PART TWO

BONDING

Chapter 6

CHEMICAL BONDS

Very few elements, exists in nature as single free atoms, example noble gases. Most atoms interact with each other or with atoms of other elements to form **chemical bonds.**

- **Chemical bonds** *are strong electrostatic force of attraction holding the atoms or ions together in a molecule or crystal.* Where *the interaction between atoms or ions in a molecule or crystal is known as* **chemical bonding**.
- Since chemical bonds are forces responsible for holding different atoms together are also known as **interatomic forces**.

Why most atoms combine?

"Atoms combine together in order to attain the strong electronic configuration of noble gases." This is the octet rule which can be derived from Kossel-Lewis theory (Kossel dealt with ionic compound while Lewis dealt with covalent compound).

KOSSEL-LEWIS THEORY

The postulates are:

1. Valence electrons (The outer most electrons of the atoms) play the most important role in a chemical bonding.
2. Chemical bonding can be formed by transferring of electrons from one atom to another. This leads to the formation of negative and positive ions which possess the electronic configuration of noble gases.
3. Chemical bonds can be formed by sharing of valence electrons. A mutual sharing of pairs of electrons between atoms leads to the formation of covalent bonds and molecules.
4. The transfer or sharing of electrons occurs in such a way that, each atom concerned acquires the stable electronic configuration of a noble gas which has an octet (eight) or duplet (two) electrons.

Exception to octet rule

Octet rule state that, *"Atoms combine by either gaining or loosing or sharing valence electrons so as to achieve stable octet (or duplet) electronic configuration of noble gases."* But this rule does not hold for a number of molecules or ions and the failure of octet rule fall under three categories.

(i) Species with more than eight valence electrons about an atom (expanded octets)

Examples: PCl_5 and SF_6

- PCl_5 is expanded acted because there are 10 valence electrons about Phosphorous atom
- SF_6 is expanded octet because there are 12 valence electrons about sulphur atom

Note that:

Each bond has two electrons. Thus in absence of unbonded electrons (**lone pair**):

$$\textbf{Number of electrons} = \textbf{Number of bonds} \times 2$$

For example, in PCl_5 there are 5 bonds about P and hence 2×5 or 10 valence electrons in P.

Expanded octet is possible only when the principal quantum number of the valence electrons of the atom at the centre is equal or greater than 3 so that the atom can use d-orbitals in covalent bond formation.

(ii) Electrons deficient compound (Incomplete octet)

Examples BF_3 and $AlCl_3$

F –B –Fis electrons deficient compound because there are six
| valence electrons about boron (B)
F

Similarly for $AlCl_3$

As result such electron deficient compounds are very reactive in order to fill their octets.

(iii) Species with an odd number of valence electrons

Examples; NO, NO_2 and ClO_2

e.g. in $\ddot{N}=O$ (NO); there are only 7 valence electrons around nitrogen one of which is unpaired.

The unpaired electron has an effect on the magnetic properties of molecules like NO, NO_2 and ClO_2. These molecules are said to be **paramagnetic** as they are attracted by magnets.

TYPES OF CHEMICAL BONDS

Chemical bonds can be classified into three common types which are:

- Ionic bonds
- Covalent bonds and
- Metallic bonds

Ionic bonds

Ionic bonds (also termed as **electrovalent bonds**) *are formed by transfer of electrons from metals to non-metals.* Metals are found at the left hand side of the periodic table while non-metals are found at the right hand side of the table.

- Metals have relatively low ionisation energy and so they can lose one or more electrons to form **cations** ('cation' is derived from two words; '**cat**hode' and '**ion'** reflecting their properties to be attracted towards cathode during electrolysis) while non-metals such as halogens have a high affinity of electrons so they can easily form **anions** (here 'anion' is derived from '**an**ode' and '**ion'** reflecting their tendency of being attracted towards anode during electrolysis).
- The cations (positively charged) and anions (negatively charged) exert an electrostatic force of attraction which is an extremely powerful and hence ionic bonds can also defined as:
  Very strong electrostatic forces of attraction holding cations and anions together in a crystal.
- In most cases, metals and non-metals have very large electronegativity difference to enable them to form ionic bonds.

Characteristics of ionic compounds

(i) Ionic compounds are crystalline solids which are non-volatile.
(ii) They exist as lattice of oppositely charged ions and not molecule.
(iii) They are generally soluble in polar solvents like water and are insoluble in non-polar solvents (organic solvents) like benzene.
(iv) When dissolved in water, they dissociate into the respective ions.
(v) Their melting and boiling points are generally high.
(vi) They are capable of doing electrolytic conduction in either molten (fused) state or aqueous solution.

Covalent bonds

The **covalent bond** *is formed when two atoms achieve noble gas electronic structure by sharing of pairs of electrons.*

- The covalent bond is formed between two atoms of high electronegativity such that their difference in the electronegativity is small or zero; example in CH_4 whereby electronegativity difference between carbon and hydrogen atom is negligible.
- Generally it can be concluded that covalent bond is formed between one non-metallic atom and another non-metallic atom; that is formed between non-metals.

Characteristics of covalent compound

(i) Covalent compounds exist as molecules.
(ii) The intermolecular force of attraction holding the molecules (covalent bonded molecules) together is Van der Waals forces of attraction which increase with an increase in their molecular weights.
(iii) The low molecular weight covalent compounds are volatile liquids or gases at room temperature. They exist as solids when their molecular weights are high.
(iv) Their melting points and boiling points are relatively low compared to ionic compounds.
(v) They are generally insoluble in non-polar solvents like water but are soluble in non-polar solvents (organic solvents).
(vi) They do not conduct electricity in molten state (they can only conduct electricity in aqueous solution if and only if they undergo **hydrolysis** in water).

Dative bond

Dative bond (also known as **coordinate bond**) *is the type of covalent bond which is formed when all the electrons shared between the bonded atoms are contributed by just one of atom.*

- It is the special case of covalent bond whereby all shared (covalent bonded) electrons comes from single atom. It is different to the **normal covalent bond** whereby each covalent bonded atom contribute single electron to the two shared electrons.

In the dative bond formation there is a **donor atom** which is an atom supplying its electron pair and an **acceptor atom** which is an atom gaining the electron pair. *The donor atoms must have **lone pair(s)** while acceptor atoms must have **empty orbital** which acts as the 'room' for the lone pair*

Definition of lone pair

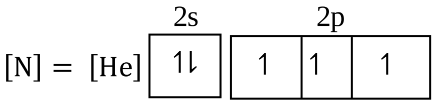
Lone pair *is valence electrons of an atom which has not participated in the bond formation.*

To understand the concept of dative bond formation, consider the formation of ammonium ion (NH_4^+):

- NH_4^+ is formed when NH_3 and H^+ combine.

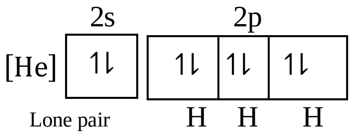
Consider electronic structure of NH_3

Electronic configuration of nitrogen:



………………………....At ground state

Presence of 3 unpaired electrons (covalency of three) makes possible for nitrogen to combine with other three monovalent atoms (atoms with valence of 1) like hydrogen atoms as follows:



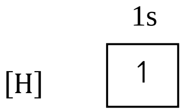
……………………....In NH_3

Where upward arrows in p-orbitals represent electrons from nitrogen and downward arrows in the same p-orbitals represent electrons from three hydrogen atoms.

- Thus NH_3 consist of three normal covalent bonds and single lone pair in nitrogen which is shown by two dots in nitrogen as $\ddot{N}H_3$.

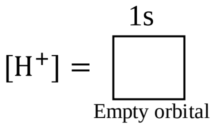
Also consider electronic structure of H^+

Electronic configuration of hydrogen



.... At ground state

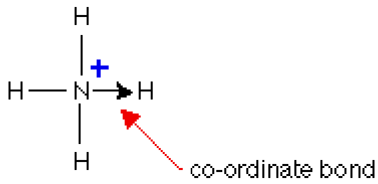
Thus removing the s-electron in H so as to get H^+ gives the following electronic structure of the ion.



- So H^+ consist of one s empty orbital

Therefore when one atomic orbital of nitrogen from NH_3 containing a lone pair is fused together with an empty atomic orbital of H^+, the molecular orbital containing two shared electrons between N and H is formed thus forming NH_4^+.

- Thus in NH_4^+, three N – H are normal covalent bonds while the remaining N – H is dative bond. The dative bond is shown by an arrow, ⟶, where the tail of the arrow **must** start at the donor atom and the head **must** direct to the acceptor atom as shown in the structure of the ammonium ion in the next page:

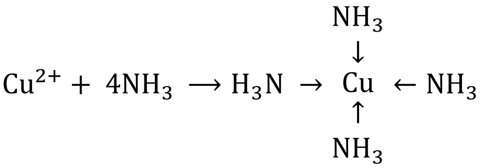


- Another example of dative bond formation is the formation of hydroxonium ion (H_3O^+) from H_2O (Has two lone pairs on O) and H^+.

$$H_2O + H^+ \longrightarrow H_3O^+$$

Dative bond is more common in the formation of complex molecules.

