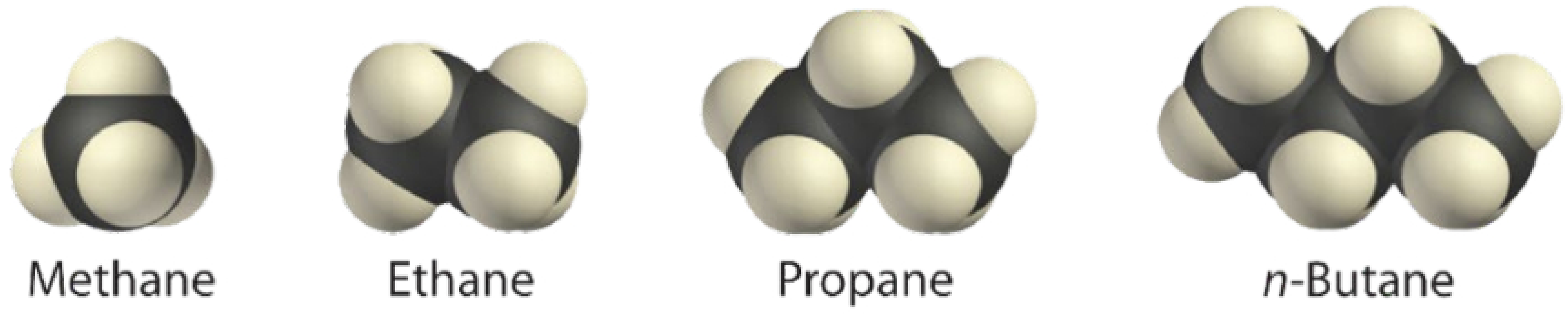


The **strength of instantaneous dipole–induced dipole interactions** is related to the ease of deformation of the electron distribution in an atom or molecule (i.e. their **polarisability**)

The polarisability of the electron cloud of a substance depends on:

(a) **Number of electrons**

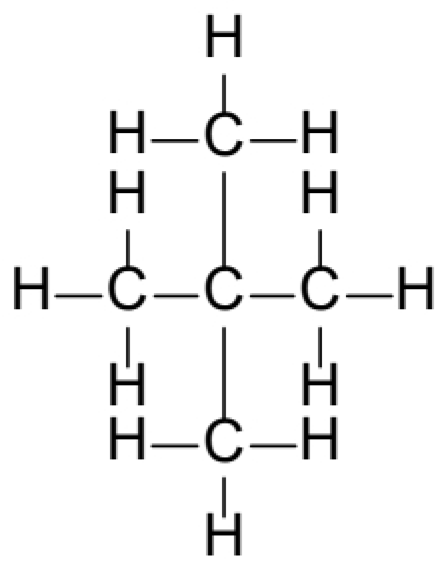
- When a molecule has **more electrons**, it will have a **bigger and more polarisable electron cloud**.
- This leads to **stronger** intermolecular instantaneous dipole–induced dipole interactions, which requires **more energy** to overcome.

molecule	boiling point / °C	reasons
CH_4	–164	These molecules have the same shape (tetrahedral), but the number of electrons increases going down the group, from 10 in CH_4 to 18 in SiH_4 to 36 in GeH_4 and 54 in SnH_4.
SiH_4	–112	
GeH_4	–89	
SnH_4	–52	
F_2	–188	All of these are linear, diatomic molecules. Down the group, the number of electrons increases, from 18 in F_2, to 34 in Cl_2, to 70 in Br_2 and 106 in I_2.
Cl_2	–35	
Br_2	59	
I_2	184	
CH_4	–164	Along the alkane series, the molecules contain more electrons (an extra 8 for each CH_2 group).
CH_3CH_3	–89	
$CH_3CH_2CH_3$	–42	
$CH_3CH_2CH_2CH_3$	–1	
		

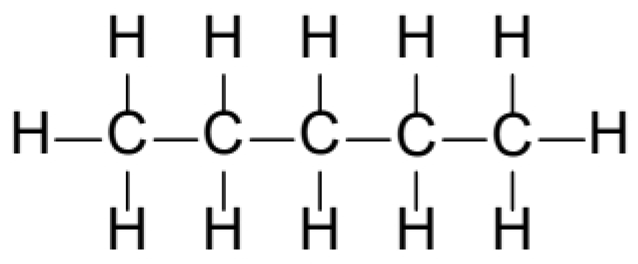
(b) **Shape of molecule** (refers to **elongated** versus **spherical** shape)

- Compared to spherical molecules, the **elongated molecules have greater surface area of contact.**
- This leads to **stronger** intermolecular instantaneous dipole–induced dipole interactions, which requires **more energy** to overcome.

For example, 2,2-dimethylpropane and pentane are **isomers** i.e. they both have the same chemical formula, C_5H_{12}, but different arrangement of atoms.

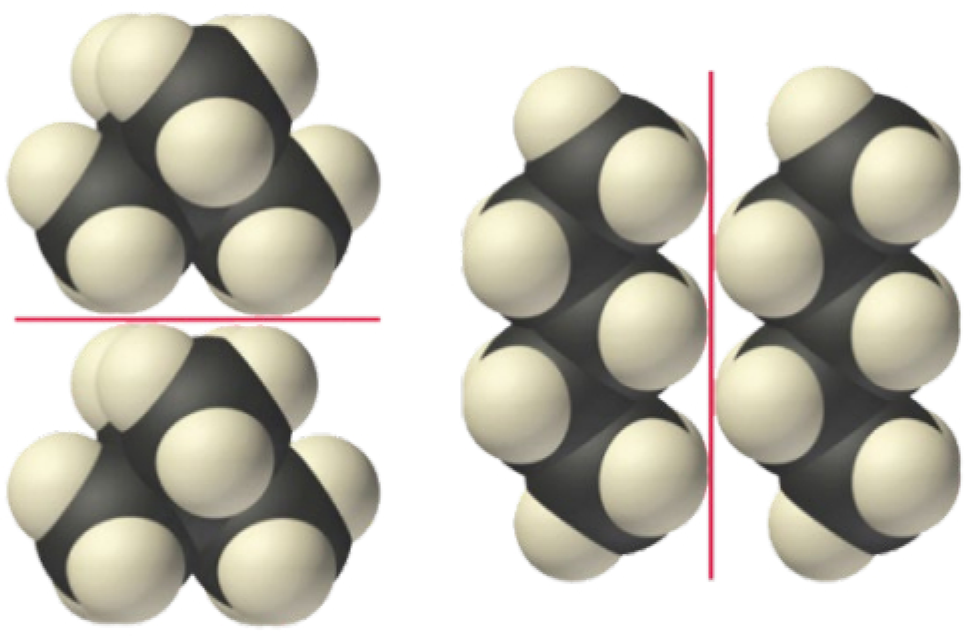


2,2-dimethylpropane



pentane

Since they have the same chemical formula, they will have the same number of electrons. However, 2,2-dimethylpropane has a lower boiling point of 9.5 °C, while pentane boils at a higher temperature of 36.1 °C. This is due to the difference in the shapes of the molecules.



branched chain
(spherical)
↓
less surface area to interact with other molecules

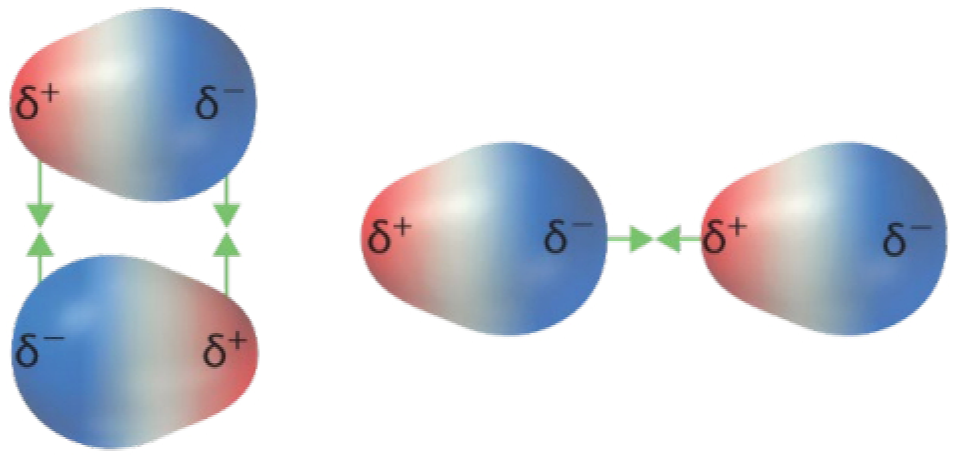
straight chain
(elongated)
↓
larger surface area to interact with other molecules

2,2-dimethylpropane

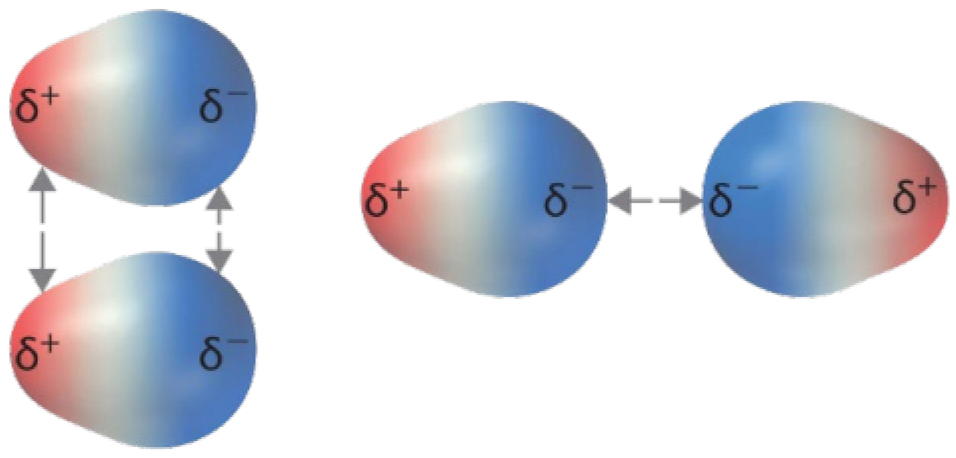
pentane

3.2 Permanent Dipole–Permanent Dipole Interactions

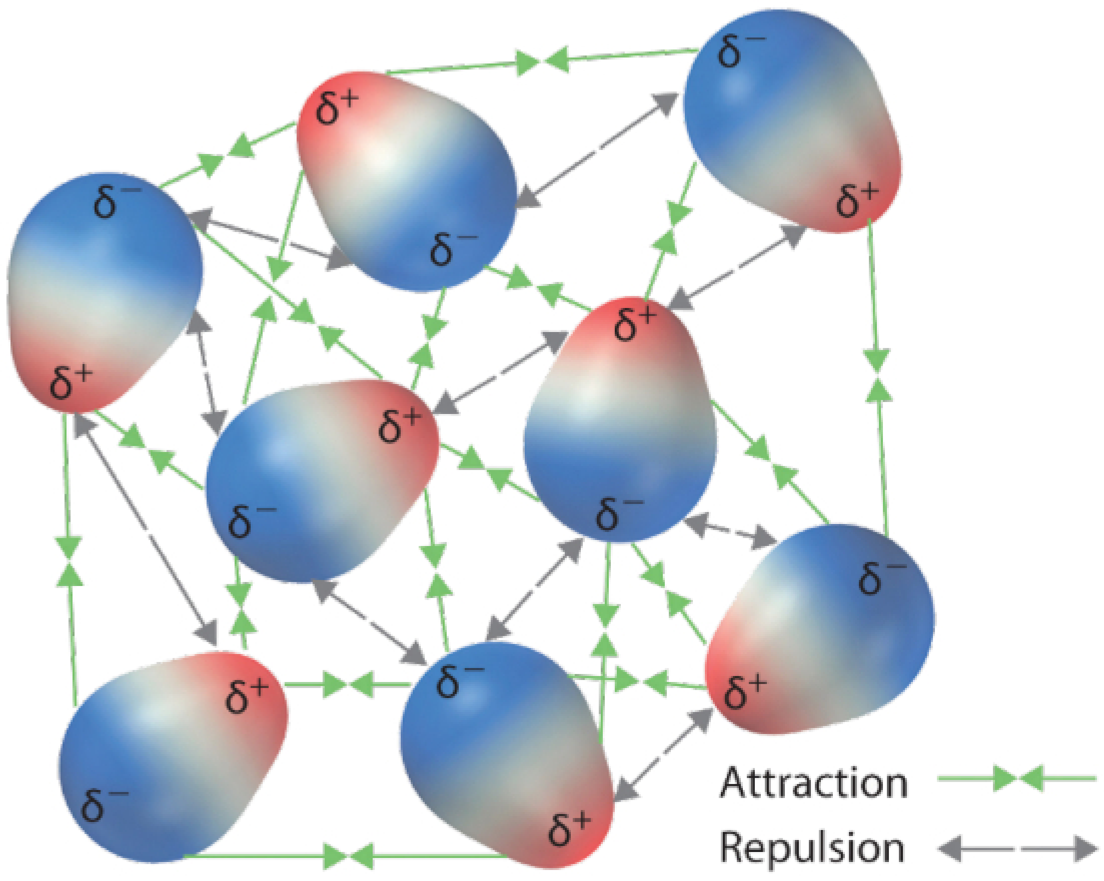
Uneven distribution of electronic charge within **polar molecules** results in a permanent dipole. The positive end of one molecule's dipole can attract the negative end of another polar molecule.



Similarly, repulsive dipole-dipole interactions can occur if two positive or two negative ends are adjacent to each other.

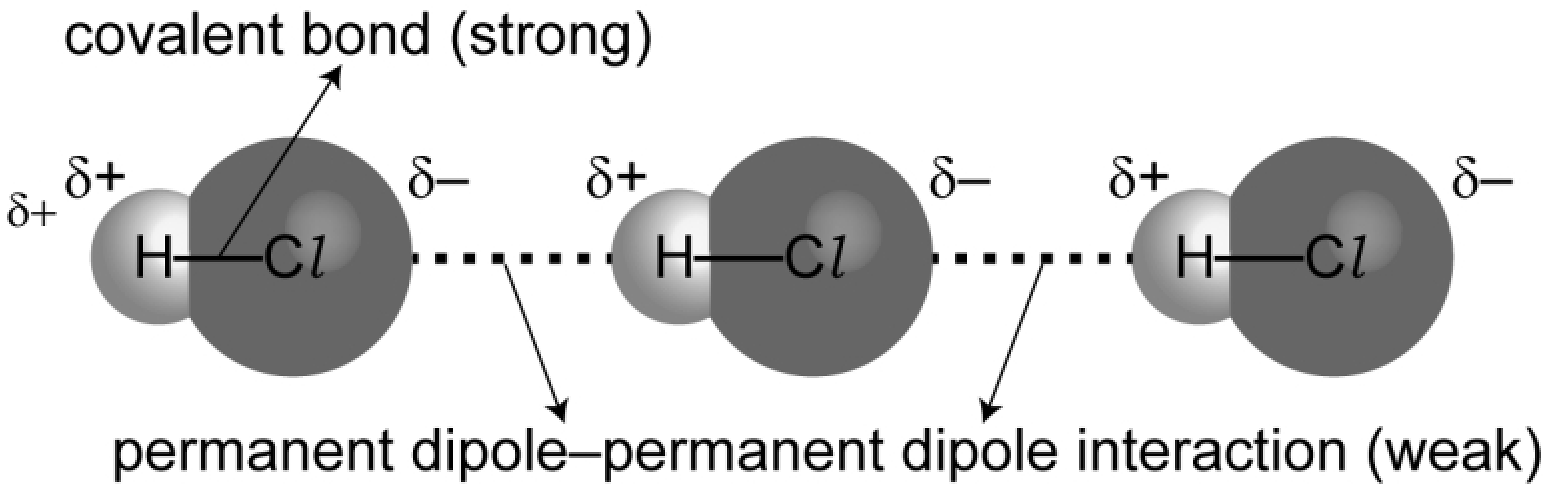


Since molecules in liquid and gas phase move freely and continuously, polar molecules always experience both attractive and repulsive dipole-dipole interactions simultaneously.



On average, however, the attractive interactions dominate, resulting in an intermolecular attraction called **permanent dipole-permanent dipole interactions**.

An example of permanent dipole-permanent dipole interactions is the attractions between HC*l* molecules.



Within a series of compounds of similar molar mass, the **strength** of the intermolecular permanent dipole–permanent dipole interactions **increases** as the **dipole moment** of the **molecules** increases, *i.e.* as the molecules become **more polar**.

compound	molar mass /g mol^{-1}	dipole moment /D	boiling point /K
$(CH_3)_3CH$ (2-methylpropane)	58	0.132	261
$C_2H_5OCH_3$ (methoxyethane)	60	1.17	281
CH_3CH_2CHO (propanal)	58	2.72	322
CH_3COCH_3 (propanone)	58	2.88	329

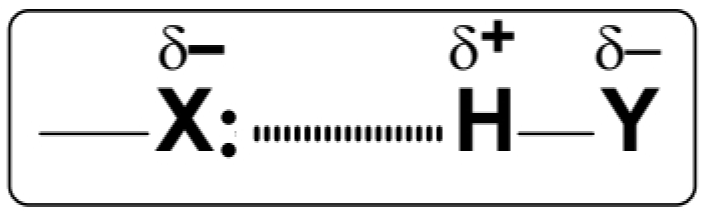
3.3 Hydrogen Bonding

When a **hydrogen atom is bonded to a very electronegative atom such as nitrogen, oxygen or fluorine**, it will have a significant partial positive charge ($\delta+$). Hence, this hydrogen atom with a large $\delta+$ can experience a particularly strong attraction to a **lone pair of electrons on a nitrogen, oxygen or fluorine atom** in an adjacent molecule, as the lone pairs of electrons in such atoms are in orbitals that are small enough to interact with the $\delta+$ hydrogen atom. An intermolecular attractive force called a **hydrogen bond** is thus created.