Example:



$$Cu^{2+} + 4NH_3 \longrightarrow H_3N \rightarrow \underset{\underset{NH_3}{\uparrow}}{\overset{\overset{NH_3}{\downarrow}}{Cu}} \leftarrow NH_3$$

Where Cu^{2+} have vacant (empty) orbitals to accept lone pairs from ammonia.

The student should understand that:

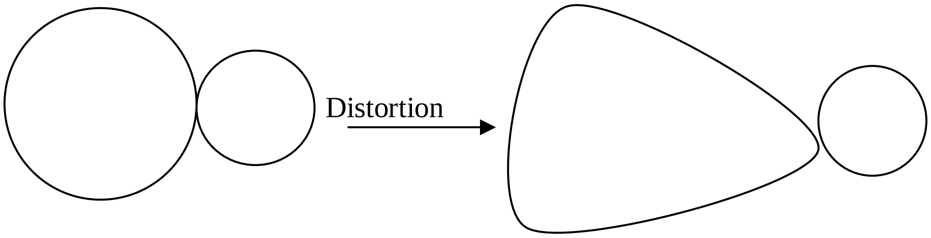
- Presence of electron pair (s) held between two atoms confirms the presence of chemical bond between the atoms.
- Any bond between two atoms means there are two electrons (one electron pair) between the atoms.
- The new orbital which is formed in the bond formation after fusing together two atomic orbitals is known as the **molecular orbital.**

Intermediate characters of ionic and covalent characters

Covalent characters in ionic compounds

Ionic compounds consist of cations and anions. In most cases cations are smaller in size than anions. The positive charge on the cation can attract electrons towards itself from the anion thus leading to distortion of the anion.

Consider a large negative ion is put near the small cation. Since the outer electrons of the large ion are for from the nucleus they are not held very tightly by the nucleus of the anion thus making easier for the nucleus of the cation to attract the electrons. So the charge cloud of the negative ion will be distorted and hence the negative ion is said to be distorted.



Undistorted molecule

Distorted molecule

Definition of terms:

Polarisation *is the distortion or deformation of valence shell of larger ion (anion) by smaller ion (cation).*

Polarising power *is the ability of smaller ion (cation) to distort the larger ion (anion).*

Polarisability *is the readiness of large ion (anion) to undergo distortion.*

- Thus ionic compounds with cation of large polarising power and anion of large polarisability are said to have very high degree of polarisation.

Polarisability is high if:

(i) Anionic radius is large
(ii) Anionic charge is more negative

Polarising power is high if:

(i) Cationic radius is small
(ii) Cationic charge is high(more positive cation)

Thus we can conclude that the degree of polarisation is high if.

(i) The cationic radius is small
(ii) The anionic radius is large
(iii) The charge on the ions are high (more negative anion and more positive cation in the compound)

What happen in ionic bonding when a cation is brought close to an anion?

The cation (small ion) starts to attracts (polarise) valence shell, that is valence electrons of the anion towards itself and as result, the negatively charged ion (anion) may partially (or even almost totally!) loose its excess electrons (which make it to be negative charged) to become neutral again and the cation regain the electrons (which originally were lost to the anion) to become neutral also. Eventually the bond between the two atoms become no longer ionic, it become covalent and the compound which was thought to be ionic starts to attain covalent characters. The extent of this distortion of ionic character will be high if the cation is small in size and high charged so that it can attracts (polarises) easily valence electrons of the anion and hence high polarising power of the cation. Also it is high if the anion is large in size and highly negative so that its valence electrons can be attracted (polarized) easily by smaller ion (cation) and hence high polarisability of the anion.

- The above discussion can be summarised by **Fajan's rule.**

According to Fajan's rule:

There is no compound which is purely ionic every compound posses some degree of covalence which increases with an increase in degree of polarisation.

Thus according to Fajan, highly polarised compound has more covalent characters and less polarised compound (compound with low degree of polarisation) has more ionic characters (less covalent in characters). Thus the degree of covalence is high if:

(i) The cationic radius is small
(ii) The anionic radius is large
(iii) the charge of the ions are large

For example:

- **AlF_3 is more ionic in characters than $AlCl_3$** because Cl^- being larger in size, has greater polarisability than F^- thus making $AlCl_3$ to have greater degree of polarisation and hence more covalent in characters in $AlCl_3$ than in AlF_3. Being more covalent in characters, in large part $AlCl_3$ exists as molecule rather than as ions while AlF_3 being ionic (less covalent in characters) exists as ions (oppositely charged ions of cations, Al^{3+} and anions, F^-) and only very small part of it exists as molecule.
- **NaCl is more ionic in characters than $AlCl_3$** because Al^{3+} being smaller in size and higher charged has greater polarising power than Na^+, thus making $AlCl_3$ to have greater degree of polarisation and hence more covalent in characters in $AlCl_3$ than in NaCl.
- **$BeCl_2$ is more covalent in characters than $BaCl_2$** because Be^{2+} (which is at the top of group IIA) being smaller in size has greater polarising power than Ba^{2+} (which is at the bottom side of group IIA) resulting to greater degree of polarisation of $BeCl_2$ and hence the compound become more covalent in characters than $BaCl_2$.

What are effects of distortion of ionic bonds on properties of compound?

Ionic compounds with high degree of polarisation have distorted ionic characters, thus they tend to exhibit some covalent characters including the following:

- They have low thermal stability (they decompose easily on heating),
- They have low melting and boiling point,
- They have low electrolytic conduction in their molten state,
- They hydrolyse in water (they react chemically with water yielding acidic solution).

Example 1

AlF_3 has higher melting point than $AlCl_3$. Explain

Solution

AlF_3 is more ionic in characters as result of its lower degree of polarisation brought about by smaller polarisability of smaller sized F^- thus making its melting point higher

Example 2

Between $AlCl_3$ and NaCl which one sublimes on heating? Give reason for your choice.

Solution

$AlCl_3$ sublimes on heating.

Reason

$AlCl_3$ is more covalent in characters as result of its higher degree of polarisation brought about by smaller in size and higher charged Al^{3+}

Example 3

Molten AlF_3 conducts electricity while molten $AlCl_3$ does not. Explain

Solution

AlF_3 is more ionic in characters as result of its lower degree of polarisation brought about by smaller polarisability of smaller sized F^- thus in molten state it has enough concentration of free ions to do electrolytic conduction while $AlCl_3$ has not

Ionic characters in covalent compounds

When the covalent bonded atoms have large difference in their electronegativities, the shared electrons spend more time under influence of the nucleus of more electronegative atom.

- Example in $H - Cl$, chlorine being more electronegative; its nuclear attractive force has more influence on shared electrons; so most of the time the electrons spend on chlorine atom resulting to partial positive and negative charges as shown below:

- Where; $\sigma +$ and $\sigma -$ are partial charges whose amount is less than the complete charge which is 1.6×10^{-19} coulombs. They are equal in magnitude but opposite in signs. In this case Cl having partial negative acts as **negative pole** while H having partial positive charge acts as **positive pole** and therefore the whole molecule is known as **dipole**.
- The covalent bond whose bonded atoms have partial charge is known as **polar covalent bond.**
- Formation of partial charges makes the compound to attain some ionic characters. Greater electronegativity difference between covalent bonded atoms, greater intensity of partial charges (the covalent bond becomes more polar) and hence the bond becomes more ionic in characters.

Dipole moments and polar molecules

Dipole moment *is the product of distance between two charges and magnitude of the charges.*

Thus for polar covalent bond, amount of dipole moment is given by the following formula:

$$\mu = qx$$

Where μ is the dipole moment in D(Debye)or Cm(Coulomb − metre)

q is the magnitude of charge coulomb, C

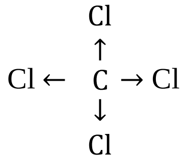
r is the distance between the charges (distance between nuclei of two covalent bonded atoms) metre, m

Dipole moment is the vector quantity (it has both magnitude and direction) and it acts towards the stronger electronegative atom.

- A covalent compound is said to be a polar molecule if it has non zero resultant of dipole moment. For the compound to have non-zero resultant of dipole moment and hence to be a polar molecule it must satisfy the following conditions:
  (i) **Its bond must be polar that is the two covalent bonded atoms must have large electronegativity difference**. Example PH_3 is non-polar because P and H have almost the same electronegativities while NH_3 is polar molecule because N has much higher electronegativity than H.

  (ii) **The structure of the molecule must be non-symmetrical so as to avoid cancellation of dipole moments in the molecule.** Example although chlorine is more electronegative than carbon, the CCl_4 molecule is non-polar due to the reason explained in the next page;

Consider the structure of CCl_4 which is shown below (dipole moments are shown by the head of arrows drawn on each of bond of the molecule)



$$\begin{array}{ccc} & Cl & \\ & \uparrow & \\ Cl \leftarrow & C & \rightarrow Cl \\ & \downarrow & \\ & Cl & \end{array}$$

Thus the structure being symmetrical and using the fact that dipole moment is vector quantity, form above structure it is clear understood that each dipole moment is cancelled by another acting at opposite direction to the direction of the dipole moment; so the resultant dipole moment become zero and hence the molecule is non-polar

Example 4

SO_2 is polar while CO_2 is non – polar although both have the similar empirical formula.Explain

Solution

CO_2 Being symmetrical (linear) in structure ($O = C = O$) has zero resultant of dipole moment thus becoming non – polar while SO_2 being bent in structure (as result of repulsion exerted by lone pair in sulphur to the bonds), is unsymmetrical so SO_2 has non – zero resultant of dipole moment and hence become polar.

METALLIC BOND

Metal atoms have lower ionisation energies compared to non-metals. **Metallic bonds** are formed when atoms lose electrons and the resulting electrons are attracted to all the resulting cations. It happens because the electrons are attracted to more than one nucleus and hence more stable.

As result the valence electrons in solid metallic crystal are free to move from one atom to another and are shared by several atoms-they are not attached to any particular atom. Thus these valence electrons are said to be **delocalised** and the spread up of electrons is known as **delocalisation**.

- So the metallic bond is thought to consist of mobile or delocalised electrons shared by virtually all atoms in a sample of metal. Therefore the metal is pictured as a network of positive ions immersed in a sea of electrons.

The above explanation can be summarised by **the electron sea-model** as shown below:

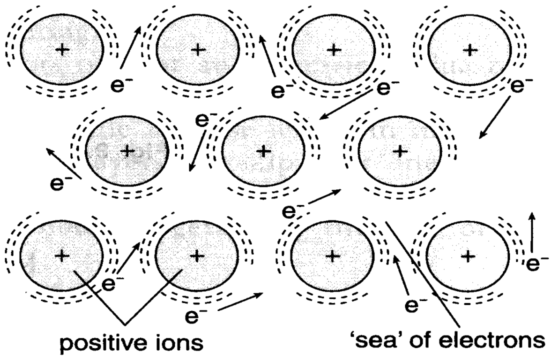


Figure: Electron sea model of the metallic bond in the two dimensional representation

Definition of metallic bond:

This is the electrostatic force of attraction between metal positive ions and the sea of negatively charged delocalised valence electrons of metal atoms which act as a 'glue' to hold the metal atoms together.

Where **metallic bonding** refers to *the interaction between the delocalised electrons and the metal nuclei.*

Metallic bond is strong if:

(i) There is small metallic radius

- This ensures enough nuclear attractive force to reach easily to the delocalised valence electrons.

(ii) There is greater number of valence electrons

- This ensures greater number of electrons the metallic atom can contribute into electronic sea of their metallic bonding.
- It also ensures higher charge to the metal ions and hence stronger delocalised electron-metal ions attraction.

The reader should understand that:

During metallic bonding, position of metal ions is fixed. Only valence electrons are free to move between the metal atoms. So the strong electrostatic of attraction between metal ions and sea of electrons (delocalised electrons) results to a giant metal lattice structure as shown in the three dimension diagram below.

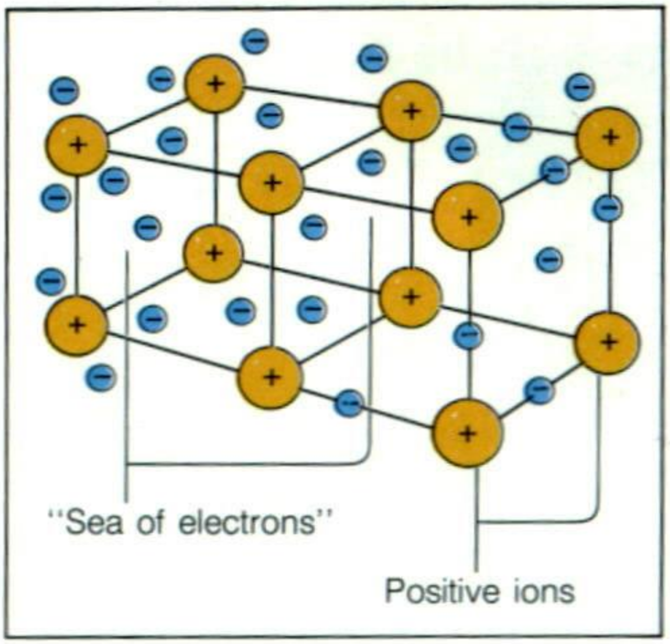


Figure: Three dimensional representation of metallic bonding

Presence of delocalised valence electrons in metals accounts for various physical properties of metals like:

- Good electrical and heat conductivity
- Malleability and ductility
- Metallic lustrous

- Metals have high heat conductivities because the thermal motion can be easily carried by the electrons within an excited state.
- Metals are good conductor of electricity because the delocalised electrons can move freely within the structure of metal when a potential difference is applied.
- Metals are very ductile and malleable because the sea of electrons is flexible.
  - So if the arrangement of atoms changes, the sea of electrons can rearrange quickly and therefore the layers of metal atoms can slide past each other without breaking the bond.
- Metals are commonly shiny coloured. ***Why coloured?***
  - They are coloured because the delocalised electrons are easily excited and on returning to the ground state or to the lower energy excited state they emit radiations with wavelength in the visible spectrum which are recognised as definite colour. That is about colour, ***what about being shiny?***
  - Also the delocalised electrons are very mobile such that there is continuously successive excitation of and de-excitation of electrons. This oscillation (continuous excitation and de-excitation) of electrons make the metals to shiny (to be lustrous).

Example 5

Why non-metals do not form metallic bond although they have large number of valence electrons accompanied with smaller atomic radii compared to metals?

Solution

Atomic radii of non-metals are so small that their ionisation energies are very high thus there are no delocalised valence electrons in non metals.

DIGGING DEEPER EXERCISE 6

Question 1

If oxygen is highly electronegative, why is a covalent bond between oxygen atoms considered non polar?

Question 2

a) Give the type of bonding present in $BeCl_2$
b) Give the type of bonding present in $BaCl_2$
c) Explain why the type of bonding is different in these two compounds.

Question 3

Classify the dipole moments of the following molecules as either "Zero" or "nonzero"

i) Hydrogen iodide
ii) Carbon dioxide
iii) Ethanol
iv) 1-chloro-2-butyne($ClCH_2C \equiv CCH_3$)
v) Nitrogen dioxide.

Question 4

Copper is ductile while copper (II) sulphate is brittle. Explain

Question 5

Compare the electrical conductivity of solid sodium metal with that $NaCl$

Question 6

Describe a co-ordinate bond with an example. How does it differs from a covalent bond.

Question 7

Do compounds with covalent bonds conduct electricity? Explain why or why not.

Question 8
Are ionic compounds known as being brittle or malleable? Explain discussing the bonds.

Question 9
Why is it that when you hit a metal such as silver with a hammer it will only deform it, whereas it would shatter $NaCl$?

Question 10
Would you expect SiO_2 to be ductile? Explain.

Question 11
Why is aluminum able to conduct heat better than quartz glass?

Question 12
Explain why third fluorine(F) cannot be added to F_2 to form F_3 despite the fact that fluorine is strongest electronegative element in the periodic table.

Question 13

Give differences in properties of ionic and covalent compounds.

Question 14

Which molecule should have the larger dipole moment HBr or HI?

Question 15
Does SO_2 have a dipole moment? If so, in which direction does the net dipole point?

Question 16

Explain the condition which must be met by a molecule with polar bonds so as to be non polar.

Question 17

Which of the following molecules are polar?

BF_3, CO, CF_4, NCl_3,SF_2

Question 18

Why are the bonds between H and Cl in HCl molecule never hundred electrovalent or covalent?

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Chapter 7

VALENCE BOND THEORY

INTRODUCTION

Valence bond theory describes the formation of covalent bonds by overlap of atomic orbitals. The theory assumes that:

- Electrons occupy atomic orbitals of individual atoms within a molecule.
- The electrons of one atom are attracted to the nucleus of another atom.
- The attraction of which the electrons in two atoms experience increases as the atoms approach one another until the nuclei of atoms reach a minimum distance apart where the two nuclei begin to experience strong repulsion.
- In the state of the minimum distance between the two nuclei, the electrostatic force of the electron-nucleus attraction between the two atoms is said to in balance with electrostatic force of repulsion between the nuclei and therefore lowest potential energy is acquired.
- The overlap of atoms is considered to form stable covalent bond to hold the two atoms after acquiring the lowest potential energy.

The two last 'dots' are very important in explaining stability state of the covalent bond and may be combined to give single statement as follows:

> *Covalent bond is in its maximum stability state when the electrostatic force of attraction between bonded nuclei and shared (covalent bonded) electrons balance with electrostatic force of repulsion between the two bonded nuclei.*

In just one line sentence, valence bond theory says that:

Covalent bond is formed as a result of overlapping of atomic or hybrid orbitals.