Hydrogen bond is defined as the **electrostatic forces of attraction** between the **partial positive** ($\delta+$) **hydrogen** atom **that is directly bonded to a very electronegative F**, **O** or **N** atom and a **lone pair of electrons** of another **F**, **O** or **N** atom.

While the name “hydrogen bond” makes such an interaction sound like it is a type of covalent bond, it is not. In fact, hydrogen bonds are about 10 times weaker than a typical covalent bond.

Hydrogen bonds are represented by dotted lines between the $\delta+$ hydrogen and the lone pair of electrons on a very electronegative element (F, O, N).



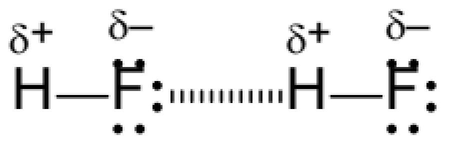
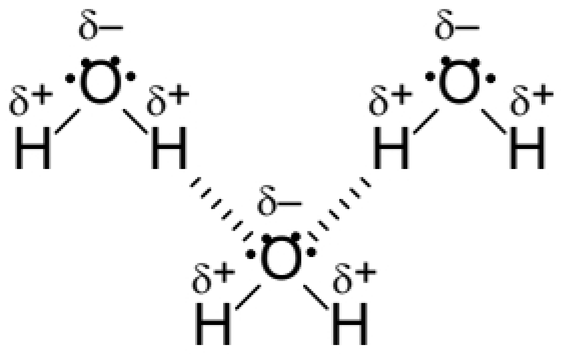
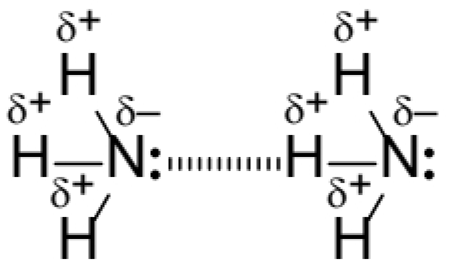
······· hydrogen bond

X, **Y** = F, O, N

Note: *Always include the **lone pair** and **partial charges*** in a diagram showing hydrogen bonds.

The **strength of hydrogen bonds increases** when the **electronegativity of the atom bonded to the $\delta+$ hydrogen atom increases**. For example, HF has higher boiling point than NH_3 because the F atom in HF is more electronegative than the N atom in NH_3. Hence, HF has stronger intermolecular hydrogen bonding than NH_3.

However, if we compare the boiling point of H_2O to that of HF, we realise that the above explanation does not work. O atom in H_2O is less electronegative than the F atom in HF, but H_2O has a higher boiling point.

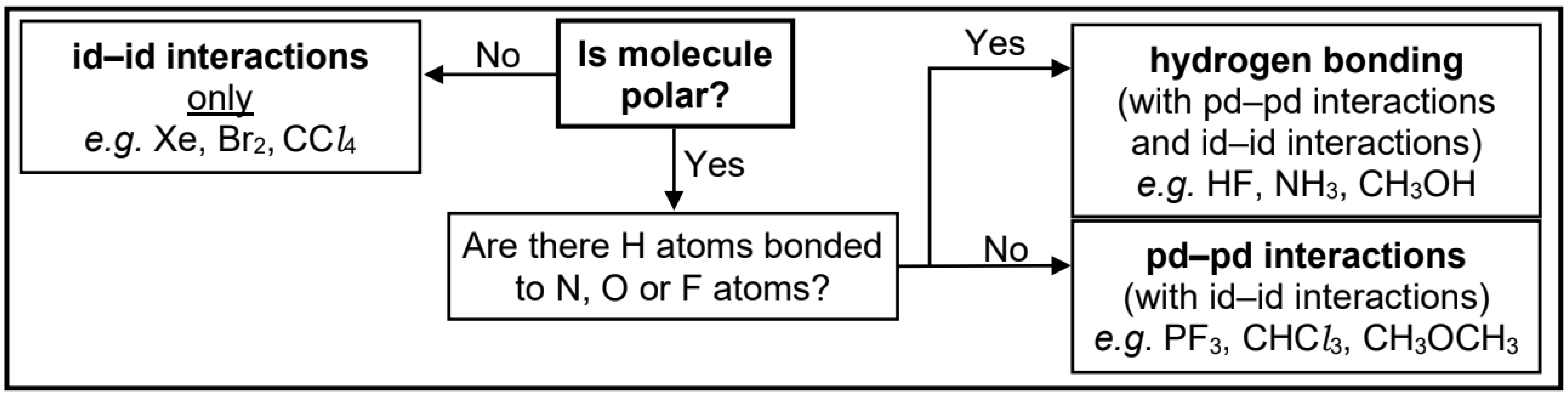
molecule (boiling point)	HF (20 ºC)	H_2O (100 ºC)	NH_3 (−33 ºC)
diagram			
no. of lone pairs (on each F/O/N)	3	**2**	**1**
no. of H atoms	**1**	**2**	3
no. of H bonds (per molecule)	**1**	**2**	**1**
electronegativity	F >	O >	N

In this case, we need to consider the number of hydrogen bonds formed per molecule, or the **extensiveness of hydrogen bonding**. H_2O has the highest boiling point because H_2O has **more extensive** intermolecular hydrogen bonding than HF and NH_3. It can form **two hydrogen bonds per water molecule** whereas both NH_3 and HF can **only form one hydrogen bond per molecule**.

3.4 Comparing the Three Types of Intermolecular Forces

The most significant intermolecular forces of attraction that exist in a species depends on the polarity of the molecule. The flow chart below shows an easy way to help you determine the intermolecular forces in a given covalent compound.

Note that instantaneous dipole–induced dipole interactions exist in **all** molecules, not just in non-polar molecules. However, due to the relative strengths of the intermolecular forces, it may not be the most significant in polar molecules.

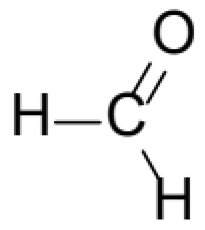
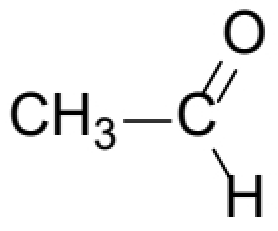
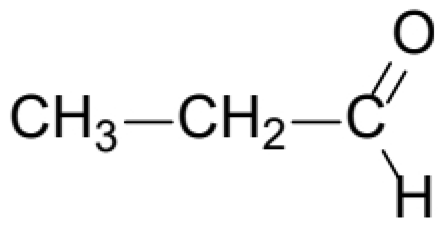


Generally, for molecules with **similar** number of electrons, the relative strengths of intermolecular forces of attraction are in the order of:

hydrogen bonds > **permanent dipole–permanent dipole interactions** > **instantaneous dipole–induced dipole interactions**

This has implications on physical properties such as boiling points of covalent compounds.

In the examples below, the compounds are grouped together by similar number of electrons. This implies that the instantaneous dipole–induced dipole interactions will be similar in strength within each grouping.

compound	formula	polarity	type of IMF	no. of electrons	boiling point / ºC
ethane	$CH_3–CH_3$	non-polar	id–id	18	–89
methanal	 $\mathrm{H{-}C({=}O){-}H}$	polar	pd–pd	16	–19
methanol	$CH_3–OH$	polar	hydrogen bonding	18	+65
propane	$CH_3–CH_2–CH_3$	non-polar	id–id	26	–42
ethanal	 $\mathrm{CH_3{-}C({=}O){-}H}$	polar	pd–pd	24	+20
ethanol	$CH_3–CH_2–OH$	polar	hydrogen bonding	26	+79
butane	$CH_3–CH_2–CH_2–CH_3$	non-polar	id–id	34	0
propanal	 $\mathrm{CH_3{-}CH_2{-}C({=}O){-}H}$	polar	pd–pd	32	+49
propan-1-ol	$CH_3–CH_2–CH_2–OH$	polar	hydrogen bonding	34	+97

The first compound in each grouping is a hydrocarbon which is essentially non-polar. Molecules of these compounds are held together by instantaneous dipole–induced dipole interactions *only*.

The second compound in each grouping is an aldehyde with a polar –CHO group. Molecules of these compounds are held together by stronger permanent dipole–permanent dipole interactions, on top of instantaneous dipole–induced dipole interactions, leading to higher boiling points.

The last compound in each grouping is an alcohol with a polar –OH group, which is capable of forming hydrogen bonds. These molecules are held together by even stronger hydrogen bonding, on top of the permanent dipole–permanent dipole interactions and instantaneous dipole–induced dipole interactions. Hence, they have the highest boiling points compared to the rest in the group.

Example 3A

1. Consider the following three compounds:

1 $(CH_3)_3CH$ **2** $CH_3CH_2CH_2OH$ **3** $CH_3CH_2CH_2CH_3$

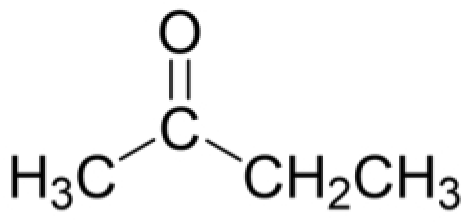
Explain why compound **3** has a higher boiling point than compound **1**.

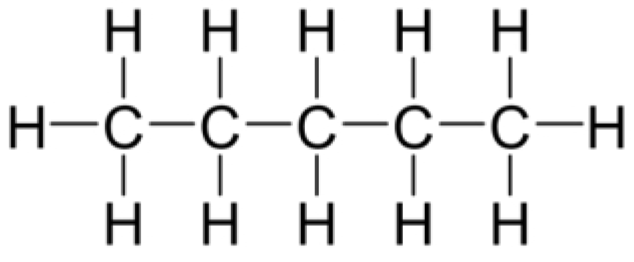
Both compounds have ____________________ structure. Compound **1** is a ________ molecule while compound 3 is a __________ molecule. Compound 3 has ____________________ compared to compound 1. Hence, Compound 3 has ____ than compound 1 which requires ____________________ to overcome.

Explain why compound **2** has a higher boiling point than compound **3**.

Compound **2** is a **simple molecular** compound with **stronger** ____________________, while compound 3 is a simple molecular compound with weaker ____.
_______________ is required to overcome the stronger
_______________________________________ of compound **2**.

2. Which of the following statements best explains why the boiling point of butanone, C_4H_8O (79.6 °C) is higher than that of pentane, C_5H_{12} (36.1 °C)?


butanone


pentane

A The relative molecular mass of butanone is higher than that of pentane.
B The butanone molecule has a larger surface area than the pentane molecule.
C There are hydrogen bonds between butanone molecules, but not between pentane molecules.
D There are permanent dipole–permanent dipole interactions between butanone molecules, but only instantaneous dipole–induced dipole interactions between pentane molecules.

Answer:
Pentane is ________ while butanone is ________. Thus, butanone will have ________________________ which are ________ and requires ________________ to overcome than the ________________________________ that pentane has. Thus, butanone would have a higher boiling point than pentane.

Self Check 3A

1. The gecko, a small lizard, can climb up a smooth glass window. The gecko has millions of microscopic hairs on its toes and each hair has thousands of pads at its tip. The result is that the molecules in the pads are extremely close to the glass surface on which the gecko is climbing.

   What is the main attractive force between the gecko's toe pads and the glass surface?

   A co-ordinate bonds
   B covalent bonds
   C ionic bonds
   D instantaneous dipole–induced dipole interactions

2. The boiling point of water (100 ºC) is greater than that of HF (20 ºC)?
   Which statement is a correct explanation of this?

   A Each hydrogen bond formed between water molecules is stronger than that formed between HF molecules.
   B There are more atoms in a water molecule than there are in a HF molecule, so the permanent dipole–permanent dipole forces are stronger in water.
   C There are, on average, more hydrogen bonds between water molecules than there are between HF molecules.
   D The water molecule has a greater permanent dipole than the HF molecule.

Checkpoint

☐ I know what the 3 types of intermolecular forces are.

☐ I know the factors that affect the strengths (and extensiveness for hydrogen bonds) of the various intermolecular forces.

☐ I am able to identify the type(s) of intermolecular forces present in any given substance.

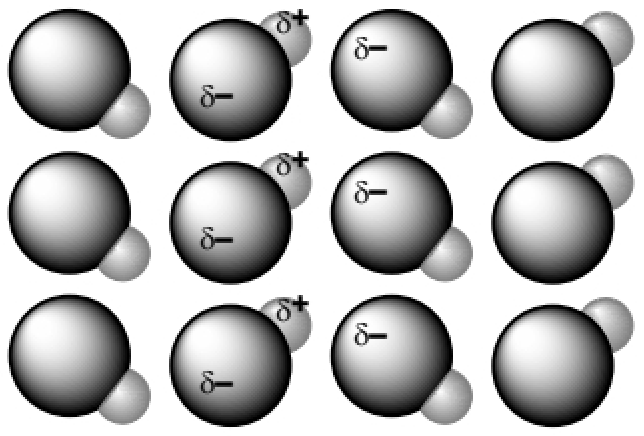
☐ I am able to explain melting and boiling point differences based on the strengths of the different intermolecular forces.

4 Covalent Substances and Their Physical Properties

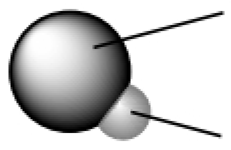
LO (i) Outline the importance of hydrogen bonding to the physical properties of substances including ice and water.
(l) Describe, in simple terms, the lattice structure of a crystalline solid which is:
  (ii) simple molecular, as in iodine
  (iii) giant molecular, as in graphite and diamond
  (iv) hydrogen-bonded, as in ice

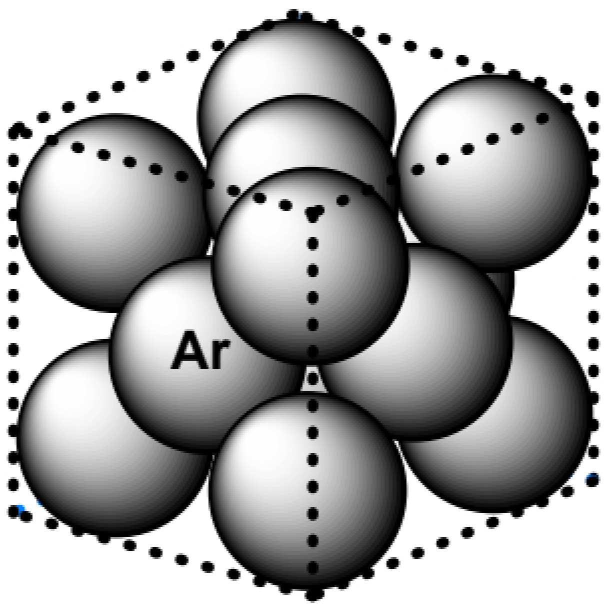
4.1 Simple Molecules

In substances with simple molecular structures (extends to monoatomic substances as well), there are intermolecular (or interatomic) interactions such as **instantaneous dipole–induced dipole interactions**, **permanent dipole–permanent dipole interactions**, and **hydrogen bonding**, which are **weak** compared to intramolecular covalent bonds.

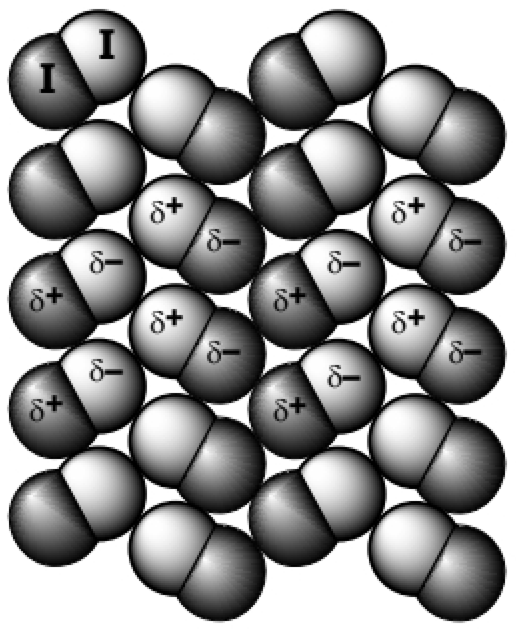


solid hydrogen chloride: stronger permanent dipole-permanent dipole interactions





solid argon: weaker instantaneous dipole-induced dipole interactions



solid iodine: stronger instantaneous dipole- induced dipole interactions

In general, substances with simple molecular structures exhibit the following physical properties:

Property	Reasons
Low melting/ boiling point	**Small** amount of energy is needed to overcome either the **weak intermolecular instantaneous dipole–induced dipole interactions/ permanent dipole–permanent dipole interactions/intermolecular hydrogen bonds**. Note: When a substance consisting of simple covalent molecules melts or boils, covalent bonds within the molecules are **NOT** broken (unless the substance decomposes).
Non-conductors of **electricity** in any state	Electrons are **localised** in **covalent bonds** and are **not mobile** to conduct electricity.

<table>
<tr><th>Property</th><th>Reasons</th></tr>
<tr><td>Generally soluble in non-polar solvents (<i>e.g.</i> benzene, CCl_4, hexane); insoluble in polar solvents (<i>e.g.</i> water)</td><td>In general, substances with similar types of intermolecular forces dissolve in each other; “like dissolves like”. Dissolution can be a physical (e.g. dissolve ethanol in water) or a chemical process (e.g. dissolve HCl in water).
To predict solubility we need to consider the relative strengths of solute–solvent interactions, solute-solute interactions and solvent–solvent interactions. For a solute to be soluble, solute–solvent interactions must be comparable in strength as solute–solute and solvent–solvent interactions.
<table>
<tr><th colspan="2">example</th><th>I_2 in water</th><th>I_2 in hexane</th><th>CH_3CH_2OH in water</th><th>HCl in water</th></tr>
<tr><td rowspan="4">interaction</td><td>solute–solute</td><td>instantaneous dipole–induced dipole</td><td>instantaneous dipole–induced dipole</td><td>hydrogen bonding</td><td>permanent dipole–permanent dipole</td></tr>
<tr><td>solvent–solvent</td><td>hydrogen bonding</td><td>instantaneous dipole–induced dipole</td><td>hydrogen bonding</td><td>hydrogen bonding</td></tr>
<tr><td>compare</td><td>stronger than</td><td>approximately the same as</td><td>approximately the same as</td><td>weaker than</td></tr>
<tr><td>solute–solvent</td><td>instantaneous dipole–induced dipole*</td><td>instantaneous dipole–induced dipole</td><td>hydrogen bonding</td><td>ion–dipole**</td></tr>
<tr><td colspan="2">solubility</td><td>insoluble</td><td>soluble</td><td>soluble</td><td>soluble</td></tr>
</table>
* The more accurate description of the interactions formed between iodine (non-polar molecule) and water (polar molecule) is actually permanent dipole-induced dipole interactions i.e. attraction between the permanent dipole on water and the induced dipole of iodine. However, at A Levels, we will accept such an interaction to be described as instantaneous dipole–induced dipole interactions.