The above explanation on the valence bond theory can be illustrated by the figure below which is known as **Morse curve.**

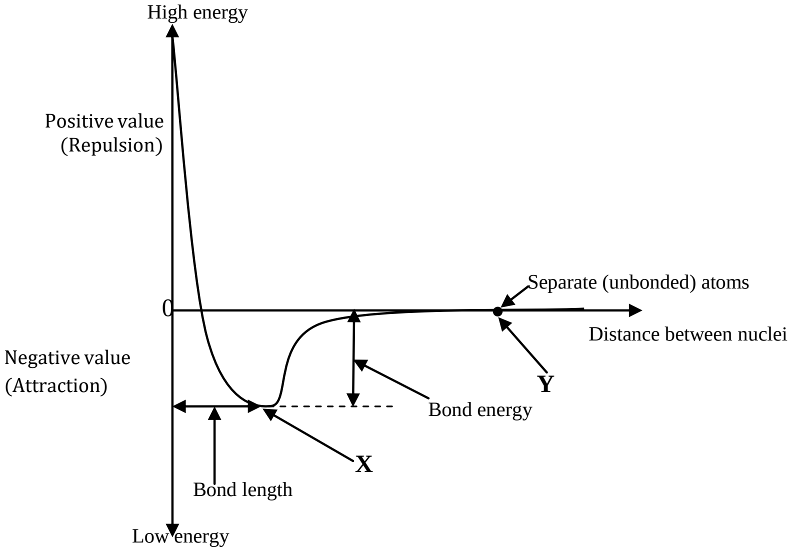


Figure: Morse curve for covalent bond formation

Interpretation from the above potential energy curve for covalent bond formation (Morse curve)

- When two atoms are very far apart, there is **neither attraction nor repulsion** between them and therefore **they have zero energy**. These **separated atoms** are said to be **unbonded**. This is shown by point **Y** on the curve.
- As the atoms start to get closer, they start to experience attraction between them due to the electrostatic force of attraction between positive charge nucleus of an atom and negatively charged valence electrons of the neighbour atom. The attraction and whence energy evolved increases as the two atoms become much closer.
- At the point **X** the attraction is maximum and therefore energy evolved is maximum too. At this point the two atoms have lowest energy possible which in turn means they are at their maximum stability state.

- The overlap between the two atoms which lead to that maximum stability state is actually the covalent bond between the two atoms and hence the distance between two nuclei is now known as **bond length**, it represents the distance between nuclei of two covalent bonded atoms.
- The energy of the two atoms in this maximum stability state is now known as **bond energy**, it represents the total energy released by the two atoms during the covalent bond formation and it is equal to the amount of energy required (to be absorbed) to separate the bonded atoms (at point **X**) to return to point **Y** where the two atoms are unbonded.

- After forming covalent bond at **X**, if the two atoms would become closer,(at the left hand side of **X**) the repulsion between the two positively charged nuclei would start to rise and therefore the potential energy start to increase again and therefore the atoms become unstable. So to avoid this instability state the two atoms cannot become closer beyond the bond length.

CONDITIONS FOR ATOMS TO FORM COVALENT BOND

There are two important conditions for atoms to form covalent bonds which are:

i) Presence of strong attraction between atoms

- An atom with small size accompanied with high electronegativity has greater ability to attract valence electrons of neighbour atom and therefore can form strong covalent bond. And these explain why covalent bond is common in non-metals only.
- Metals do not normally form covalent bond they have large atomic size accompanied with low electronegativity and therefore no strong attraction between them.

ii) Presence of unpaired or empty orbital

- Unpaired or empty orbital acts as a room for shared electrons in the covalent bond.
- If the orbitals employed are two unpaired orbitals, then normal covalent bond is formed while the employment of empty orbital results to the formation of dative covalent bond.
- In absence of unpaired or empty orbital (if all orbitals are full occupied with electrons), no covalent bond is formed even if the atom exerts very strong nuclear attraction. This explains why third hydrogen cannot be added to H_2 to form H_3.

SIGMA AND PI BOND

Based on the way atomic orbitals overlap, covalent bonds can be classified into two categories which are:

- Sigma (σ) bond
- Pi (π) bond

Sigma (σ) bond

Sigma bond *is strong covalent bond formed by maximum overlap of two atomic orbitals to make molecular orbital through head to head (end to end) overlapping.*

Sigma (δ) bonds have one region electron density on the **internuclear axis.**

- Whereas **internuclear axis** *is the line joining nuclei of the two bonded atoms.*
- *The intersectional region with high electron density formed after overlapping of adjacent atomic orbitals where covalent bonded electrons are more likely to be found is known as* **molecular orbital.**

The sigma bond is formed when:

(i) Two s-orbitals overlaps

Example: Formation of hydrogen molecule

H atom H atom
$1s^1$ $1s^1$
End to end overlap

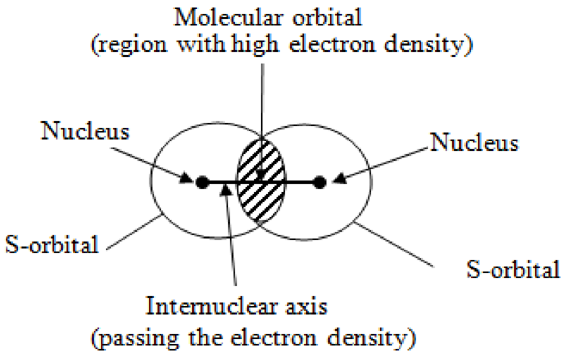


Figure: Formation of sigma bond between two s-orbitals

(ii) s-orbital overlaps with p-orbital

Example: Formation of hydrogen fluoride

H atom F atom
$1s^1$ $2p_z^1 2p_y^2 2p_z^2 2s^2 1s^2$
End to end overlap

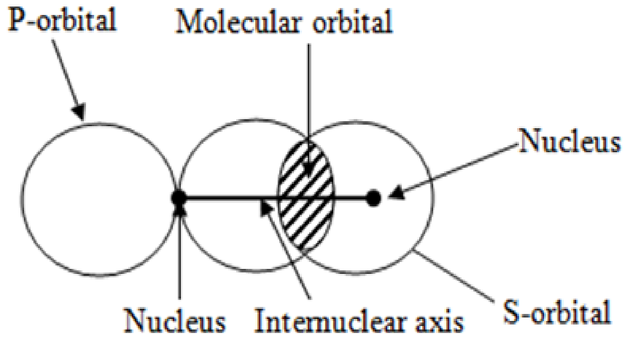


Figure: Formation of sigma bond between s-orbital and p-orbital

(iii) Two p-orbitals overlap by end to end

Example: Formation of fluorine molecule.

F atom F atom

$1s^1 2s^2 2p_y^2 2p_z^1$ $2p_z^1 p_y^2 2s^2 1s^2$

End to end overlap

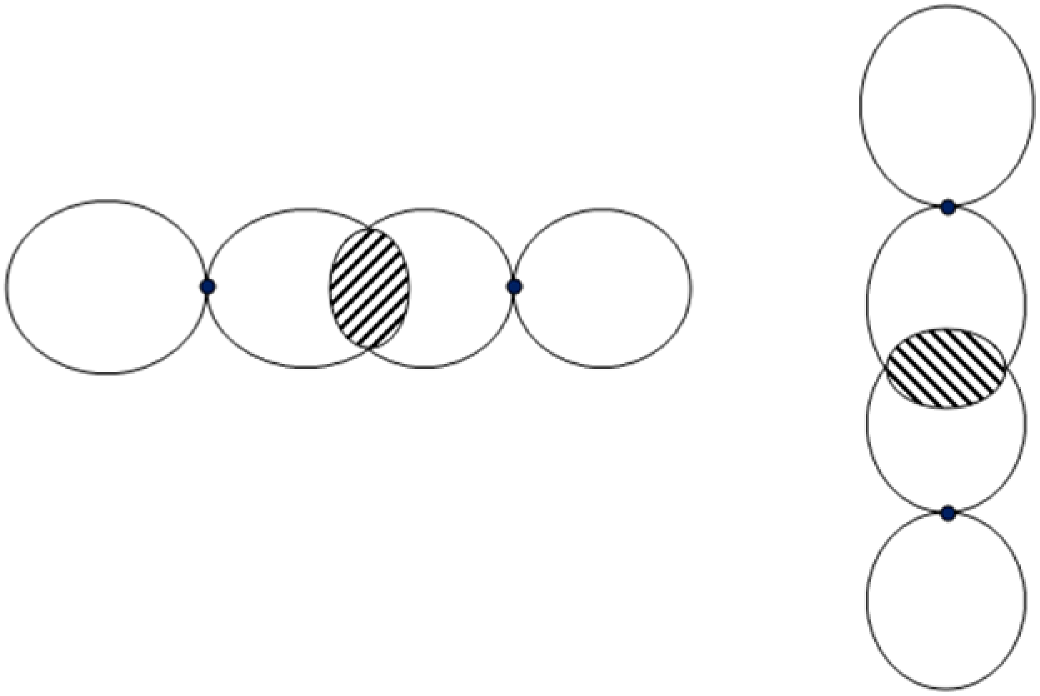


Figure: Formation of sigma bond between p orbitals

(iv) Hybrid orbital overlap with another atomic orbital (hybrid or unhybrid)

The concept of hybridisation of atomic orbitals will be discussed later.

Another possibility of sigma bond formation is when: an s-orbital of one atom overlaps with d-orbital of another atom or an s-orbital of one atom overlap with f-orbital of another atom.

Pi (π) bond

Pi bond *is the weak covalent bond formed by minimum overlap of two atomic orbitals to make molecular orbital through the side way (lateral) overlapping*.

- Unlike sigma bond whose molecular orbital is of one electron density, the molecular orbital of pi bond has two regions of electron density (in two opposite sides of the internuclear axis).

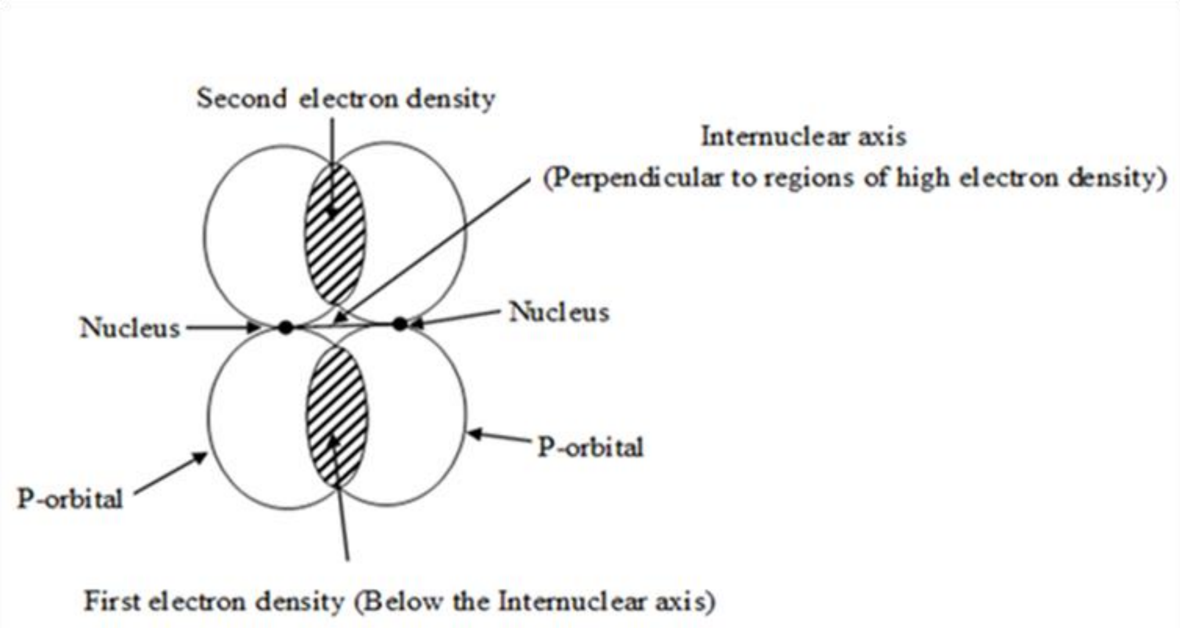


Figure: Formation of **π**-bond between **p_z**-orbitals

Similarly;

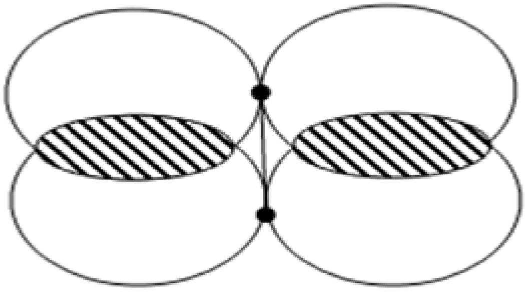


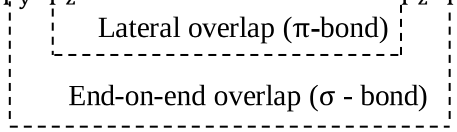
Figure: Formation of **π**-bond between **p_x**-orbitals

Examples:

(i) Formation of oxygen molecule (O_2 in $O = O$)

O atom O-atom

$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ $2p_z^1 2p_y^1 2p_x^2 2s^2 1s^2$

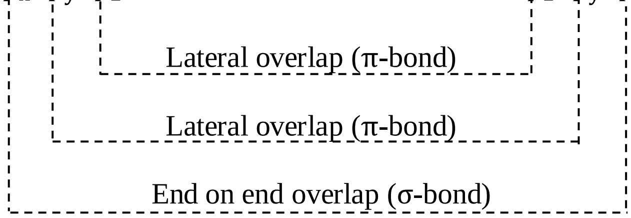


The preference of forming sigma bond is according to the following order: $P_x > P_y > P_z$. Thus with two p orbitals, P_y and P_z; P_y must form sigma bond while P_z forms pi bond. Similarly for P_x and P_y; P_x would form sigma bond while P_y form pi bond. s-orbital does not form pi bond at all, it forms the sigma bond only.

(ii) Formation of nitrogen molecule(N_2 in $N \equiv N$)

N atom N atom

$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ $2p_z^1 2p_y^1 2p_x^1 2s^2 1s^2$



Generally pi bond is formed by lateral overlapping of **unyhbridised** p-orbitals. It can also be formed by lateral overlapping of unyhbridised p-orbital and unyhbridised d or f orbital; and all other remaining possibilities of atomic orbitals overlapping are for sigma bond formation.

Important point to understand!

An atom will form π bond if and only if its atomic size is small enough to enable side-way (lateral) overlapping of atomic orbitals.

- These small size atoms have outermost energy level with smaller principle quantum number and therefore smaller atomic orbitals.

So in other words it can be said that: **Orbitals with lower principle quantum numbers are smaller in size and hence have greater ability to undergo sideways overlapping to form π bond.**

- This explain why nitrogen can form triple bond in $N \equiv N$ of N_2 while phosphorous cannot (N has smaller size than P).
- It also explain why carbon C, form $\pi -$ bond with oxygen, O, ($O = C = O$) in CO_2 while silicon, Si form sigma bonds only in SiO_2 (C has smaller size than Si).

Differences between sigma (σ) and pi (π) bond

	SIGMA BOND		Pi BOND
1	Formed by end to end overlapping of atomic orbitals	1	Formed by lateral overlapping of atomic orbitals
2	Stretches along the direct line joining the atomic nuclei so their molecular orbital is symmetrical about this axis (internuclear axis).	2	Is perpendicular to the internuclear axis of the bonding atoms thus shortening the internuclear distance (bond length)
3	Free rotation about sigma bond is possible	3	Free rotation about pi bond is not possible
4	Molecular orbital consist of a single electron cloud.	4	The molecular orbital consist of two electron clouds
5	It is stronger due to greater overlapping of electronic charge cloud and its lower energy level	5	It is weak compared to sigma bond due to poor overlapping and its higher energy level
6	Only **one** sigma bond can exist between atoms	6	There can be more than one pi bond between the two atoms (in triple bond)

Attention!

- You cannot form multiple bonds with sigma bonds alone.
- If there is double bond, that means one bond is sigma and another is pi.
- If there is triple bond, that means one bond is sigma and other two bonds are pi.
- If one of the atoms in the pi bond is rotated, there will be no overlap between their orbitals and therefore the bond will break. So free rotation of atoms in π bond is not allowed.
- This is different to sigma bond where atoms in the bond are free to rotate without breaking the bond.

Don't forget that:

The ability to form sigma bond is according to the following order:

$$s > p_x > p_y > p_z$$

Thus:

(i) s-orbital can never form π – bond at all, it must form sigma bond.

(ii) Whenever there is unpaired p_x orbital and p_y - orbital (or p_z orbital) is the p_x orbital which forms sigma bond and p_y (or p_z) form pi bond.

(iii) Whenever there is unpaired p_y and p_z orbitals; p_y form sigma bond while P_z form pi bond

(iv) P_z will form sigma bond if and only if all s, p_x and p_y orbitals are paired with electrons; that is the only unpaired orbital is P_z orbital.

HYBRIDISATION

Consider the typical bonding pattern of carbon (a $1s^2 2s^2 2p_x^1 2p_y^1$ atom). If you went only with the idea of atomic orbital overlap (valence bond theory), it would seem that when carbon bonds there would be only two bonds forming – one from each half filled 2p orbital. *But there is a problem with this assumption; what is this problem?*

- The problem lies on the fact that: **carbon usually not form stable compound with two covalent bonds!** Carbon always forms stable compounds with four covalent bonds.

If you consider electron promotion (**excitation**) to move an electron from the $2s -$ orbital to the $2p_z -$ orbital, you would achieve 4 half filled orbitals (one 2s-orbital and three 2p-orbitals) and now with the covalence of four, the carbon could bond via orbital overlap to form four covalent bonds. *However, when you consider the shape and orientation of the s and p orbitals you still have other two problems***.** *What are other problems?*

- To understand other problems, consider the structure of CH_4 with four $C - H$ covalent bonds about the carbon. Since s and p orbitals in the carbon have slightly different energies, the three 2p-orbitals overlapping with the 1s-orbital of hydrogen atoms and one 2s orbital overlapping with the 1s-orbital of the hydrogen. You would have the following two expectations from such overlapping.

First expectation:

Such overlapping would seem to imply a significant energy difference in one of the four $C - H$ bonds where the 2s-orbital being closer to nucleus would form more stable sigma bond with the hydrogen through $s - s$ overlapping of the atomic orbitals than other three 2p-orbitals could form through $s - p$ overlapping. **However, methane is known to have four identical energy $C - H$ bonds.**

Second expectation:

Also since the 2p orbitals$(p_x, p_y \text{and } p_z)$ are perpendicular to each other, one might expect three $C - H$ bonds (formed through $s - p$ overlapping) to be oriented at 90° (the p orbitals orientation). **Experiments, however, confirms CH_4 to be tetrahedral molecule with identical bond angles of 109.5°.**

So what is the correct explanation for such observations?