** HCl ionises in water : $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
(refer to pg. 49 for more information about ion-dipole interactions)</td></tr>
</table>

Example 4A

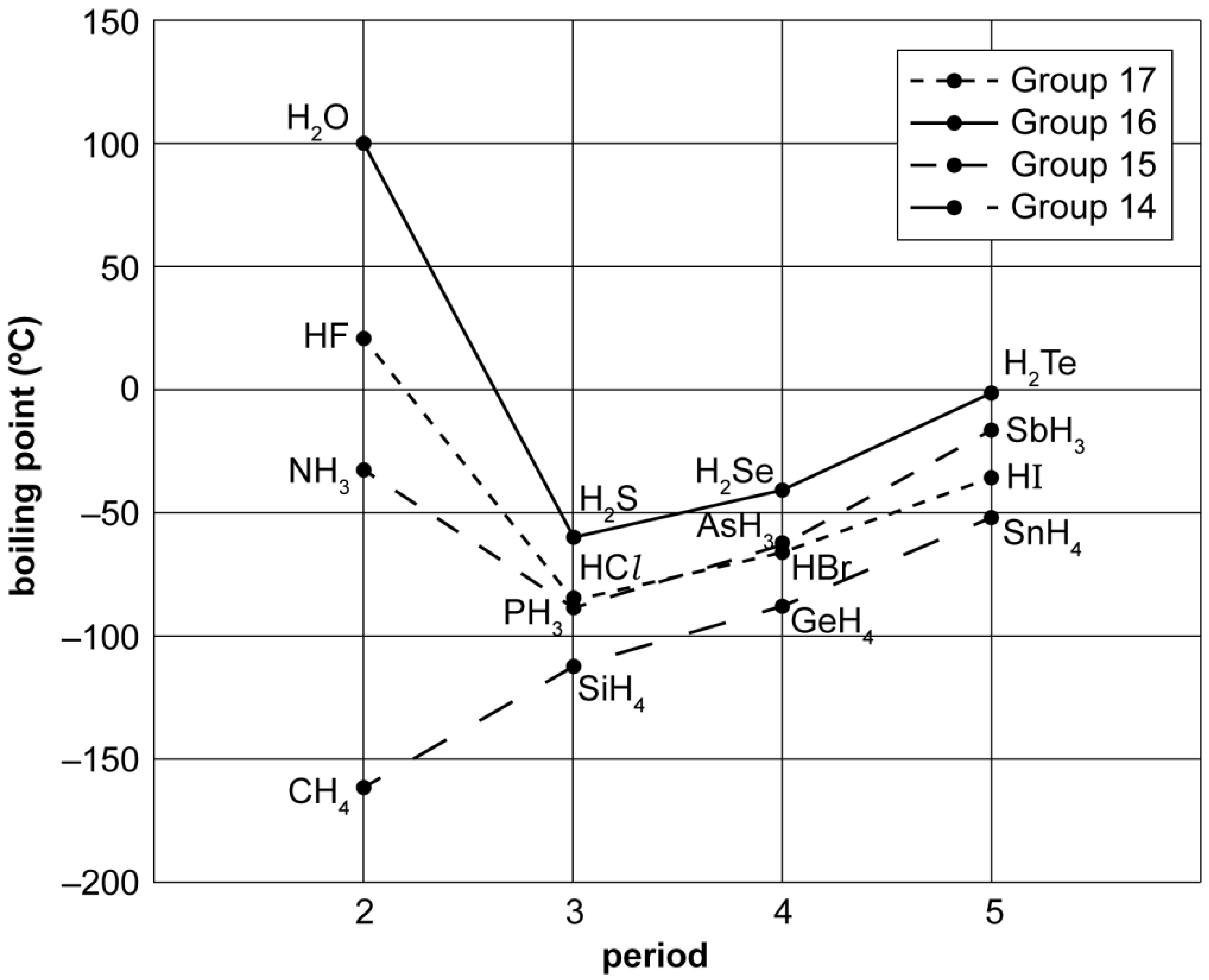
Explain why CH_3CH_2OH is soluble in CH_3COCH_3.

The energy ____________ in forming ________________________ between the CH_3CH_2OH and CH_3COCH_3 molecules (i.e. solute-solvent interactions) is ____________ to ____________ the ________________________ between the CH_3CH_2OH molecules (i.e. solute-solute interactions) and ____________________________________ between the CH_3COCH_3 molecules (i.e. solvent–solvent interactions). Thus CH_3CH_2OH is soluble in CH_3COCH.

4.2 Influence of Hydrogen Bonding on Physical Properties of Molecules

4.2.1 Unusually high boiling points of ammonia, water and hydrogen fluoride

when compared to other hydrides in the same group:



All hydrides in each group have **simple molecular** structures.

As **number of electrons increases** down each group, **strength of intermolecular instantaneous dipole–induced dipole interactions increases**. A **larger amount of energy** is required to overcome the stronger intermolecular instantaneous dipole–induced dipole interactions. Hence, boiling point of hydrides increases down the group.

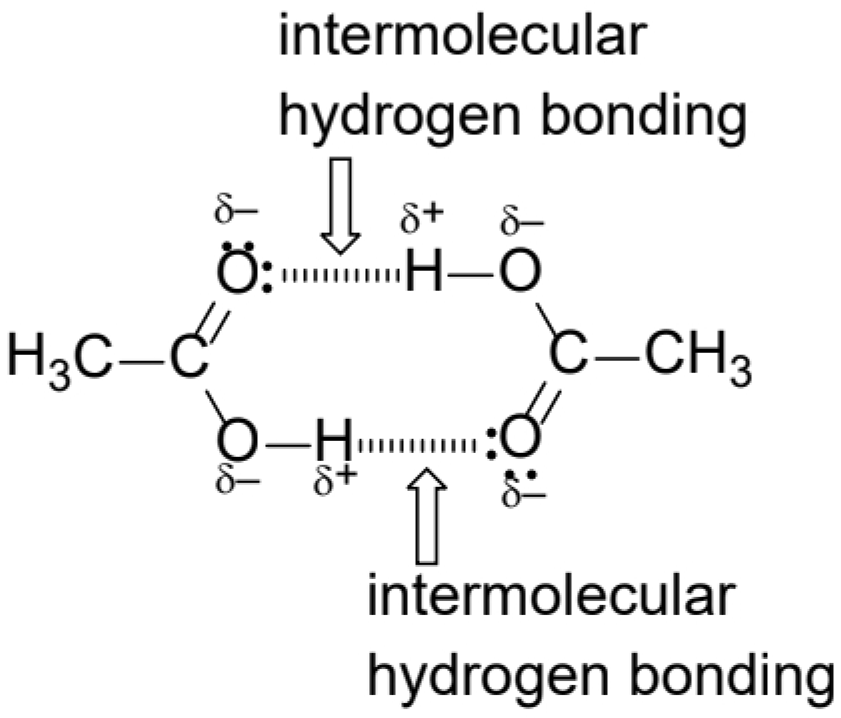
However, boiling points of ammonia, water and hydrogen fluoride are **higher than expected**. This is because **more** energy is needed to overcome the **stronger** intermolecular **hydrogen bonds** in **ammonia**, **water** and **hydrogen fluoride** compared to the **weaker** intermolecular **instantaneous dipole–induced dipole interactions** in other hydrides.

(See Section 3.3 for the comparison between the boiling points of ammonia, water and hydrogen fluoride.)

4.2.2 Anomalous relative molecular masses of organic acids (R–CO_2H)

Ethanoic acid, CH_3CO_2H, has an **apparent M_r of 120.0** which is **double** the expected M_r of 60.0 in the gas phase or when dissolved in benzene.

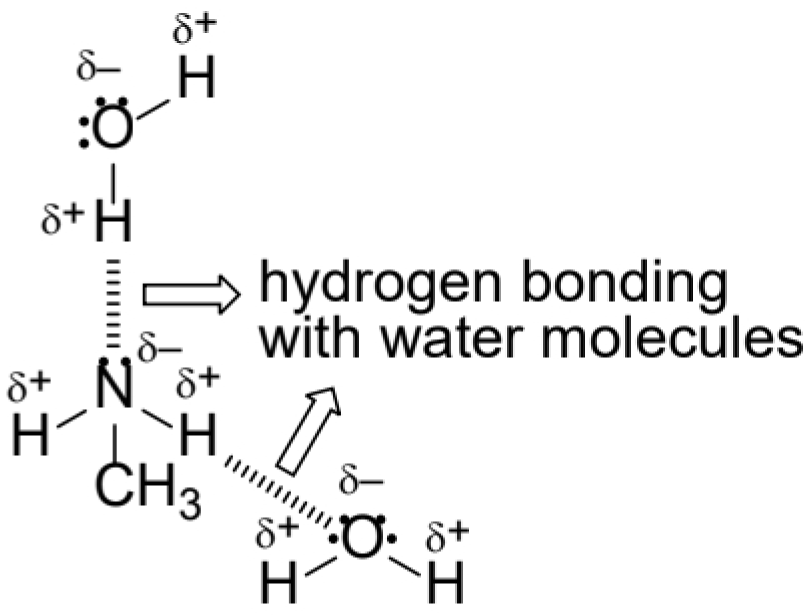
This is due to each acid molecule pairing up to form a **cyclic** (closed ring) **dimer** *via* intermolecular **hydrogen bonds**.



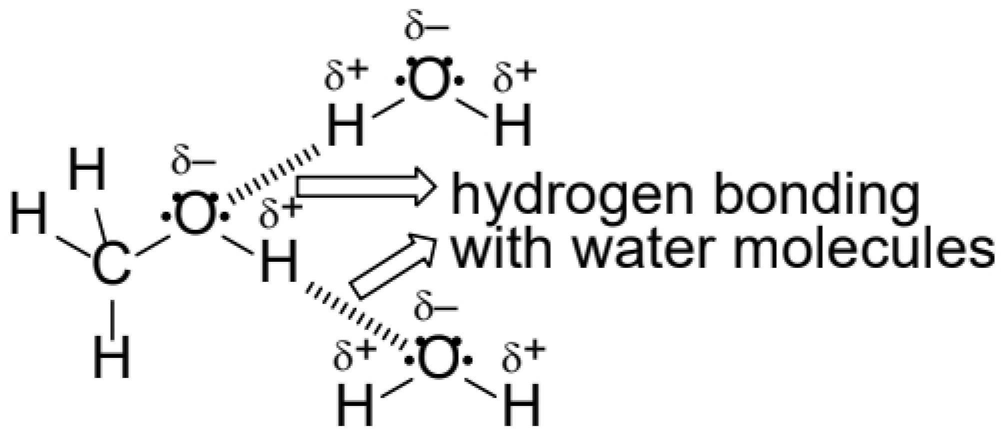
4.2.3 High solubility of ammonia, alcohols (R–OH), organic acids and amines (R–NH_2) in water

These substances can form **intermolecular hydrogen bonds** with water molecules as shown below:

CH_3NH_2 soluble in H_2O



CH_3OH (methanol) soluble in H_2O

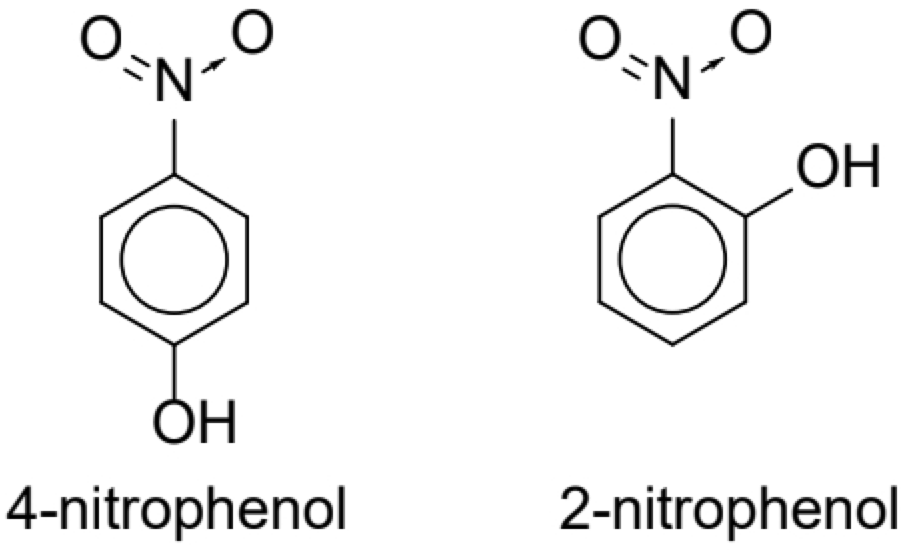


Note: When illustrating solubility in water via hydrogen bonding, show:

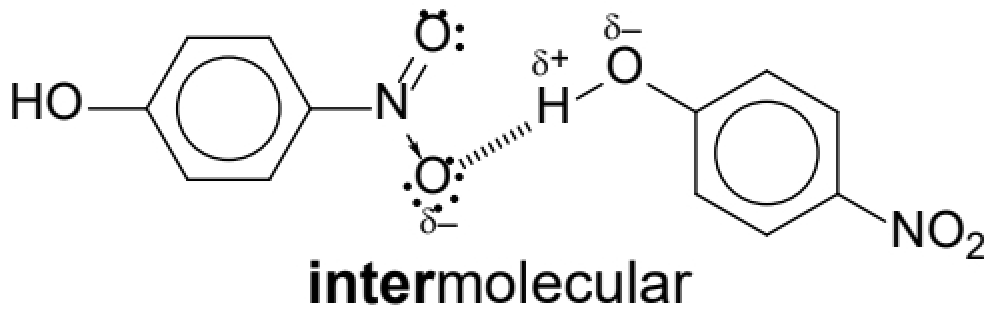
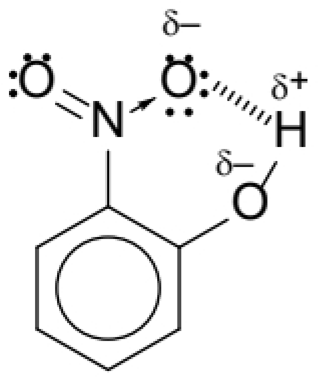
1 at least 1 solute molecule and 1 water molecule
2 hydrogen bonds,
3 lone pair of electrons,
4 partial charges (dipoles)

4.2.4 Different physical properties of isomers

4-nitrophenol has a boiling point of 279 ºC, while that of 2-nitrophenol is **lower** at 216 ºC. Also, 4-nitrophenol is **more soluble in water** compared to 2-nitrophenol.

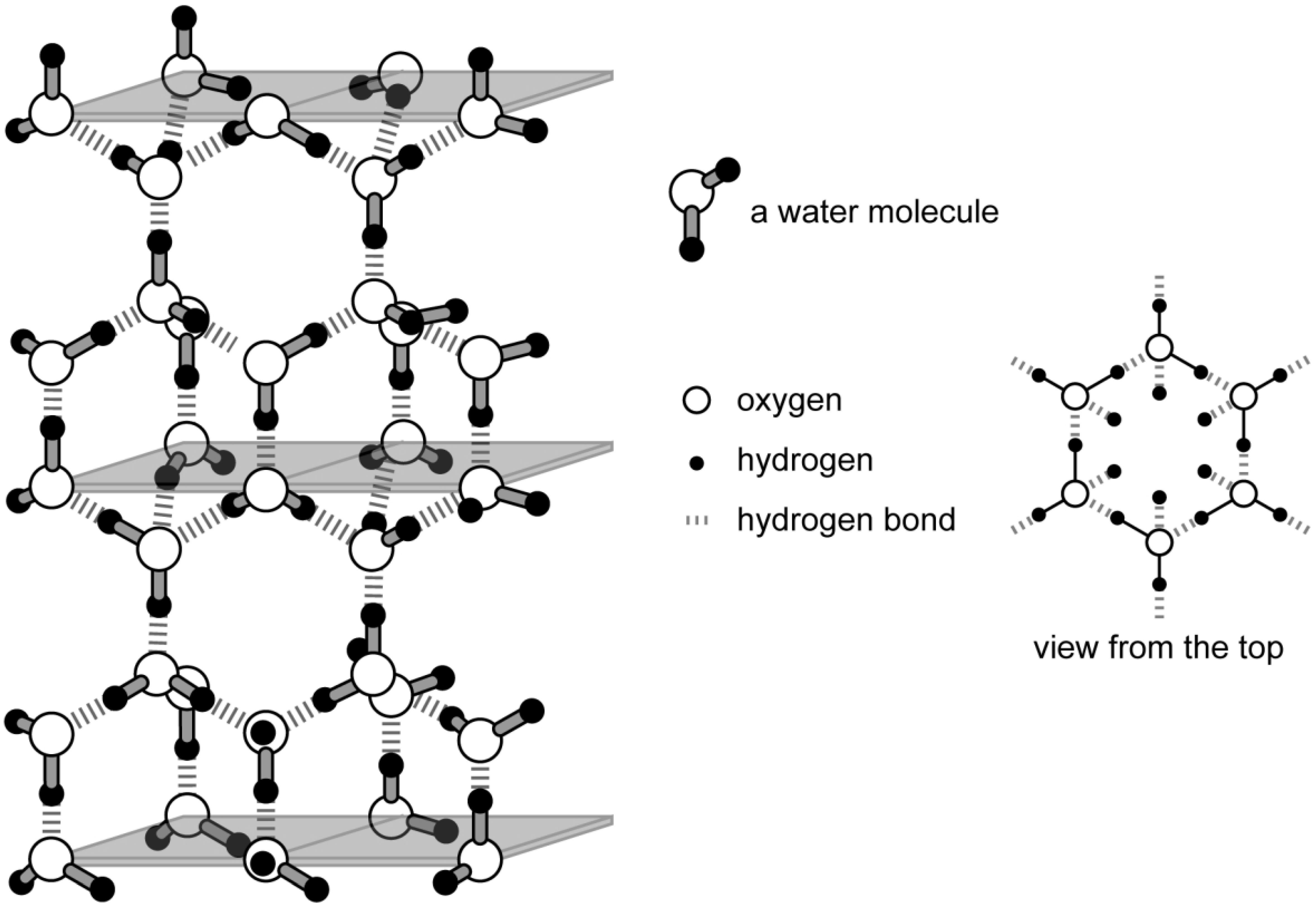


- **<u>Inter</u>molecular** hydrogen bond: formed **BETWEEN different molecules**.
- **<u>Intra</u>molecular** hydrogen bond: formed **WITHIN the same molecule**.