To account for the known structure of methane, it makes sense to assume that the carbon atom has four equivalent energy atomic orbitals, arranged tetrahedrally as revealed by experiments.

- Such a set of orbitals can be obtained by **mathematically** combining the carbon's 2s and 2p orbitals. This mixing of the atomic orbitals to form special identical orbitals for covalent bonding is called **hybridisation**. These four new orbitals are called **sp^3** (pronounce as **'s**, p three' and **not** s, p cubic) **orbitals** because they are formed from one 2s and three 2p orbitals.

By definition:

Hybridisation *is the theoretical mixing up of orbitals having different energy and shape to give orbitals of the same energy and shape.* Hybridisation increases combining power of an element (it increases the ability of an element to form covalent bond).

- It is 'theoretical' because the **hybridisation is not physical process**; it is just mathematical process of mixing atomic orbitals.

Avoid these misconceptions!

Many students make mistake by wrongly relating hybridisation and excitation of electrons. They think that:

- Hybridisation process must be accompanied with excitation of electrons; and
- Whenever there is excited electron(s), then the orbitals with excited electrons must be involved in the hybridisation process.

The above two 'dashes' are totally misconception!

- As we will see later, the truth lies in the following two 'dots'!
- Not necessary for hybridisation process to be accompanied with excitation of electrons (Although some hybridisations do).
- Not necessary for orbitals with excited electrons to be involved in the hybridisation (Although some orbitals with excited electrons do).

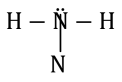
Hybridisation rules for common covalent compounds

i) Orbitals of a central atom only undergo hybridisation

By definition:

Central atom *is an atom in a molecule or polyatomic ion that is bonded to more than one other atom.*

- For example in ammonia NH_3, all three hydrogen atoms are bonded to nitrogen and hence the nitrogen atom is the central atom in ammonia.



$$\begin{array}{c} H-\ddot{N}-H \\ | \\ N \end{array}$$

Figure: Structure of ammonia

So by this rule, we have no hybridisation of H but that of N. If you are asked about hybridisation of ammonia that means you are actually asked about hybridisation of nitrogen in ammonia.

ii) Only valence orbitals can be used in hybridisation

- This means orbitals in inner shells are not used in hybridisation. Only orbitals in outermost shell may be used (Exceptional of this in complexes of transition elements where orbitals in penultimate shell are also used in hybridisation process. You have not to worry about this; will be discussed in Inorganic chemistry).

iii) Complete filled orbitals, half filled orbitals and empty orbitals may be used in the hybridisation process

- This means that, there is no any orbital which cannot be used in the hybridisation in accordance to your requirement provided that the orbitals are found in the outermost energy level

iv) The orbitals of almost same energy can be mixed to form hybrid orbitals

- This means if for example you have s, p and d orbitals available for hybridisation and you are intending to have four hybrid orbitals; the preferred choice would be to use s and p orbitals and not s and d orbitals because the energy difference between s and p orbitals is smaller than that found between s and d orbital.

- Another reason favouring this choice (in preference to any other possible combination like p and d orbitals) is that hybrid orbitals obtained from s and p orbitals have lower energy of all other choices and hence most stable.

v) The numbers of atomic orbitals mixed together are always equal to the number of hybrid orbitals

- This means no orbital get destroyed or created during hybridisation process. It is actually the principle of conservation of orbital during the hybridisation process.
- For example, if **one** s-orbital is mixed with **three** p-orbital (Total of **four** atomic orbitals) in hybridisation, it always result to **four** hybrid orbitals.

vi) During the hybridisation, the mixing number of atomic orbitals is as per requirement

- This means, you take appropriate number of atomic orbitals to mix (hybridise) according to the number of hybrid bonds you wish to form. If you wish to form 4 hybrid bonds you will need four atomic orbitals so as to form 4 hybrid orbitals or if 6 hybrid bonds are required, then 6 hybrid orbitals would be formed from 6 atomic orbitals. In other words

$$\textbf{Number of hybrid bonds} = \textbf{Number of hybrid orbitals} = \textbf{Number of atomic orbitals to be mixed}$$

Where, **hybrid bonds** *are covalent bonds whose bonding (molecular) orbitals resulted from hybridisation of atomic orbitals.*

Characteristics of hybrid orbitals

i) The number of hybridised orbitals formed is equal to the number of orbitals that get hybridised

ii) The hybrid orbitals have equal energy and shape

iii) The hybrid orbitals form more stable covalent bond than the pure atomic orbitals (because they have lower potential energy than unhybridised atomic orbital) and hence the hybridisation increases ability of an element to form covalent compound as we had noted earlier.

iv) The hybrid orbitals are arranged in space such that there is maximum distance apart between them so that they have minimum repulsion between them (and therefore giving stable arrangement of the orbitals).

TYPES OF HYBRIDISATION

The common types of hybridisation are:

(i) sp^3 hybridisation
(ii) sp^2 hybridisation
(iii) sp hybridisation

The student should understand that superscript in identification of hybridisation show number of orbitals in particular energy sublevel which were used for mixing up in hybridisation e.g. sp^3 hybridisation imply **one** s-orbital and **three** p-orbitals were used in the hybridisation, sp^2 hybridisation imply **one** s-orbital and **two** p-orbitals were used and so on.

sp^3 hybridisation

This is formed when one s- orbital is mixed up with three p-orbitals to give four sp^3 hybrid orbitals. To understand this considers formation of methane (CH_4).

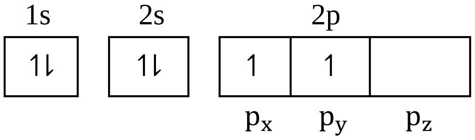
- In methane (CH_4), carbon has bonded to hydrogen making a total of four covalent bonds contrary to the bonding capacity of carbon as observed in its electronic configuration.

$$[C] = 1s^2 2s^2 2p_x^1 2p_y^1$$

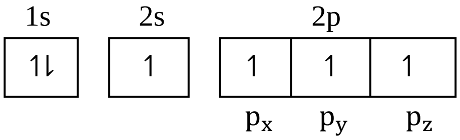
Form above electronic configuration of ${}_6C$; it is clear that carbon is able to form two covalent bonds due to presence of two unpaired electrons in p_x and p_y (one electron in each orbital).

- However it forms four covalent bonds in methane. The four bonds formed have the same bond length, bond angle and the same energy; so the only sensible explanation to the capacity of bonding of carbon is hybridisation

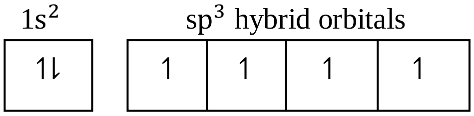
Electronic configuration of carbon at ground state is;



Supply of energy to carbon atom, excite one 2s – electron to p_z -orbital to give the following electronic configuration of carbon at excited state with the required four unpaired orbitals:



Application of some more energy to the excited carbon atom results into the mixing of the 2s – orbital and three 2p-orbitals forming four equivalent orbitals in terms of energy and shape as illustrated below:



Each of the sp^3 hybrid orbital can overlap with unpaired 1s orbital of hydrogen thus forming **four C-H sigma bonds**.

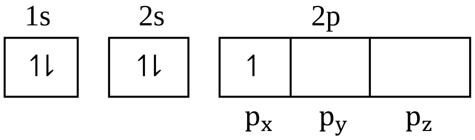
- sp^3 hybrid orbitals are **tetrahedral** in shape and hence the term **tetrahedral hybridisation** for sp^3 hybridisation. The angle between the hybrid orbitals is 109.5°.

sp^2 hybridisation

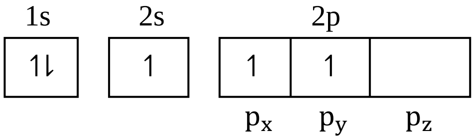
This is formed when one s-orbital is mixed with two p-orbitals to give three sp^2 hybrid orbitals.

- To understand this consider formation of BF_3.

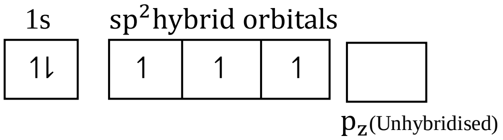
Electronic configuration of boron at ground state is;



Then its electronic configuration at excited state becomes;



After sp^2 hybridisation it becomes;



Thus for boron to form three equivalent bonds in BF_3, boron use the three unpaired sp^2 hybrid orbitals to overlap with unpaired $2p_z$ orbitals of fluorine atom to form **three B-F sigma bonds.**

- sp^2 hybrid orbitals are **trigonal planar** in shape and hence the term **trigonal planar hybridisation** for sp^2 hybridisation. The angle between the hybrid orbitals is 120°.

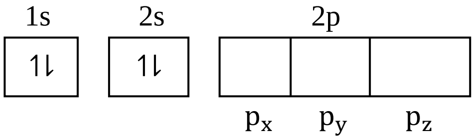
As it is formed by sp^2 hybridisation with no lone pair in boron, BF_3 is trigonal planar in shape.

sp hybridisation

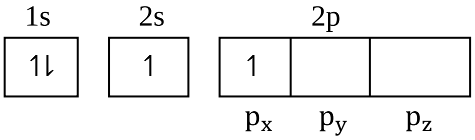
This is formed when one s-orbital is mixed with one p-orbital to give two sp hybrid orbitals.

- To understand this consider the formation of $BeCl_2$

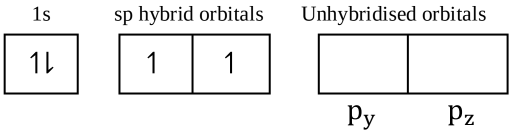
Electronic configuration of Be ground state is;



Then its electronic configuration at excited state becomes;



And after sp hybridisation it becomes;



Thus each unpaired sp hybrid orbital overlaps with unpaired $3p_z$ orbital of chlorine to form **two Be – Cl sigma** bonds in $Be-Cl_2$.

- sp hybrid orbitals are **linear** in shape and hence the term **linear hybridisation** for sp hybridisation. It is also known as **diagonal hybridisation.** The angle between the orbitals is 180°.

Other types of hybridisation

This includes hybridisation involving d-orbitals to give expanded octet molecule (molecules which contain an atom at the centre with more than eight valence electrons).

- The types of hybridisation include **sp^3d hybridisation** and **sp^3d^2 hybridisation.**

Consider formation of PCl_5

At ground state:

	3s	3p			3d				
$[_{15}P]$ = [Ne]	1⇂	1	1	1					

At excited state:

	3s	3p			3d				
$[_{15}P]$ = [Ne]	1	1	1	1	1				

After hybridisation (sp^3d hybridisation)

	sp^3d hybrid orbitals					Unhybridised 3d-orbitals			
$[_{15}P]$ = [Ne]	1	1	1	1	1				

With sp^3d hybridisation phosphorous is able to form five equivalent bonds (each unpaired sp^3d hybrid orbital overlap with unpaired $3p_z$ orbital of chlorine to give **five P-Cl sigma bonds**).

- sp^3d hybrid orbitals are **trigonal bipyramidal** in shape and hence the term **trigonal bipyramidal hybridisation** for sp^3d hybridisation. The angles between the hybrid orbitals are 120° in the trigonal plane and 90° between the hybrid orbitals in the plane and those above and below the plane.

Consider formation of SF_6

At ground state:

	3s	3p			3d				
$[_{16}S]$ = [Ne]	1⇂	1⇂	1	1					

At excited state:

	3s	3p			3d				
$[_{16}S]$ = [Ne]	1	1	1	1	1	1			

After hybridisation (sp^3d^2 hybridisation)

	sp^3d^2 hybrid orbitals						Unhybridised 3d-orbitals		
$[_{16}S]$ = [Ne]	1	1	1	1	1	1			

With sp^3d^2 hybridisation sulphur is able to form six equivalent bonds (each of unpaired sp^3d^2 hybrid orbital overlap with unpaired $2p_z$ orbital of fluorine to give **six S-F sigma bonds**).

- sp^3d^2 hybrid orbitals are **octahedral** in shape and hence the term **octahedral hybridisation** for sp^3d^2 hybridisation. The angles between the hybrid orbitals are 90°.

QUICK WAY TO KNOW TYPE OF HYBRIDISATION

Quick way to know number of lone pairs in the atom

Knowing number of lone pairs present in an atom is very important in deducing the type of hybridisation in the atom. So before studying how to deduce the type of hybridisation of the atom it is firstly better to study how to deduce the number of lone pairs present in the atom.

You may quickly find number of lone pairs present in the given atom by following the following procedures:

- Firstly know number of valence electrons present in the atom before forming bond(s).
- Then count number of bonds, both sigma and pi bond where each bond is equivalent to one valence electron contributed by the atom in the bond formation.
- Then find the difference between the number of valence electrons and that of bonds. The difference is equal to the number of unbonded electrons.
- Finally divide the difference (number of unbonded electrons) by 2 to get number of pairs of unbonded electrons, that is number of lone pairs.

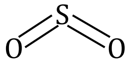
So by putting all above four 'dashes' together, memorise the following formula to make things simpler!

$$\textbf{Number of lone pairs in an atom} = \frac{\textbf{Number of valence electrons of the atom} - \textbf{Number of bonds in the atom}}{\textbf{2}}$$

To ensure good understanding of the concept, consider number of lone pairs of atom in the bracket for the following species:

i) SO_2 (sulphur)
ii) IBr_3(Iodine)
iii) CO_3^{2-}(carbon)

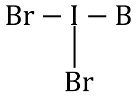
- For (i) structure of SO_2 is



- number of valence electron in S=6
- Number of bonds in S=4
- So number of lone pair in s $= \frac{6-4}{2} = 1$

Hence there is one lone pair in S of SO_2

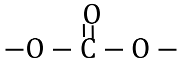
- For (ii): structure of IBr_3 is



$$\begin{array}{c} \mathrm{Br} - \mathrm{I} - \mathrm{B} \\ | \\ \mathrm{Br} \end{array}$$

- Number of valence electrons in I=7
- Number of bonds in I=3
- Number of lone pairs in I $= \frac{7-3}{2} = 2$

Hence there are two lone pairs in I of IBr_3



$$-O-\overset{\overset{O}{\|}}{C}-O-$$

- Number of valence electrons of C = 4
- Number of bonds in C = 4
- Number of lone pairs $= \frac{4-4}{2} = 0$

Hence there is no lone pair in the carbon of CO_3^{2-}

Deducing type of hybridisation

The type of hybridisation of a particular atom can be easily deduced if you understand all bonds and lone pairs present in the atom.

- After understanding bonds and lone pairs present in the atom the process of deducing type of hybridisation for the atom is more than simple! It can be explained in just single sentence rule as written below:

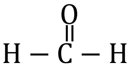
  Count total number of sigma bonds and lone pairs in the atom and then assign one hybrid orbital for each starting from s, p and then d orbital.

The rule can be written as arithmetic equation as follows:

$$\textbf{Number of hybrid orbitals} = \textbf{number of } \boldsymbol{\delta} \textbf{ bonds } + \textbf{Number of lone pairs}$$

The total number of lone pairs and sigma bonds is known as **steric number**.

To have better understanding of the above rule, consider hybridisation in the following compounds:

i) 

$$H-\overset{\overset{O}{\|}}{C}-H$$

(methanal)

ii) NH_3 (ammonia)

- For (i), the central atom carbon has **3 sigma bonds** without any lone pair on it. So we need **three (3) hybrid orbitals**; **one s-orbital** and **two p-orbitals** and hence the type of hybridisation of C in the given compound is $\mathbf{sp^2-hybridisation.}$

- For (ii), the central atom nitrogen has **three (3) sigma bonds** and **one (1) lone pair** making a total of four (4) electron pairs on it. So we need **four (4) hybrid orbitals**; **one s-orbital** and **three p-orbitals** and hence the type of hybridisation of N in the given compound is $\mathbf{sp^3 - hybridisation.}$

The reader should remember that:

In the **page number 107** (**dative bond** section of **chapter 6**), we saw electronic structure of NH_3 which did not involve excitation of electrons in nitrogen because the nitrogen atom has already 3unpaired orbitals (required to form 3 covalent bonds with H) in its ground state. So hybridisation of N in NH_3 is the clear example of what we had noted earlier that the **process of hybridisation may occur without excitation of electrons!**

Two more facts to deduce from above hybridisations!

- If total number of hybrid orbitals in an atom is equal to the total number of sigma bonds in it, then there is no lone pair in that atom.

- In (i), there were **three sigma bonds** on C of methanal and **three** $\mathbf{sp^2}$ **hybrid orbitals** and therefore no lone pair in the carbon C.
- The above fact can be easily deduced from our rule:

$$\textbf{Number of hybrid orbital} = \textbf{Number of } \boldsymbol{\delta} \textbf{ bonds} + \textbf{Number of lone pairs}$$

- From which it clearly understood that; if $\text{Number of lone pairs} = 0$

$$\textbf{Then number of hybrid orbitals} = \textbf{Number of } \boldsymbol{\delta} \textbf{ bonds}$$

- If the total number of hybrid orbitals in an atom is not equal to the total number of sigma bond in it, there is at least one lone pair in that atom.

The number of lone pairs may be given by the following formula;

$$\textbf{Total number of lone pairs} = \textbf{Total number of hybrid orbitals} - \textbf{Total number of sigma bonds}$$

- so in (ii); while there were just **three sigma bonds**, there were **four** $\mathbf{sp^3}$ **hybrid orbitals** suggesting that there is **one** (4 minus 3) **lone pair** in the nitrogen.

Again this can easily be deduced from our equation:

$$\textbf{Number of hybrid orbitals} = \textbf{Number of } \boldsymbol{\delta} \textbf{ bonds} + \textbf{Number of lone pairs}$$

(By just making the number of lone pairs as the subject of the formula)!

The reader should understand that:

π bonds are not included in assigning hybrid orbitals because they are formed between **unhybridised** atomic orbitals.

- Keeping in mind that unhybridised orbitals have more energy and therefore are less stable is another reason why sigma bond (which are commonly formed between hybridised orbitals) are more stable than π-bond.