	4-nitrophenol	**2-nitrophenol**
type of interactions	 **inter**molecular hydrogen bonding Hydrogen bonds formed **<u>between two</u>** 4-nitrophenol molecules. ⇒ <u>more extensive</u> **inter**molecular hydrogen bonding	 **intra**molecular hydrogen bonding Hydrogen bond formed **<u>within one</u>** 2-nitrophenol molecule due to the $-NO_2$ and –OH groups being close together in 2-nitrophenol. ⇒ more extensive **intra**molecular hydrogen bonding ⇒ <u>less extensive</u> **inter**molecular hydrogen bonding
boiling point	**More energy** is needed to overcome the **more extensive <u>inter</u>**molecular hydrogen bonds in **4-nitrophenol.** Hence, 4-nitrophenol has a **higher boiling point**	**Less energy** is needed to overcome the **less extensive <u>inter</u>**molecular hydrogen bonds in **2-nitrophenol.** Hence, 2-nitrophenol has a **lower boiling point**
solubility	**More extensive <u>inter</u>**molecular hydrogen bonds can be formed between molecules of 4-nitrophenol and water. Hence, 4-nitrophenol is **more soluble in water**.	**Less extensive <u>inter</u>**molecular hydrogen bonds can be formed between molecules of 2-nitrophenol and water. Hence, 2-nitrophenol is **less soluble in water**.

4.2.5 Higher density of water compared to ice

Intermolecular hydrogen bonding holds ice molecules in place in an **orderly open structure** with **large amount of empty spaces** in between.



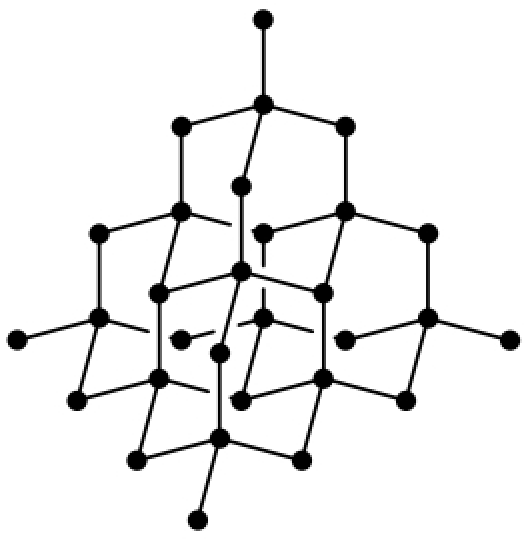
In this extended network, each water molecule forms **two** hydrogen bonds with its neighbouring water molecules such that each oxygen atom is surrounded by **four** hydrogen atoms.

Water molecules in the liquid state are able to occupy the spaces in between when ice melts. More molecules present in a fixed volume accounts for the higher density of water.

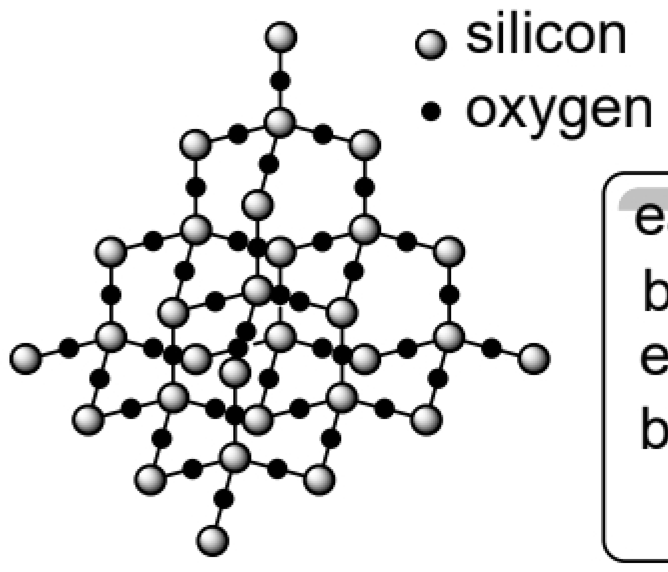
4.3 Giant Molecules

Giant molecules can have **giant covalent** or **macromolecular lattices**. Such lattices consist of an **extensive three-dimensional arrays of atoms**, which can either be all of the same type, as in the elements carbon (diamond and graphite) and silicon, or of two different elements such as in silicon(IV) oxide, SiO_2, and boron(III) nitride, BN.

each **C/Si** atom is tetrahedrally bonded to **4** other **C/Si** by **strong covalent bonds** forming a giant 3-dimensional network



diamond / silicon



silicon(IV) oxide

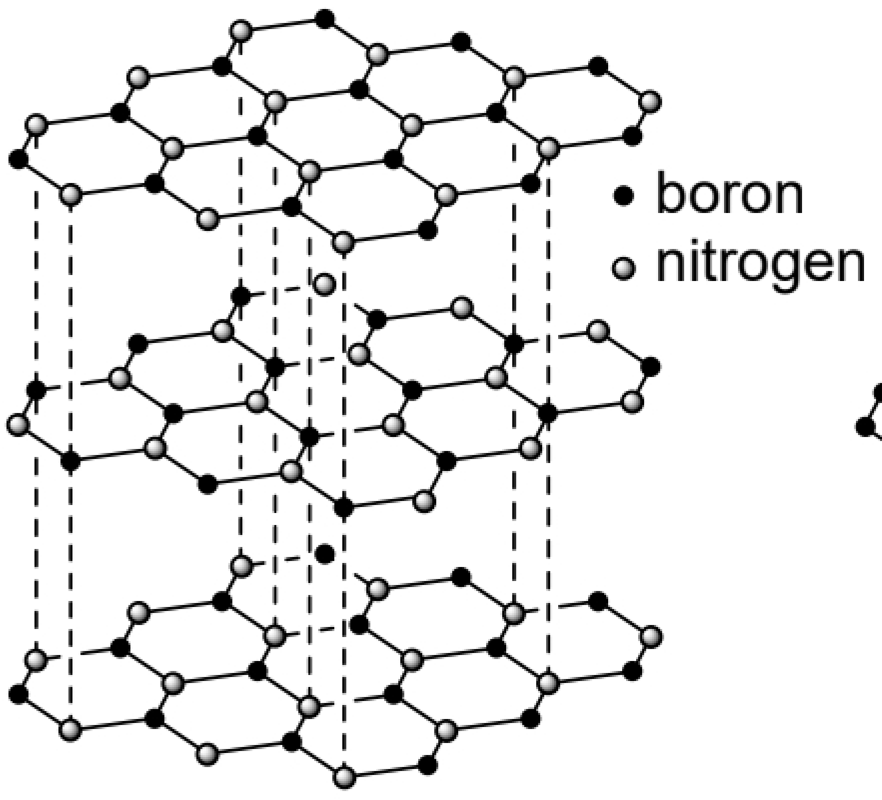
each **Si** atom is bonded to **4** O; each **O** atom is bonded to **2** Si; hence **SiO_2**

The **atoms are all joined to one another by strong covalent bonds**. So a single crystal of diamond or quartz is in fact a single molecule. For atoms to become free from the lattice, these strong bonds have to be broken. Substances containing this type of lattice therefore have very high melting and boiling points:

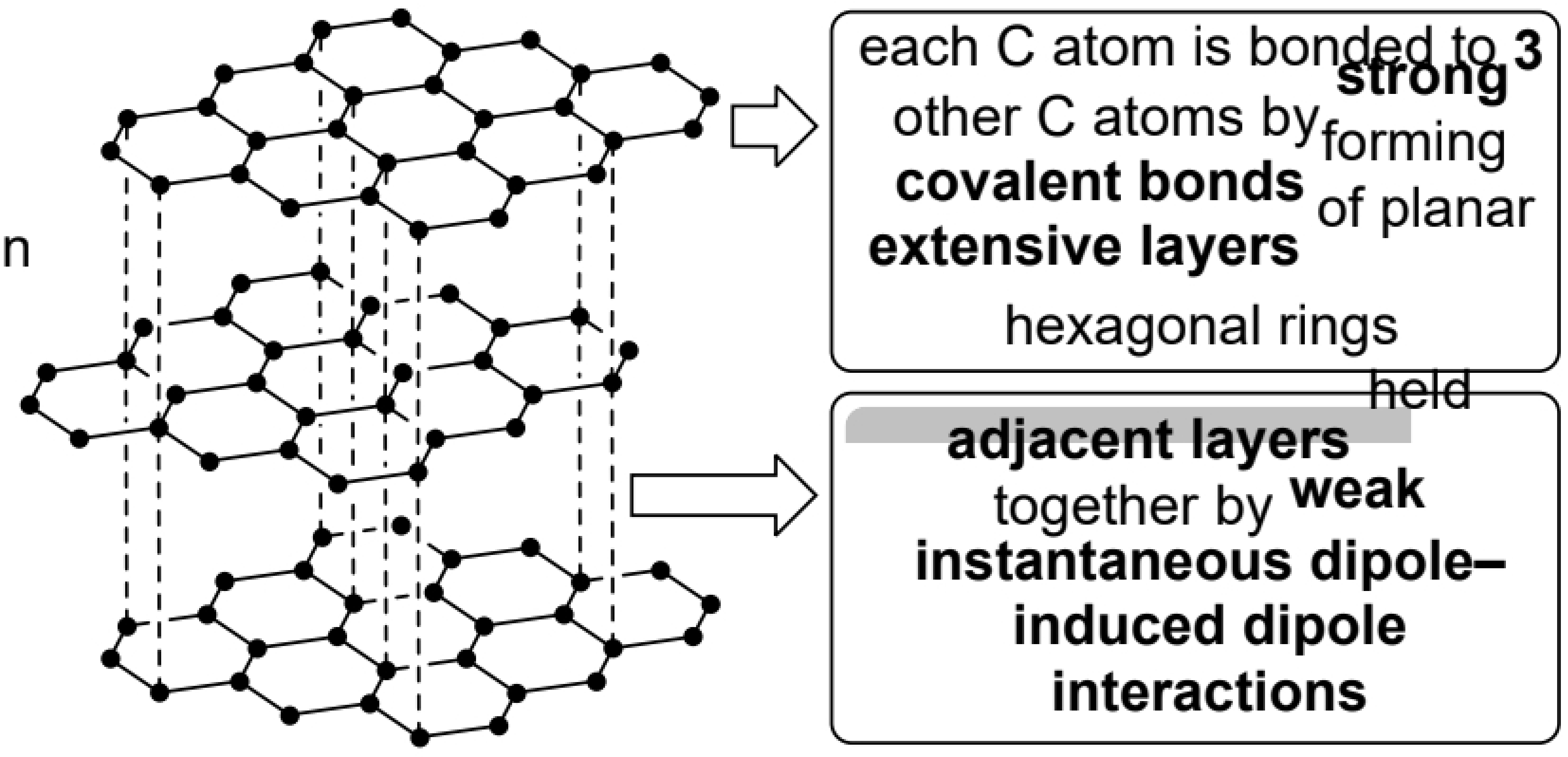
substance	formula	type of interatomic attraction	melting point/ºC	boiling point/ºC
silicon	Si	covalent	1412	3265
silicon(IV) oxide	SiO_2	covalent	1610	2959
diamond	C	covalent	3500	3930

Property	Reasons
High melting / boiling point	**Large** amount of energy is needed to **overcome** the **strong covalent bonds between atoms** in a **giant molecular structure**.
Non-conductors of **electricity** in any state	Electrons are **localised** in **covalent bonds** and are **not mobile** to conduct electricity.
Insoluble in both **water** and **non-polar** solvents	**No favourable solute–solvent interactions** between solute particles and water / solvent molecules can be formed to **break down the giant molecular structure** for hydration / solvation.
Hard, **strong** and **non-malleable**	**Atoms** are held closely together by **strong covalent bonds** in a **giant molecular structure**. (Can be used as **abrasives** due to their **hardness** and **high melting points**, *e.g.* diamond-tipped tools is used to cut rocks)

Giant molecular layered structure consists of **atoms** held together by **strong covalent bonds** in **giant extensive planar layers** with the **adjacent layers** held together by **weak instantaneous dipole–induced dipole interactions**.



boron(III) nitride

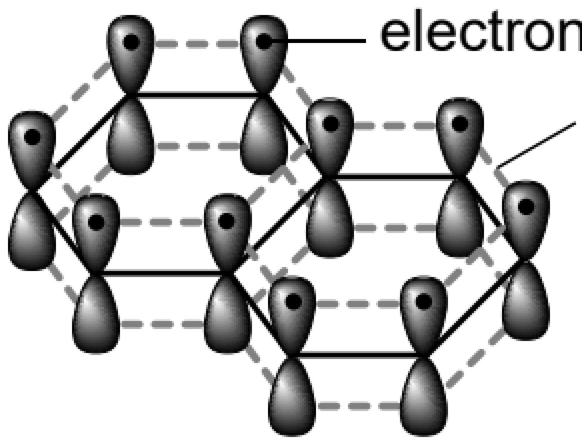

each C atom is bonded to **3**
strong
other C atoms by forming
covalent bonds of planar
extensive layers
hexagonal rings

held
adjacent layers
together by **weak**
instantaneous dipole–
induced dipole
interactions

graphite

<u>Note</u>: Drawing to include **at least 2 layers** with **3 hexagonal rings each.**

substance	formula	type of interatomic attraction	melting point/ºC	boiling point/ºC
boron(III) nitride	BN	covalent	2967	2500 (sublime)
graphite	C	covalent	–	3915 (sublime)

<table>
<tr><th>Property of graphite</th><th>Reasons</th></tr>
<tr><td>High melting/boiling point</td><td>Large amount of energy is needed to overcome the <u>strong covalent bonds between atoms</u> in the giant molecular layered structure.</td></tr>
<tr><td>Good conductors of electricity parallel to the layers but non-conductors of electricity perpendicular to the layers</td><td>3 of the 4 valence electrons are used to form covalent bonds, the 4th electron is delocalised parallel to the whole layer. The presence of delocalised electrons act as mobile charge carriers to conduct electricity.


overlap of 2p orbitals on adjacent carbon atoms lead to delocalisation of electrons within each layer
Electrons cannot delocalise between the layers.</td></tr>
<tr><td>Insoluble in both water and non-polar solvents</td><td>No favourable solute–solvent interactions between solute particles and water / solvent molecules can be formed to break down the giant molecular layered structure for hydration / solvation.</td></tr>
<tr><td>Soft and slippery</td><td>Adjacent layers are held together by weak instantaneous dipole–induced dipole interactions and so the layers can easily slide over one another.
(Can be used as a lubricant because of this property, as well as its ability to withstand high temperatures due to its high melting point).</td></tr>
</table>

Self Check 4A

1. Silicon carbide (carborundum) is a shiny, hard, chemically inert material with a very high melting point. It can be used to sharpen knives and make crucibles.
   Which type of structure explains these properties?

   A a giant structure with covalent bonds between silicon and carbon atoms
   B a giant structure containing metallic bonding
   C a giant layered structure with covalent bonds between atoms and instantaneous dipole-induced dipole interactions between the layers
   D a simple molecular structure with covalent bonds between the atoms of silicon and carbon

2. Which of the following statements correctly describe the graphite lattice?

   1 The lattice contains delocalised electrons.
   2 Each carbon atom in the lattice has three closest neighbours.
   3 The layers of carbon atoms are held together by strong covalent bonds.

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

Checkpoint

☐ I am able to explain the physical properties observed in substances with simple molecular structure by relating to the structure and bonding of these substances.

☐ I am able to use hydrogen bonding to explain certain unusual physical properties *e.g.* boiling points, anomalous relative molecular mass, solubility and density differences.

☐ I am able to explain the physical properties observed in substances with giant molecular structure by relating to the structure and bonding of these substances.

5 Ionic Bonding

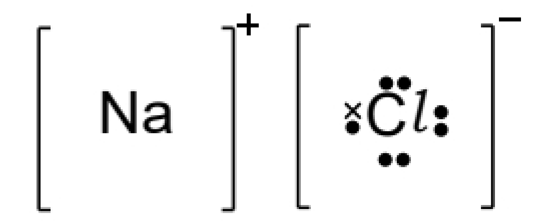
LO (a) Show understanding that all chemical bonds are electrostatic in nature and describe:
  (i) ionic bond as the electrostatic attraction between oppositely charged ions;
(b) Describe, including the use of ‘dot-and-cross’ diagrams:
  (ii) ionic bonding, as in sodium chloride and magnesium oxide;
(l) Describe, in simple terms, the lattice structure of a crystalline solid which is:
  (i) ionic, as in sodium chloride and magnesium oxide

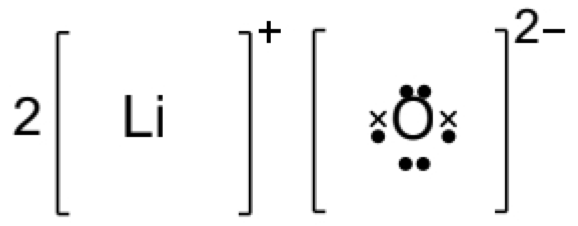
5.1 Formation of Ionic Bond

Ionic bonds are **strong electrostatic forces of attraction** between **oppositely charged ions** in a giant ionic lattice structure

Ionic bonds are typically formed between a metallic element and a non-metallic element, when one atom (the metal) totally gives away one or more electrons to the non-metallic atom. This results in **ions** being formed.

Atoms with *low ionisation energies* can lose valence electrons to become positive ions, known as **cations**. The electrons are donated to atoms to form negative ions, known as **anions**. This can be represented using a **‘dot-and-cross’ diagram**:





Dots and crosses distinguish where the electron comes from, although in reality there is no difference between them. The charge on the ion should be shown as a superscript outside the square bracket.

The ions that make up ionic compounds are not always monatomic, *i.e.*, they do not always contain *only one atom*. Several common ions contain *groups* of atoms which are covalently bonded together, and which have an overall positive or negative charge e.g. SO_4^{2-} and NH_4^+.

5.2 Factors affecting Ionic Bond Strength

The strength of an **ionic bond** is measured by the **magnitude** of **lattice energy** (ΔH_{latt}) of the ionic compound.

Lattice energy, ΔH_{latt} of an ionic crystal is the **energy released** when **one mole** of the **solid ionic compound** is **formed from** its **constituent gaseous ions**.

e.g. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ $\Delta H < 0$

$$|\Delta H_{latt}| \propto \left|\frac{q^+ \times q^-}{r_+ + r_-}\right|$$

where q^+ and q^- : charges on the cation and anion respectively
r_+ and r_- : ionic radii of cation and anion respectively

Generally, the **greater** the **magnitude of lattice energy**, the **stronger** the ionic bonds. Also, generally the **difference in charge is more important than the difference in radius**.

Example 5A

In terms of structure and bonding, explain why MgO (m.p. 2850 ºC) has a higher melting point than Na_2O (m.p. 1130 ºC).

Both MgO and Na_2O have ________________________ held together by ________________ ________________________________.

$$|\Delta H_{latt}| \propto \left|\frac{q^+ \times q^-}{r_+ + r_-}\right|$$

Both compounds have the same anionic charge and radius.

However, Mg^{2+} has a ____________ ionic charge and ____________ ionic radius than Na^+.

________________________ is required to overcome the ________________________ in MgO. Hence, MgO has a higher melting point.

For Your Info

Ionic bonding involves a separation of charge, which is usually an unfavourable endothermic process. The reason why it becomes more favourable with metals is their comparatively low ionisation energies. In sodium chloride, NaC*l*, for example, the outer electron is fairly easily lost from the sodium atom, and becomes more attracted to the chlorine nucleus than to its original sodium nucleus.

$\text{Na}(g) \rightarrow \text{Na}^+(g) + e^-$ $\quad\Delta H^{\ominus} = +494\ \text{kJ mol}^{-1}$ (ionisation energy)
$\text{C}l(g) + e^- \rightarrow \text{C}l^-(g)$ $\quad\Delta H^{\ominus} = -349\ \text{kJ mol}^{-1}$ (electron affinity)

Therefore in the gas phase:

$\text{Na}(g) + \text{C}l(g) \rightarrow \text{Na}^+(g) + \text{C}l^-(g)$ $\quad\Delta H^{\ominus} = 494 - 349 = \mathbf{+145\ kJ\ mol^{-1}}$

The fact that $\Delta H^{\ominus}$ is positive means that this is an energetically unfavourable process.

But when the ions form a solid lattice, the ions attract one another, and much energy is released:

$\text{Na}^+(g) + \text{C}l^-(g) \rightarrow \text{Na}^+\text{C}l^-(s)$ $\quad\Delta H^{\ominus} = -787\ \text{kJ mol}^{-1}$ (lattice energy)

Hence, the overall energy change, from gas-phase atoms to solid compound, is:

$\text{Na}(g) + \text{C}l(g) \rightarrow \text{Na}^+\text{C}l^-(s)$ $\quad\Delta H^{\ominus} = 145 - 787 = \mathbf{-642\ kJ\ mol^{-1}}$

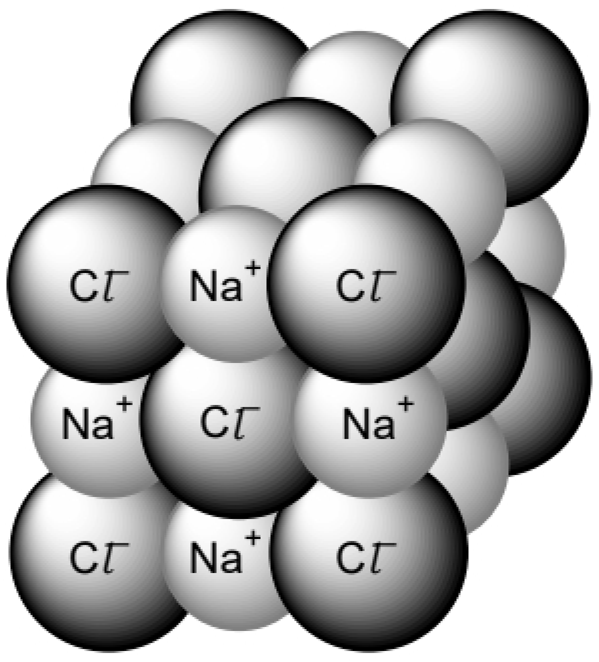
The complete process is seen to be highly exothermic, and therefore favourable. The benefits of total electron transfer are completed by the resulting electrostatic attraction between the cation and anion that are formed.

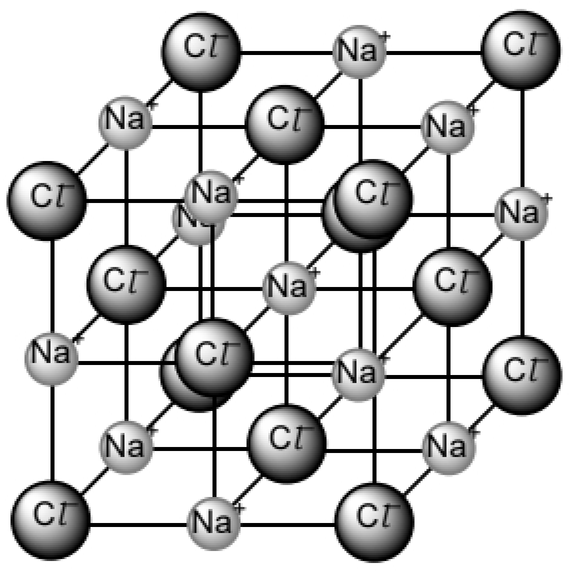
5.3 Giant Ionic Lattice

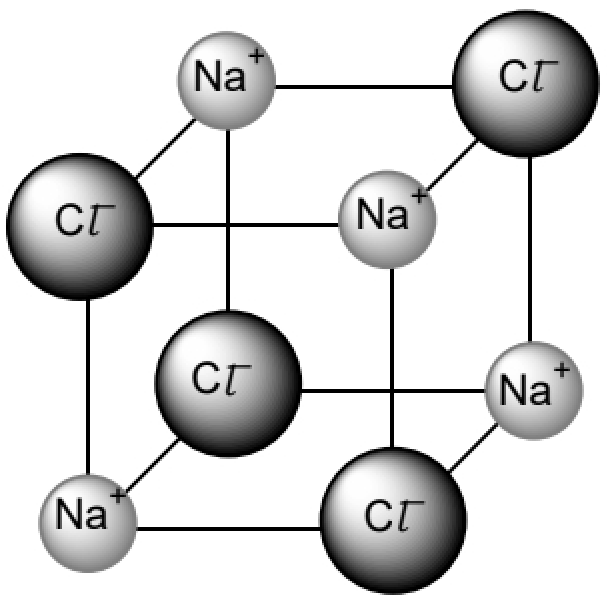
In an ionic lattice of a solid, ions are arranged in a **fixed**, **orderly** manner in a **giant ionic lattice** structure.

- Each cation is surrounded by a number of anions as its closest neighbours.
- Each anion is surrounded by a number of cations as its closest neighbours.
- No two cations or anions will be adjacent to each other.
- The electrostatic force of attraction exists between any two adjacent ions of opposite charge. Hence, an ionic bond is said to be **non-directional**.

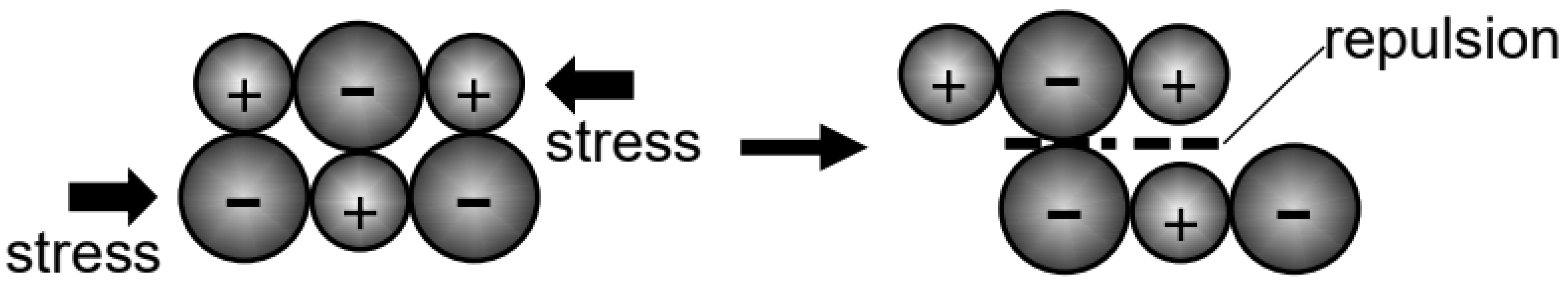
In the case of sodium chloride, $NaCl$, each Na^+ ion is surrounded by six of the larger Cl^- ions while each Cl^- ion is surrounded by six Na^+ ions. (Refer to Appendix 5 for information on Coordination Number for ionic compounds)

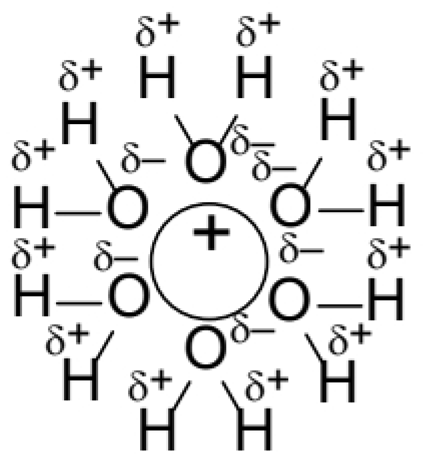


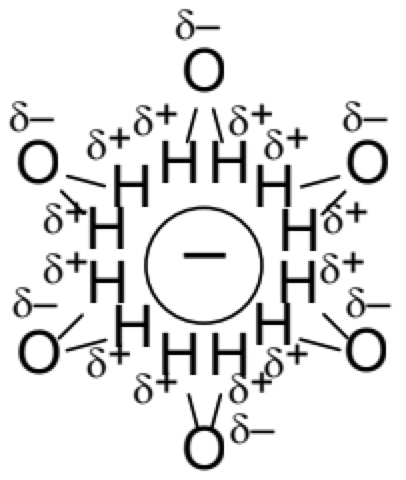




5.4 Physical Properties of Ionic Compounds

<table>
<tr><th>Physical property</th><th>Reasons</th></tr>
<tr><td>**High** melting/ boiling point</td><td>**Large** amount of energy is needed to **overcome** the **strong electrostatic forces of attraction** between **oppositely charged ions**.</td></tr>
<tr><td>**Strong**, **hard** but **brittle**</td><td>**Hard**: **oppositely charged ions** are held closely together by **strong electrostatic forces of attraction** in a **giant ionic lattice** structure.


Brittle: stress applied on the ionic lattice with regular pattern causes **sliding** of layers of ions resulting in **ions of similar charges coming together** and resultant **repulsion** shatters the ionic lattice structure.</td></tr>
<tr><td>**Non electrical conductors** in **solid** state</td><td>**Ions** can only **vibrate about fixed positions** and hence are **not mobile** to conduct electricity.</td></tr>
<tr><td>**Good electrical conductors** in **molten/aqueous** state</td><td>Presence of **ions** as **mobile charge carriers** to conduct electricity under the influence of an electric current/ field.
Electrical conductivity increases with increasing concentration of the ions in the solution.</td></tr>
<tr><td>Generally, **soluble** in **polar** solvent (*e.g.* water)
i.e. solute particles surrounded by solvent (water) molecules</td><td>**Favourable ion–dipole interactions form between ions and water molecules**. Hydration, whereby the ions are surrounded by water molecules, has occurred.
The interactions formed will **release energy** to **overcome** the **strong electrostatic forces of attraction** between **oppositely charged ions** in the giant ionic lattice structure.
The giant ionic lattice structure breaks down, and the solid dissolves.</td></tr>
<tr><td colspan="2">**Diagrammatic representation of ion–dipole interactions**
$\delta-$ end of water attracted to positive ions and $\delta+$ end of water attracted to negative ions forming ion-dipole interactions:


The "δ–" oxygen ends in H_2O are attracted to the cations
The "δ+" hydrogen ends in H_2O are attracted to the anions

 </td></tr>
<tr><td>**Insoluble** in **non-polar** solvents
(*e.g.* benzene, CCl_4, hexane)</td><td>**No favourable ion–dipole interactions** between ions and non-polar solvent molecules can be formed. The **giant ionic lattice** structure does not break down.</td></tr>
</table>

Self Check 5B

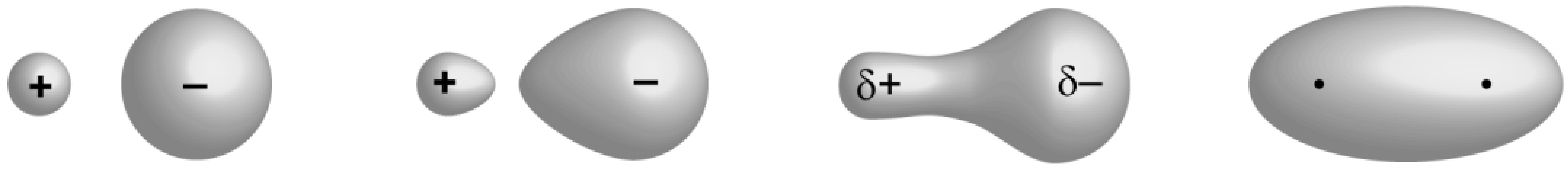
Electric cable, as used in houses, is made of copper wire surrounded by poly(chloroethene) also called polyvinylchloride or PVC. However, electric cable used in fire alarm systems has copper wire surrounded by magnesium oxide which acts as an insulator. The whole cable is encased in thin copper tubing.

(i) Describe the bonding in magnesium oxide and explain why it acts as an insulator.

(ii) Suggest a reason why copper is suitable for encasing the magnesium oxide.

6 Intermediate Bond Types

Many covalent and ionic bonds have **intermediate bond character** – some covalent bonds have **ionic character** and some ionic bonds have **covalent character**



"Pure" ionic bond	ionic bonds with **covalent character**	covalent bond with **ionic character**	"Pure" covalent bond
e.g. $\mathrm{NaC}l$	*e.g.* $\mathrm{A}l_2\mathrm{O}_3$	*e.g.* polar molecules like $\mathrm{HC}l$	*e.g.* non-polar molecules like $\mathrm{C}l_2$

← increasing % ionic character, increasing electronegativity difference

→ increasing % covalent character, decreasing electronegativity difference

6.1 Ionic Character in Covalent Bond

Ionic character in a covalent bond arises due to sharing of electrons between atoms with a **considerable electronegativity difference**.

The **more electronegative** atom acquires a **partial negative charge** (denoted by δ–), the **less electronegative** atom acquires a **partial positive charge** (denoted by δ+), forming a **dipole moment** in a **polar** covalent bond

The extent of **ionic character** in a covalent bond **increases** with an **increase in electronegativity difference** between the covalently bonded atoms.

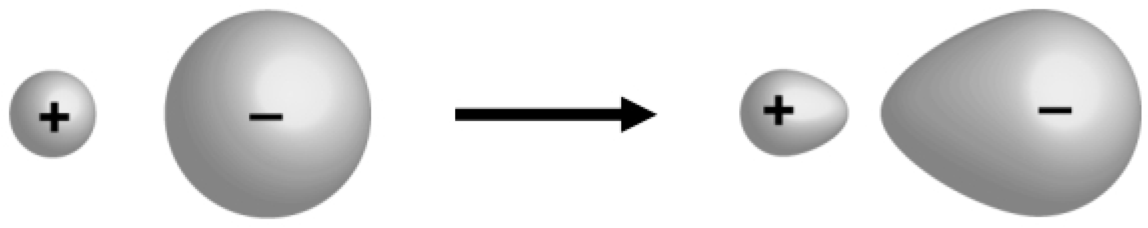
If we compare HBr and HI, both are simple molecular compounds with weak intermolecular permanent dipole-permanent dipole interactions between molecules.

As electronegativity of iodine is lower than that of bromine (as electronegativity decreases down a group), the electronegativity difference between the atoms in HI is smaller than that between HBr. Hence, HI has a smaller degree of ionic character.

6.2 Covalent Character in Ionic Bond

In a pure ionic bond, there is complete transfer of electrons and the electron clouds of both the cation and anion remain intact.

Covalent character in an ionic bond arises due to **polarisation**, which refers to the **distortion of anion electron cloud by a neighbouring cation** in an ionic compound. Due to this, there is some form of "electron sharing" between oppositely charged ions, leading to some covalent character being induced in the ionic bond



Fajans' rules can be used to predict the extent of polarisation, which depends on the **charge on the cation** and the **relative sizes of the cation and anion**:

Low ← Polarisation → High	
Low positive charge	High positive charge
Large cation	Small cation
Small anion	Large anion

The concept of **charge density** is useful for explaining the influence that an ion (usually a cation) has on the electrons in adjacent ions or molecules.

The extent of polarisation (and hence attraction) of the electrons in adjacent anions depends on the charge density and, in turn, the **polarising power of the cation**.

- Small, highly charged ions (*e.g.* Al^{3+}) have **greater charge densities** and hence **higher polarising powers** than large, singly charged ions (*e.g.* Cs^{+}).
- If two ions have similar charge densities, their compounds often have similar properties (e.g. $AlCl_3$ and $BeCl_2$).

The extent of polarisation also depends on the **polarisability of the anion**. The **larger the anionic radius**, the **more polarisable** the anion is.

Hence, the extent of covalent character in an ionic bond is larger when:

- The cation has a high charge and a small radius i.e. high charge density (highly polarising).
- The anion has a large radius (highly polarisable).

The idea of ion polarisation is important in explaining the thermal decomposition of Group 2 carbonates under the topic of 'Periodic Table'.

Example 6A

In terms of structure and bonding, account for the following observation:

compound	**melting point / ºC**
AlF_3	1090
$AlCl_3$	193

Understanding the context:

Due to the larger size of Cl^- $\left(r_{Cl^-} = 0.181\ \text{nm}\right)$ compared to F^- $\left(r_{F^-} = 0.136\ \text{nm}\right)$, the Cl^- ion is ________________________ than F^-, leading to substantial polarisation of the Al–Cl bond in $AlCl_3$.

Since Al^{3+} has ________________________ and is ________________________, this results in ____________________________________ to the Al–Cl bond. Hence $AlCl_3$ has a ____________________________________ while AlF_3 is essentially ionic.

AlF_3 has ________________________ while $AlCl_3$ has a ________________________. ________ energy is required to break the ____________________________________ in AlF_3 than the ____________________________________ between $AlCl_3$ molecules. Thus, AlF_3 has a higher melting point that $AlCl_3$.

7 Metallic Bonding

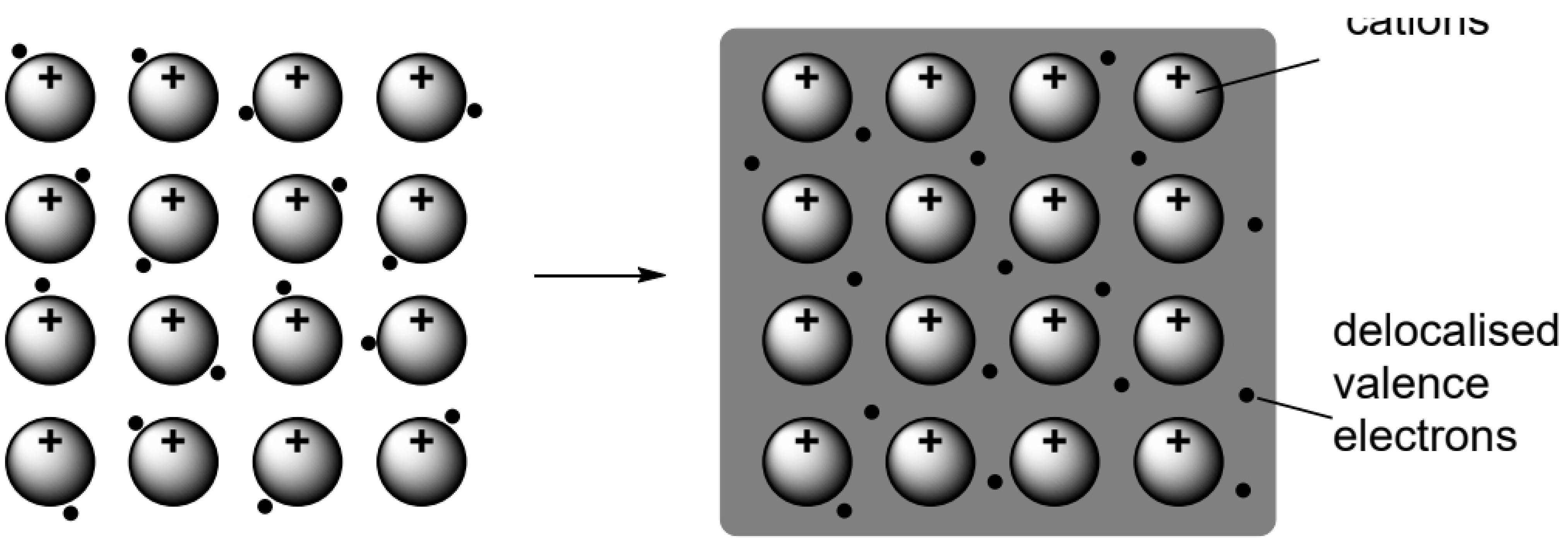
LO (a) Show understanding that all chemical bonds are electrostatic in nature and describe:
  (ii) metallic bond as the electrostatic attraction between a lattice of positive ions and delocalised electrons.
 (l) Describe, in simple terms, the lattice structure of a crystalline solid which is:
  (v) metallic, as in copper

7.1 Definition of Metallic Bond

Metallic bonds are **strong electrostatic forces of attraction** between **metal cations and sea of delocalised electrons** in a **giant metallic lattice** structure

The metal atoms contribute their valence electrons to form cations in a **sea of delocalised electrons**. The **valence electrons** are **delocalised** due to the weak electrostatic forces of attraction between them and the nucleus.

In any given piece of metal, the **metallic lattice** is **electrically neutral** as the number of positive and negative charges balance out.



7.2 Factors affecting Metallic Bond Strength

The strength of metallic bonds is:

- **proportional** to **number of delocalised valence electrons** contributed per atom
- **proportional** to the **charge density of metal cation,** $\boldsymbol{\frac{q^+}{r_+}}$

where q^+ is the charge of the cation, r_+ is the cationic radius.

In comparing two metals, the **difference in cationic charge tends to have a greater effect on metallic bond strength than the difference in cationic radius**.

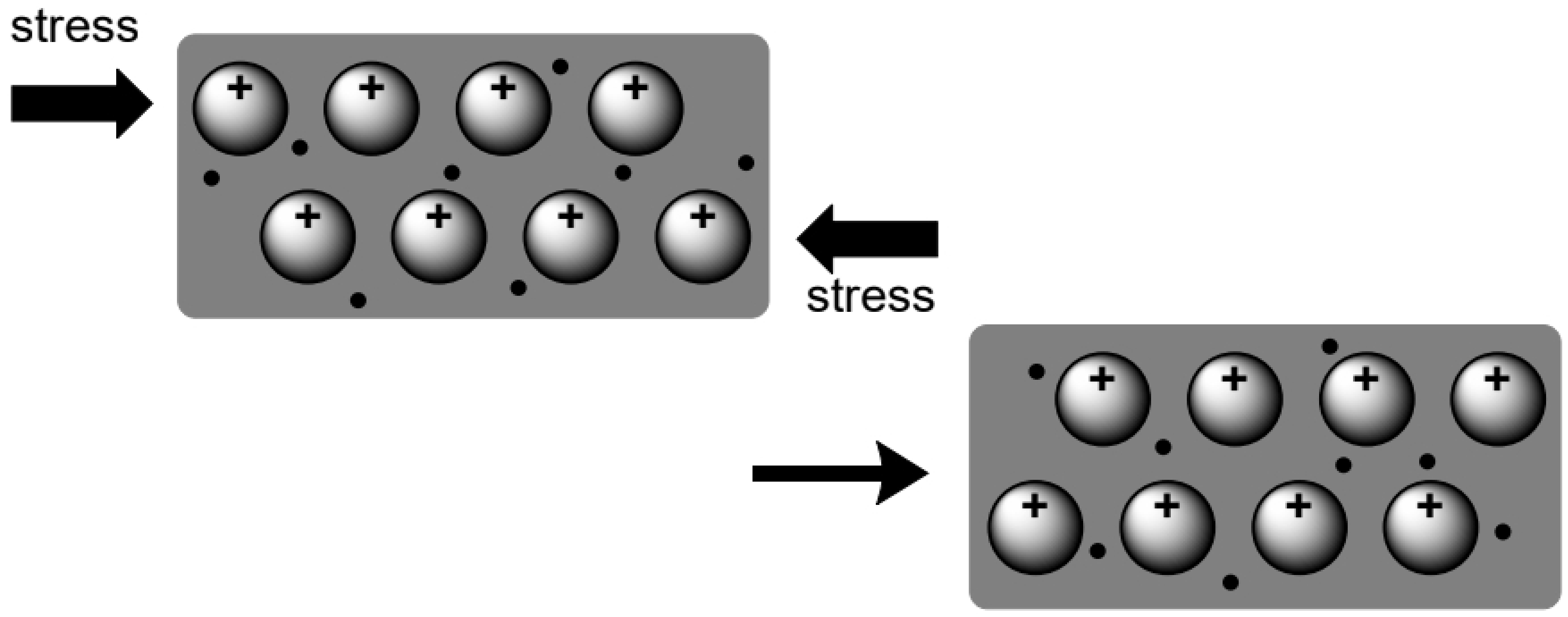
The metallic bond strength is reflected in the boiling point of the metal.

E.g. Comparing the metallic bond strength of sodium, magnesium and aluminium

metal	**sodium (Na)**		**magnesium (Mg)**		**aluminium (A*l*)**
boiling point / °C	883		1091		2519
no. of delocalised valence electrons	1 (Group 1)		2 (Group 2)		3 (Group 13)
cationic charge, q^+	+1		+2		+3
cation radius, r_+ / nm	0.095		0.065		0.050
metallic bond strength	Na	<	Mg	<	A*l*

> ***Note:***
> **Transition metals** tend to have particularly high melting and boiling points. The reason is that they can involve the **3d** electrons in the delocalisation as well as the **4s**. We will talk about this again in the topic of 'Chemistry of Transition Elements'.

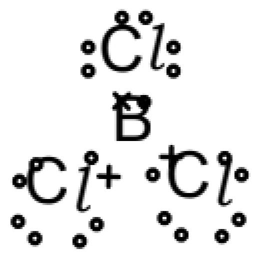
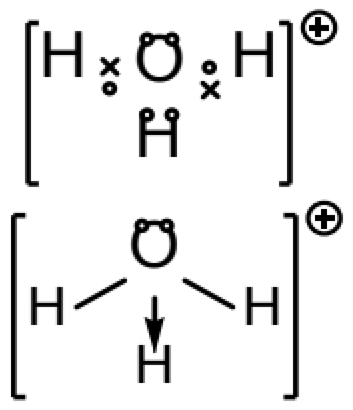
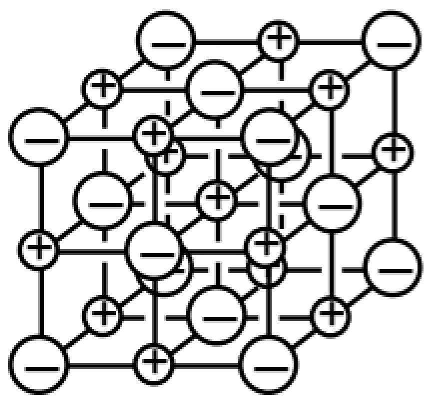
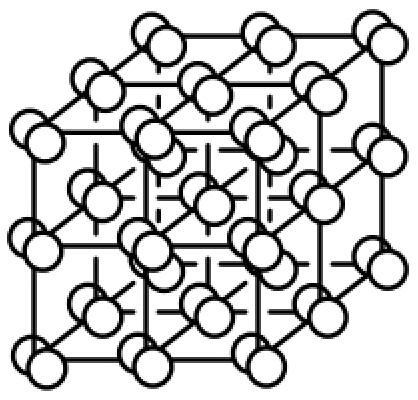
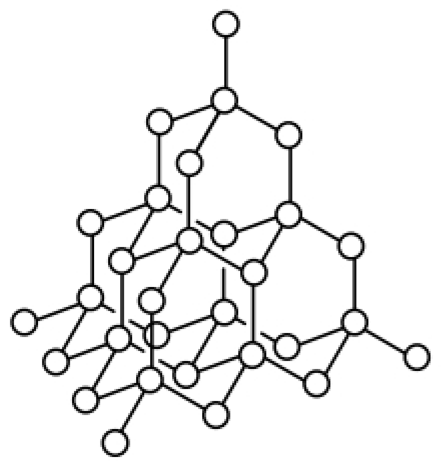
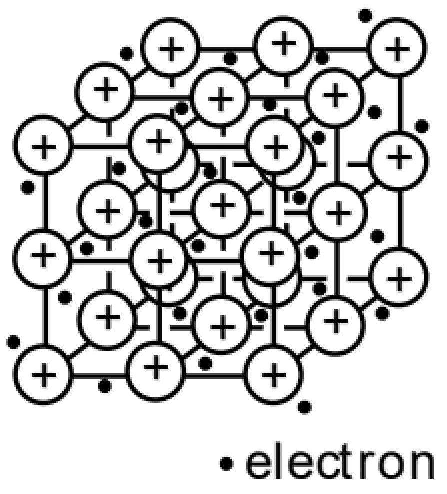
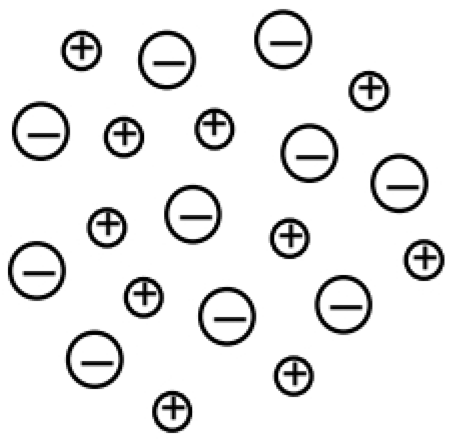
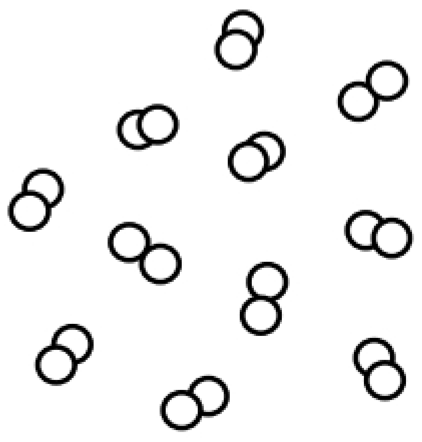
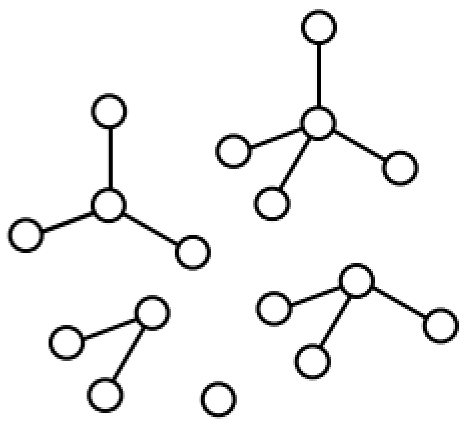
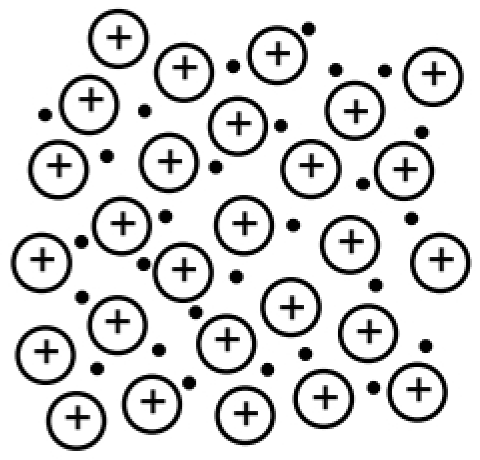
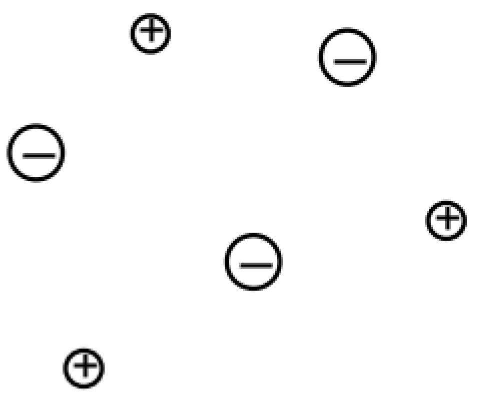
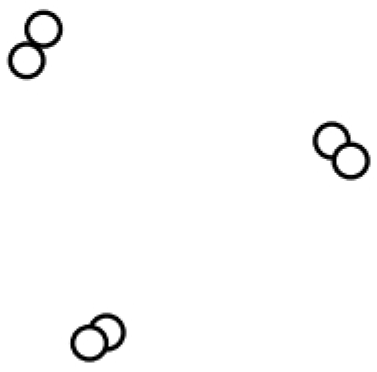
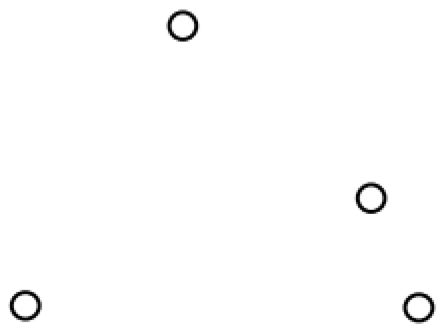
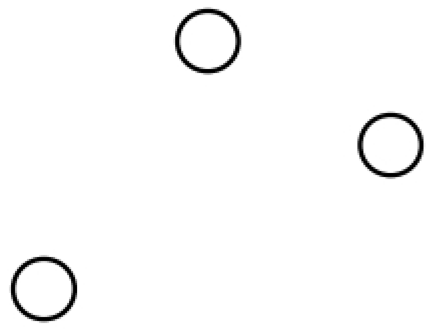
7.3 Physical Properties of Metals

Property / use	Reasons
High melting/boiling point	**Large** amount of energy is needed to **overcome** the **strong electrostatic forces of attraction** between **metal cations and sea of delocalised electrons** during melting / boiling.
Good conductors of **electricity** in **solid and liquid states**	Presence of sea of **delocalised electrons** as **mobile charge carriers** to conduct electricity under the influence of an electric current/field.
Good conductors of **heat**	The sea of **delocalised electrons** transfer the **heat energy** quickly throughout the metallic structure.
Malleable (can be beaten into sheets) **Ductile** (can be pulled out into wires)	**Stress** applied on a metallic lattice causes **sliding of layers of cations** over one another without causing the metallic structure to break down as the **sea of delocalised electrons** are holding the cations together to **prevent repulsion between the cations**. 
Alloy formation, *e.g.* brass (copper and zinc) steel (iron and carbon)	Presence of **cations (metals)/atoms (non-metals) of different sizes** in the metallic **lattice inhibits sliding of layers**, hence **tensile strength** of alloy is **increased**.

Checkpoint

- ☐ I am able to explain the physical properties observed in ionic compounds by relating to the structure and bonding of these substances.
- ☐ I understand the concept that covalent and ionic bonds can have intermediate bond character.
- ☐ I am able to compare the extent of covalent character between two ionic compounds based on the charge and size of the ions.
- ☐ I am able to explain the physical properties observed in metals by relating to the structure and bonding of these substances.

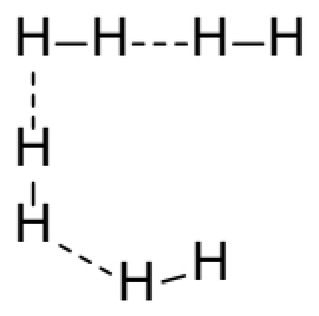
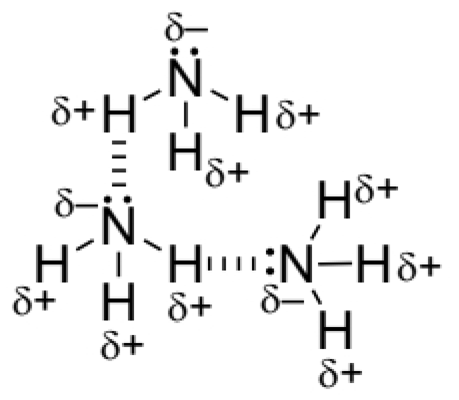
Chemical Bonds Summary

		ionic bonding	covalent bonding		metallic bonding
written description		**electrostatic force of attraction** between **oppositely charged ions**	**electrostatic force of attraction** between the **shared electrons** and **positively charged nuclei** between **2 atoms.** ↓ *covalent* ↓ overlapping of 2 *half-filled* orbitals	↓ *dative / coordinate* ↓ overlapping of 1 *filled* and 1 *empty* orbital	**electrostatic force of attraction** between **metal cation** and **sea of delocalised electrons**.
dot-and-cross diagram		*e.g.* KCl 	*e.g.* BCl_3 	*e.g.* H_3O^+ 	
directionality		non-directional	directional		non-directional
structures		giant ionic lattice	simple molecular	giant covalent / giant molecular	giant metallic lattice
physical properties	**m.p. / b.p.**	high / non-volatile	low / volatile	high / non-volatile	high / non-volatile
	hardness	hard and brittle	soft	hard	hard but malleable & ductile
	electrical conductivity	conducts in liquid and aqueous states (*mobile ions*)	non-conductor	non-conductor (except those with layers e.g. graphite)	conducts in solid and liquid states (*mobile electrons*)
	solubility	*generally* soluble in polar solvents but insoluble in non-polar solvents	*generally* insoluble in polar solvents but soluble in non-polar solvents	*generally* insoluble in all solvents	*generally* insoluble in all solvents (Note that some metals can react with solvents e.g. H_2O)
pictorial representation	**solid**		 (This diagram is for diatomic molecules)	 e.g. C or Si	
	liquid				
	gas				

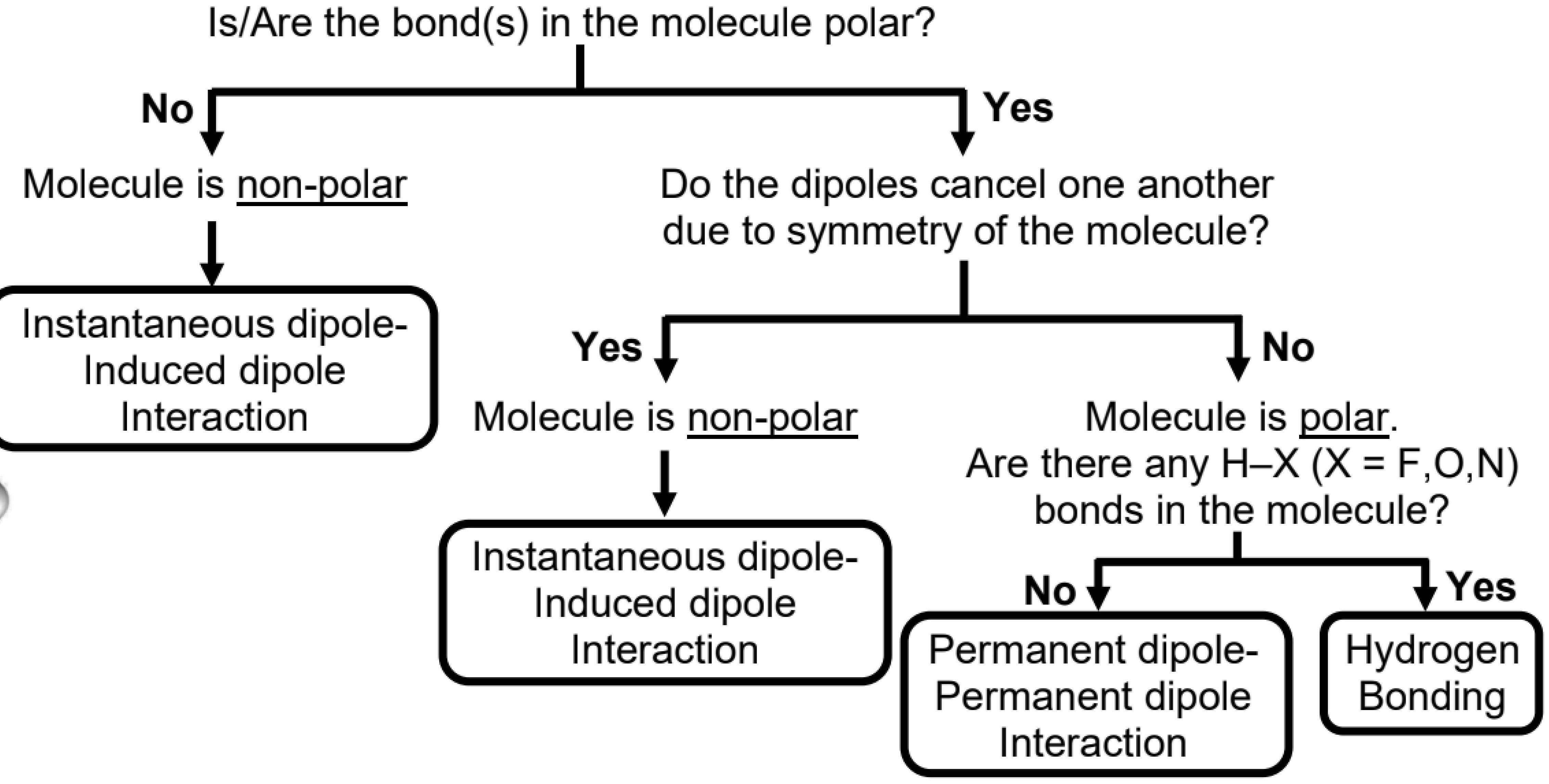
Intermolecular Forces

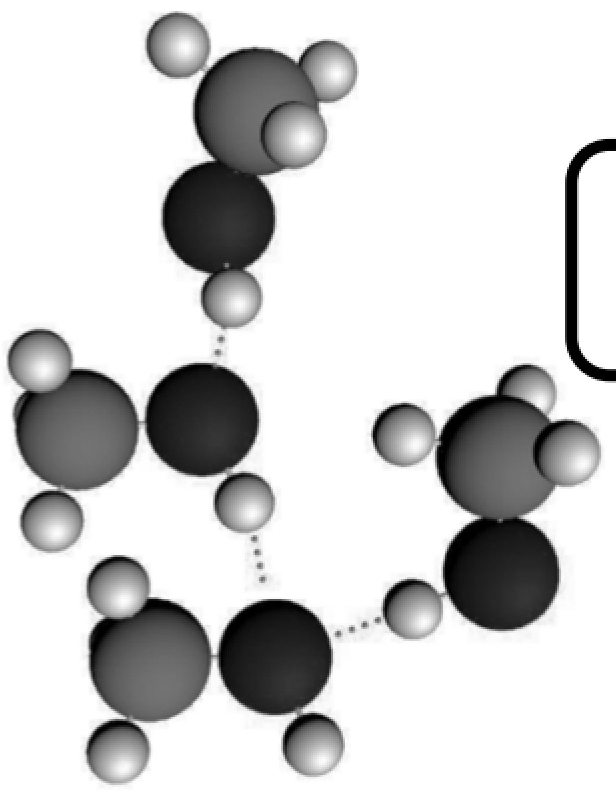
(for simple molecular substances)

(3 types)

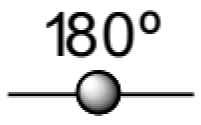
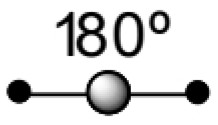
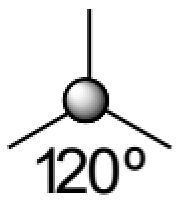
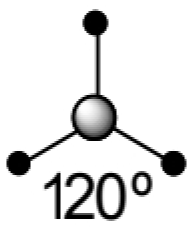
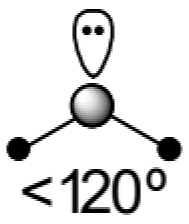
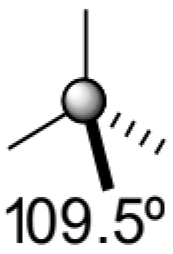
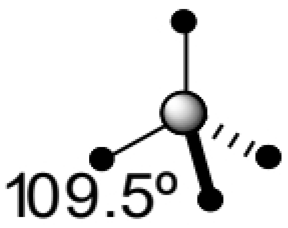
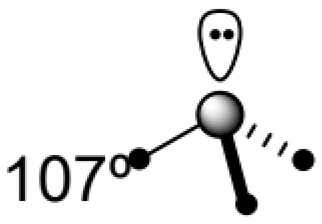
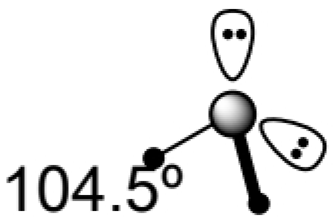
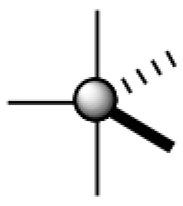
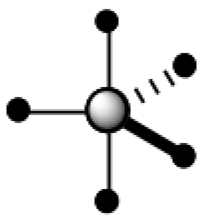
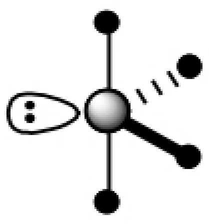
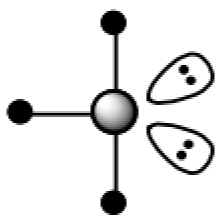
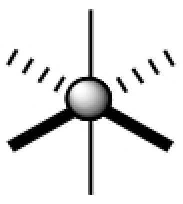
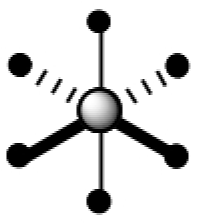
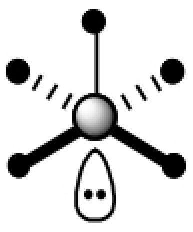
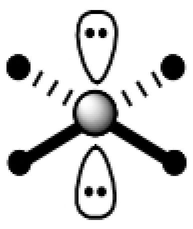
		instantaneous dipole–induced dipole interactions *(present in all molecules)*	**permanent dipole–permanent dipole interactions**	**hydrogen bonding**
strength (similar M_r)		Usually very weak small M_r < Large M_r branched molecule < straight molecule.	weak	moderate
molecules involved		non-polar	polar *(atoms of different electronegativities **and** molecule with a net dipole moment)*	Molecules consist of H–F bonds H–O bonds H–N bonds **and** an electronegative atom with at least one lone pair of electrons, *e.g.* alcohols, RCOOH, amines, NH_3, H_2O
diagrammatic representation			$\overset{\delta+}{H}–\overset{\delta-}{Br}---\overset{\delta+}{H}–\overset{\delta-}{Br}$	
effects on physical properties	**m.p./ b.p.**	very low	low	moderate
	solubility	soluble in non-polar solvents *generally* insoluble in polar solvents	intermediate solubilities	*generally* soluble in water

Flowchart:





Shapes of Molecules

VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR) THEORY				
electron pairs	**arrangement**	**bond pairs**	**lone pairs**	**molecular shape**
2		2	0	linear *e.g.* $BeCl_2$, CO_2 
3		3	0	trigonal planar *e.g.* BF_3, SO_3 
		2	1	bent *e.g.* SO_2 
4		4	0	tetrahedral *e.g.* CH_4 
		3	1	trigonal pyramidal *e.g.* NH_3 
		2	2	bent *e.g.* H_2O 
5		5	0	trigonal bipyramidal *e.g.* PCl_5 
		4	1	see-saw *e.g.* SF_4 
		3	2	T-shaped *e.g.* ClF_3 
6		6	0	octahedral *e.g.* SF_6 
		5	1	square pyramidal *e.g.* IF_5, SF_5^{2-} 
		4	2	square planar *e.g.* XeF_4, ICl_4^- 

Strength of electron pair repulsion: lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

Appendix 1: A Little Bit of History……

In the early 20th century, the American chemist Gilbert N. Lewis began to use dots in lecture, while teaching undergraduates at Harvard, to represent the electrons around atoms. His students favoured these drawings, which stimulated him in this direction. From these lectures, Lewis noted that elements with a certain number of electrons seemed to have a special stability: it appeared that once a core of ***eight electrons*** has formed around a nucleus, the layer is filled, and a new layer is started. Lewis also noted that various ions with eight electrons also seemed to have a special stability. On these views, he proposed the rule of eight or octet rule: ions or atoms with a filled layer of eight electrons have a special stability.

Moreover, noting that a cube has eight corners Lewis envisioned an atom as having eight sides available for electrons, like the corner of a cube. Subsequently, in 1902 he devised a conception in which cubic atoms can bond on their sides to form cubic-structured molecules.

In 1913, while working as the chair of the department of chemistry at the University of California, Berkeley, Lewis read a preliminary outline of paper by an English graduate student, Alfred Lauck Parson, who was visiting Berkeley for a year. In this paper, Parson suggested that the electron is not merely an electric charge but is also a small magnet (or "magneton" as he called it) and furthermore that a chemical bond results from two electrons being shared between two atoms.

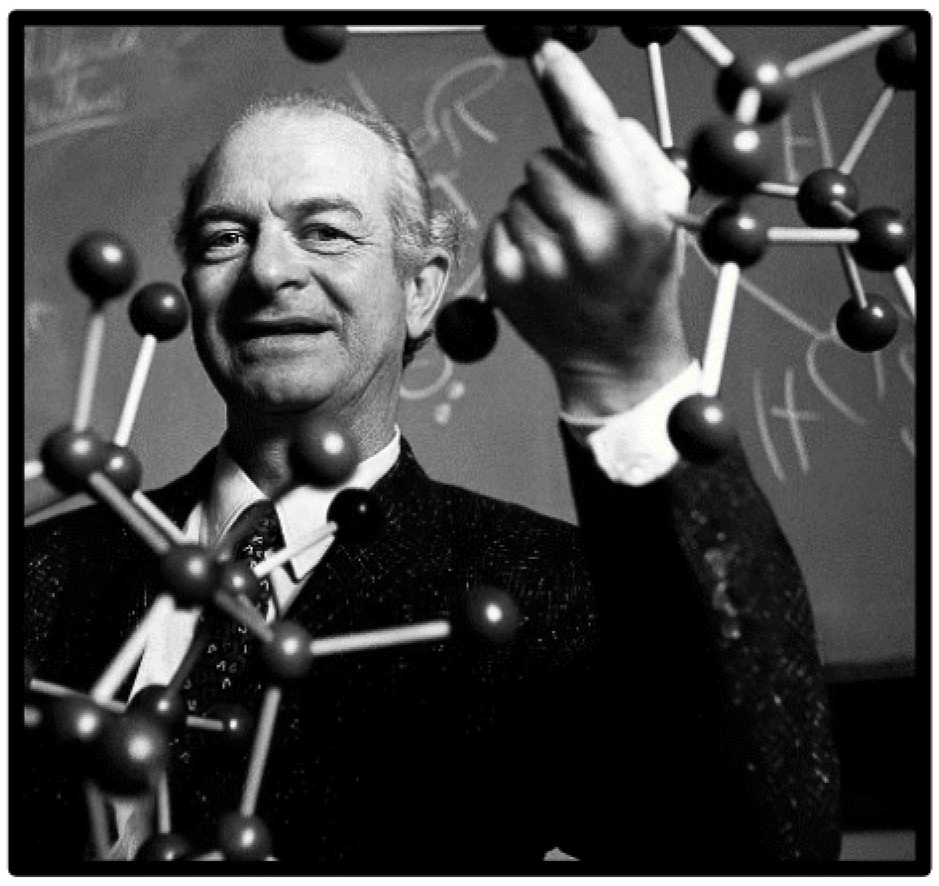
Moreover, he proposed that an atom tended to form an ion by gaining or losing the number of electrons needed to complete a cube. Thus, Lewis structures show each atom in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another; occasionally, pairs of dots are used instead of lines. Excess electrons that form lone pairs are represented as pair of dots, and are placed next to the atoms on which they reside.

To summarise his views on his new bonding model, Lewis states:

> Two atoms may conform to the rule of eight, or the octet rule, not only by the transfer of electrons from one atom to another, but also by sharing one or more pairs of electrons...Two electrons thus coupled together, when lying between two atomic centres, and held jointly in the shells of the two atoms, I have considered to be the chemical bond. We thus have a concrete picture of that physical entity, that "hook and eye" which is part of the creed of the organic chemist.

The following year, in 1917, an unknown American undergraduate chemical engineer named Linus Pauling was learning the Dalton hook-and-eye bonding method at the Oregon Agricultural College, which was the vogue description of bonds between atoms at the time. Each atom had a certain number of hooks that allowed it to attach to other atoms, and a certain number of eyes that allowed other atoms to attach to it. A chemical bond resulted when a hook and eye connected. Pauling, however, wasn't satisfied with this archaic method and looked to the newly emerging field of quantum physics for a new method.

In 1927, the physicists Fritz London and Walter Heitler applied the new quantum mechanics to the deal with the saturable, non-dynamic forces of attraction and repulsion, *i.e.*, exchange forces, of the hydrogen molecule. Their valence bond treatment of this problem, in their joint paper, was a landmark in that it *brought chemistry under quantum mechanics*. Their work was an influence on Pauling, who had just received his doctorate and visited Heitler and London in Zürich on a Guggenheim Fellowship.



Subsequently, in 1931, building on the work of Heitler and London and on theories found in Lewis' famous article, Pauling published his ground-breaking article "The Nature of the Chemical Bond" in which he used quantum mechanics to calculate properties and structures of molecules, such as angles between bonds and rotation about bonds. On these concepts, Pauling developed hybridisation theory to account for bonds in molecules such as CH_4, in which four sp^3 hybridised orbitals are overlapped by hydrogen's 1s orbital, yielding four sigma (σ) bonds.

(Taken from wikipedia : https://en.wikipedia.org/wiki/History_of_molecular_theory)

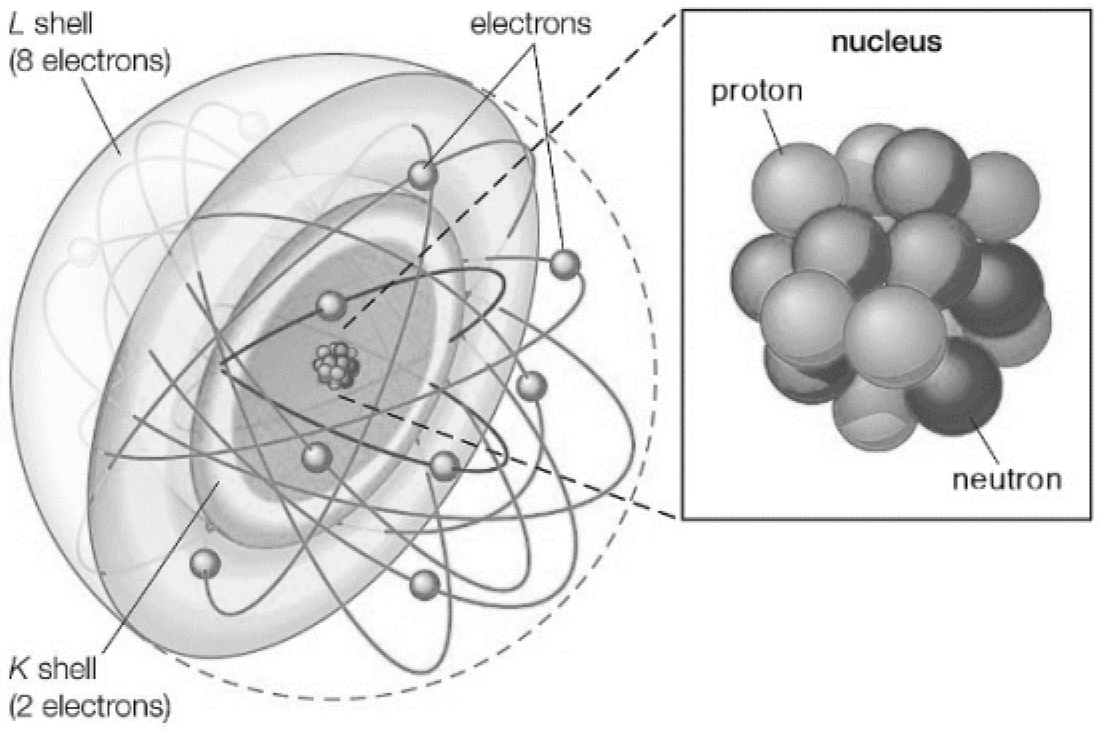
Why are We Studying This?

Molecular structure is the foundation on which chemistry, the study of matter and the changes it undergoes, rests. Much of chemistry is concerned with changes at the molecular level as structures are elucidated and chemical reactions occur.

Appendix 2: Structure of the Atom

Understanding the nature of the chemical bond relies on knowledge of the composition and structure of the atom. The model of the atom that emerged from the early work of Thomson, Rutherford, Moseley, and Bohr was of a central, very small, positively charged nucleus composed of positively charged protons and neutral neutrons, surrounded by one or more negatively charged electrons moving at high speed and effectively occupying a volume much larger than that of the nucleus.

The lack of reactivity of the noble gases – no known compounds at that time – led both Walther Kossel and Lewis to conclude in 1916 that these substances have a particularly stable arrangement of electrons. This in turn led to the development of the shell model of the atom. In the shell model, the electrons in an atom are arranged in successive spherical layers or shells surrounding the nucleus. The outer shell is never found to contain more than the number of electrons in the valence shell of a noble gas. The outer shell is called the valence shell because it is these electrons that are involved in bond formation and give the atom its valence.



Experimental support for the shell model has been provided by the determination of the ionisation energies of free atoms in the gas phase and by the analysis of the spectra of such atoms. These measurements have given a picture of the arrangement of the electrons in an atom in terms of their energies, which can also be deduced from the quantum mechanical description of an atom. Quantum mechanics also shows us that electrons do not have fixed positions in space but are in constant motion, following paths that cannot be determined. Hence, it is strictly not correct to talk about the *arrangement* of the electrons. It is their energy, not their positions, which can be determined.

On the basis of the shell mode, two apparently different models of the chemical bond were proposed, the ionic model and the covalent model.

Appendix 3: Ionic Bonding – Prelude

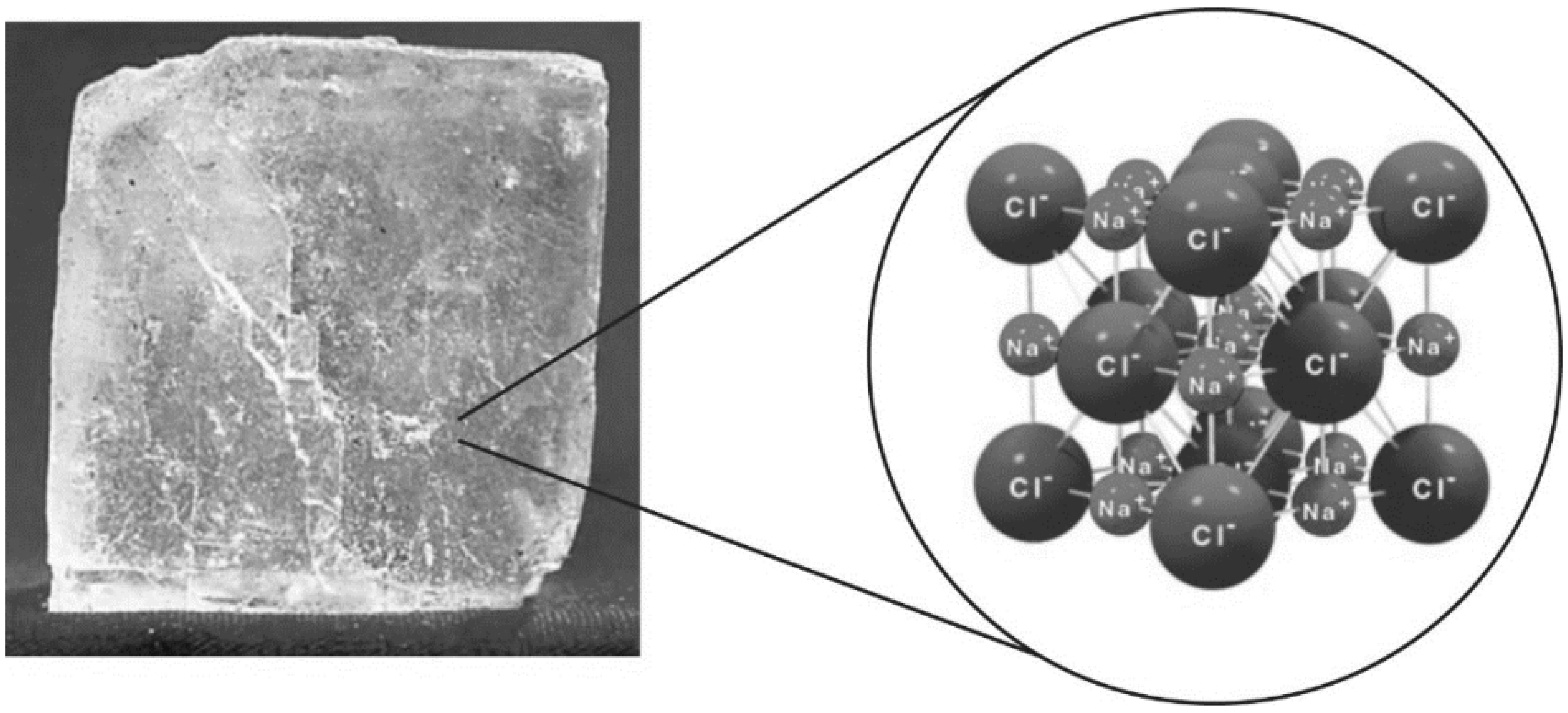
In 1916, W. Kossel noted that the loss of an electron by an alkali metal gives a positive ion, such as Na^+ (2,8) or K^+ (2,8,8), where the numbers in parentheses represent the number of electrons in successive shells. Hence, these ions have the same electron arrangement as a noble gas. Similarly, the gain of an electron by a halogen gives a negative ion, such as a fluoride ion, F^-, (2,8) or a chloride ion, Cl^-, (2,8,8), also with the electron arrangement of a noble gas: that is, an outer shell containing eight electrons.

Kossel proposed that these ions are formed because their valence shell electrons have the same stable arrangements as a noble gas. He considered solid sodium chloride to consist of positive sodium ions (cations) and negative chloride ions (anions) held together in a regular pattern by electrostatic attraction. Each crystal of solid sodium chloride can be regarded as a single giant molecule, in which a very large number of ions are arranged in a regular manner that continues through the crystal.

Misconception

Misconception: Atoms form stable ions by losing or gaining one or more electron to have the same stable arrangements as a noble gas.

Correction: The formation of ions does not necessarily lead to greater stability. Metal atoms take in energy (ionisation energy) to free the electrons from attraction by the nucleus, which means that the resulting cations (and isolated electrons) are less stable than the atoms.



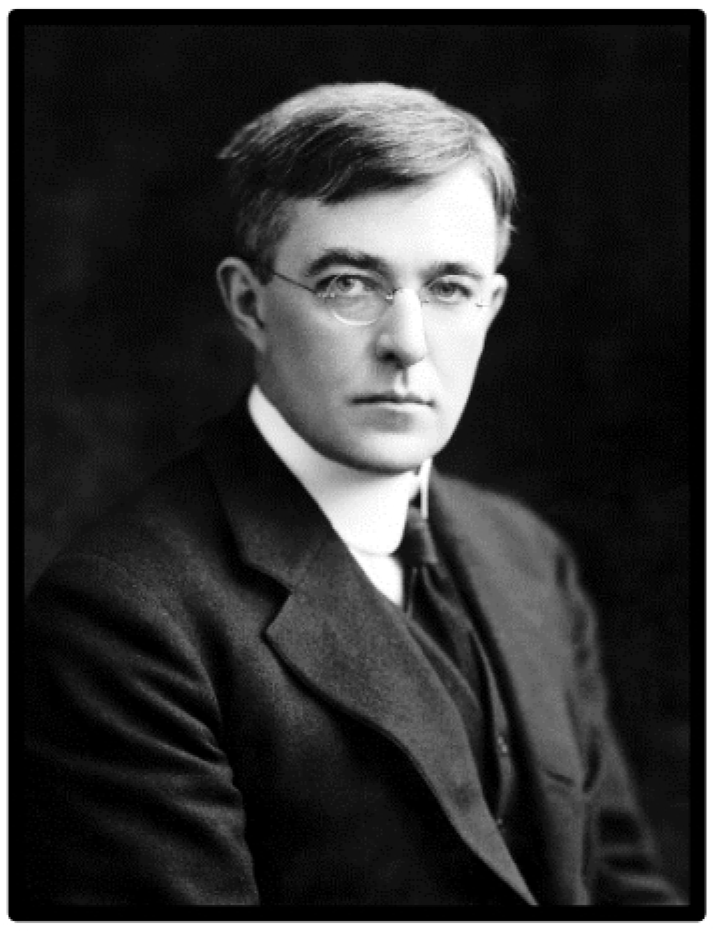
Evidence that solids such as $NaCl$ do consist of ions was provided by the observation that these materials are conducting in the molten state and in solution such as water. In these states the ions are free to move independently of each other under the action of an applied electric field. Sodium chloride is a non-conductor in the solid state, because the ions are fixed in position.

Sodium chloride and many similar compounds are said to be ionic compounds held together by ionic bonds. However, even though the term “ionic bond” is widely used, it is a vague and ill-defined concept. Electrostatic forces act in all directions and through relatively long distances so that the *attractive forces are not confined to just two neighbouring oppositely charge ions*. Moreover, there are also *repulsive forces between ions of like charge*.

Appendix 4: Covalent Bonding – Prelude

Clearly the explanation of the chemical bond given by Kossel cannot apply to homonuclear molecules (*i.e.* molecules comprising of the same type of atoms) such as Cl_2. Almost simultaneously with the publication of Kossel's theory, G. N. Lewis published a theory that could account for such molecules. Like Kossel, Lewis was impressed with the lack of reactivity of the noble gases. But he was also impressed by the observation that the vast majority of molecules have an even number of electrons, which led him to suggest that in molecules, electrons are usually present in pairs. In particular, he proposed that in a molecule such as Cl_2 the two atoms are held together by sharing a pair of electrons because in this way each atom can obtain a noble gas electron arrangement, as in the following examples:

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \qquad H:H$$



Diagrams of this type are called Lewis diagrams or Lewis structures. The bond between the two atoms could be called a shared-electron-pair bond but it is now universally called a covalent bond – a term introduced by Irving Langmuir (1919). In a Lewis diagram, the pairs of electrons that are not forming bonds are called nonbonding pairs or, more usually, lone pairs.

Although Lewis had no clear idea of why electrons are found in molecules as pairs, or how a shared pair of electrons holds two atoms together, the ideas of the shared electron pair, the covalent bond and the octet rule enable us to understand the formulas of a vast number of molecules and their relationship to the positions of the elements in the periodic table.

Because the formation of electron pairs seemed to contradict Coulomb's law, according to which electrons repel each other so that they should keep as far apart as possible, Lewis even suggested that Coulomb's law is not obeyed over the very short distances between electrons in atoms and molecules. Although we now know that Coulomb's law is obeyed for all distances between charges, in making the assumption about the importance of electron pairs, Lewis displayed remarkable *intuition*: electrons do indeed form pairs in most molecules, despite their mutual electrostatic repulsion. Nonetheless Lewis diagrams showing bonding pairs and lone pairs are still widely us ed today, and the electron pair remains a central concept in chemistry.

Lewis called the apparent tendency of atoms to acquire a noble gas electron arrangement, either by forming ions or by sharing electron pairs, the rule of eight. Later Langmuir called it the octet rule, and this is the term that is now generally used. Lewis did not regard the rule of eight as being as important as the rule of two, according to which electrons are present in molecules in pairs, because he found more exceptions to the octet rule than to the rule of two. There are only a few exceptions to the rule of two, such as molecules with an odd number of electrons (free radicals), whereas there are a large number of exceptions to the octet rule.

Appendix 5: Coordination Number

- Coordination number, with regards to an ionic lattice, refers to the number of oppositely charged ions that surrounds the ion of concern.
  The factors that affect coordination number are:

  - Relative size of the ions
    For any given ionic compound,
    - Typical coordination numbers to be considered are 4, 6 and 8.
    - There are 3 possible scenarios as shown below:

scenarios	consequence	coordination number
one ion is very much smaller in size than the other	region of space around the small ion is limited, hence reducing the number of oppositely charged ions around it	4
one ion is slightly smaller in size than the other	intermediate between the other two scenarios.	6
both cations and anions are similar in size	region of space around both ions are optimised, hence maximising the number of oppositely charged ions around it.	8

  - Relative charge
    To achieve electrical neutrality,
    - Cation with +2 charge will need twice as many anions with –1 charge, when compared to a cation with +1 charge

compound	cationic charge	cationic radius/ nm	anionic charge	anionic radius/ nm	$\frac{\text{anionic radius}}{\text{cationic radius}}$	coordination number of cation	coordination number of anion
ZnS	+2	0.08	–2	0.19	2.4	4	4
NaCl	+1	0.10	–1	0.18	1.8	6	6
MgO	+2	0.07	–2	0.14	2.0	6	6
CsCl	+1	0.17	–1	0.18	1.1	8	8
CaF_2	+2	0.10	–1	0.13	1.3	8	4