To keep all reasons together, sigma bonds are more stable than π-bonds because:

i) Sigma bonds are formed by head to head overlapping of atomic orbitals which have greater region of interaction than π-bond which is formed through side-way overlapping.

ii) Sigma bonds are commonly formed between hybrid orbitals which have lower energy than unhybridised orbitals used to form pi bond.

PERCENTANGE OF S AND P CHARACTERS IN HYBRID ORBITALS

Generally with $\mathbf{sp^n}$ hybridisation, where n may be 1, 2or 3 there are **1** s-orbital and **n** p-orbitals and total number of hybrid orbitals will be **(n+1).**

- The ratio of number of s-orbital to the total number of hybrid orbitals reflects s-character in the hybrid orbitals. It is known as percentage of s-character if it converted to percentage.

That is: $\mathbf{percentage\ of\ s-character} = \frac{\mathbf{Number\ of\ s-orbital}}{\mathbf{Total\ number\ of\ hybrid\ orbitals}} \times \mathbf{100}\%$

Where in $\mathrm{sp^n}$ hybridisation, the percentage of s-character will be given by the following formula;

$$\text{Percentage of s} - \text{character in sp}^{\text{n}} \text{ hybridisation} = \left(\frac{\mathbf{1}}{\mathbf{n+1}}\right) \times \mathbf{100}\%$$

For example:

- For $\mathrm{sp^3}$ hybridisation, n = 3 and therefore:

$$\%\ \text{s} - \text{character} = \frac{1}{4} \times 100\% = 25\%$$

- For $\mathrm{sp^2}$ hybridisation, n = 2 and therefore:

$$\%\ \text{s} - \text{character} = \frac{1}{3} \times 100\% = 33.3\%$$

- And for sp hybridisation

$$\%\ \text{s} - \text{character} = \frac{1}{2} \times 100\% = 50\%$$

Similarly, the percentage of p-characters is given by;

$$\text{Percentage of p} - \text{ character} = \frac{\mathbf{number\ or\ p-orbitals}}{\mathbf{Total\ number\ of\ hybrid\ orbitals}} \times \mathbf{100}\%$$

$$= \left(\frac{\mathbf{n}}{\mathbf{n+1}}\right) \times \mathbf{100}\%$$

It could worth to understand this term too!

The ratio of number of p-orbitals to the number of s-orbital in sp hybridisation is known as **hybridisation index**.

$$\text{That is hybridisation index} = \frac{\text{Number of p}-\text{orbitals}}{\text{Number of s}-\text{orbital}}$$

$$= \frac{\text{n}}{1} = \text{n}$$

- Hence in $\mathrm{sp^n}$ hybridisation, n is an integer (may be 1, 2, or 3) standing for the hybridisation index.
- **Greater value of the hybridisation index means smaller percentage of s-character and vice-versa.**

Significance of percentage of s-character

Understanding the percentage of s-characters in given hybrid orbitals is useful in deducing various useful information including the following:

i) Determination of energy of hybrid orbitals
ii) Determination of electronegativity of atoms with hybrid orbitals
iii) Determination of bond length between bonded atoms with hybrid orbitals

i) The determination of energy

Hybrid orbitals with greater percentage of s-character are closer to nucleus and therefore have lower energy because with given principle quantum number, s-orbitals are always closer to the nucleus (And don't forget that: lower energy orbitals means the orbitals are more stable).

- Therefore among the three common types of hybridisation, sp^3 hybrid orbitals having smallest percentage of s-character have highest energy while sp hybrid orbitals (which have greatest percentage of s-character) have lowest energy and hence most stable orbitals.

Don't misunderstand!

The rule applies if and only if the comparison involves two difference kinds of hybrid orbitals of the **same** principal quantum number.

- For example; it is clearly wrong to say that because both NH_3 and PH_3 are formed by the same type of sp^3 hybridisation with the same percentage of s-character, their sp^3 hybrid orbitals have equal energy. This is totally false! Nitrogen has outermost energy level with $n = 2$ while phosphorus has the level with $n = 3$. So sp^3 hybrid orbitals of N has principal quantum number of 2 and those of P have principal quantum of 3 and it is clear that principal quantum number (the main determinant of energy of orbital) of 3 has more energy than 2 and hence sp^3 hybrid orbitals of P in PH_3 has higher energy!

ii) The determination of electronegativity of atoms with hybrid orbitals

As we have seen earlier hybrid orbitals with greater percentage of s-character are closer to nucleus. So these hybrid orbitals experience stronger nuclear attractive forces.

- This means **for two atoms of the same element** but with different types of hybridisation, the atom with hybrid orbitals of higher percentage of s-character will be more electronegative. As an example;
- Carbon with double bond like in $CH_2 = CH_2$ is sp^2 hybridised while carbon in $CH_3 - CH_3$ is sp^3 hybridised.

This means the carbon atom in double bond has greater percentage of s-character and therefore more electronegative than the carbon in the single bond.

- The same reason explains why carbon in triple bond (like C in $CH \equiv CH$) is more electronegative than carbon in the double bond.

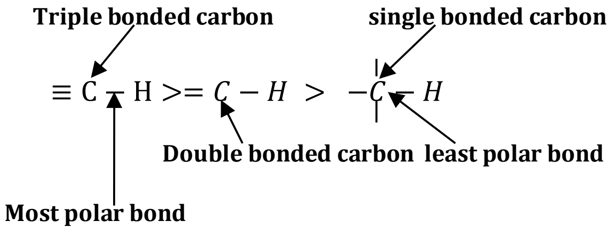
That is:

$$\underset{\textbf{Strongest electronegative}}{\text{C in triple bond}} > \text{C in double} > \underset{\textbf{weakest electronegative}}{\text{C in single bond}}$$

(The concept apply effectively in comparing electronegativity of atoms of the same element only)

High electronegativity of carbon with triple bond (as result of its highest percentage of s-character) explains why $\mathrm{C-H}$ bond in the carbon with triple bond is polar although normally the bond is non-polar.

- Generally the polarity of $\mathrm{C-H}$ bond is according to the following order.



$$\equiv \mathrm{C-H} >= C-H > -\overset{|}{\underset{|}{C}}-H$$

iii) The determination of bond length

Bond length (also termed as **bond distance**) *is the average distance between nuclei of two bonded atoms.*

- If bonded (fused) orbitals of atoms are closer to the nuclei of their respective atoms then the bond will be shorter and vice-versa.
- Since s-orbital is closer to nucleus than p-orbital, the hybrid orbital with greater percentage of s-character leads to shorter bond and vice-versa and this **explains why bond length of $\mathrm{C-C}$ is greater than $\mathrm{C=C}$ and that of $\mathrm{C=C}$ is greater than $\mathrm{C\equiv C}$. This is simply because**, C in $\mathrm{C-C}$ is sp^3 hybridised which has smaller percentage of s-character than sp^2 hybridised carbon in $\mathrm{C=C}$. And sp^2 hybridised carbon in $\mathrm{C=C}$ has smaller percentage of s-character than sp hybridised carbon in $\mathrm{C\equiv C}$.

DIGGING DEEPER EXERCISE 7

Question 1

For each of the entities listed, give the hybrid state of the selected atom(s) shown in the parenthesis beside it.

a) Iodine pentafluoride molecule(I)
b) Nitrous acid molecule (N)
c) Acetic (ethanoic) acid molecule(C_1 and C_2)
d) Hydrogen peroxide molecule(O)
e) Formic (methanoic)acid molecule(C)
f) Mercury(II) bromide molecule(Hg)

Question 2

Explain why PCl_5 exist while NCl_5 is not known.

Question 3

Why PCl_5 is more reactive than PCl_3?

Question 4

Indicate the type of hybridisation of orbitals by the central atom in each of the following:

a) SO_3^{2-}
b) SO_3
c) PCl_4^-
d) ClF_2^-
e) SCl_2

Question 5

What types of hybridised orbitals can be formed by elements of the third period that cannot be formed by elements in the second period?

Chapter 8

SHAPES OF COVALENT MOLECULES

A type of hybridisation gives geometry of the molecule. When the concept of hybridisation is combined with the valence shell electron pair repulsion (VSEPR) theory, geometric shape of various molecules and their bond angles can be described.

ELECTRON PAIR GEOMETRY AND MOLECULAR GEOMETRY

Geometry of a compound (or ion) may be **electron pair geometry** or **molecular geometry**.

- **Electron pair geometric shape** considers arrangement of **all bonded and unbonded electron pairs** (lone pairs) in a molecule of the compound

By definition:

Electron pair geometry *is the three dimensional arrangement of all electron pairs around the central atom.*

- On another hand, **molecular geometric shape** (or simply **molecular shape**) considers arrangement of atoms around the central atom. **It considers arrangement of bonded electron pairs only excluding unbonded electron pairs (lone pairs).**

By definition:

Molecular geometry *is the three dimensional arrangement of atoms around the central atom.*

- It can be deduced by eliminating lone pairs from electron pair(s) from electrons pair geometric shape leaving bonded electrons only.

Electron pair geometric shape only depend on the type of hybridisation

- It is not affected by presence or absence of lone pair. It remains the same provided that the types of hybridisation remain unchanged.

This is different to the molecular geometry whose shape and bond angle depend on the number of lone pair where the bond angle of molecules decrease with an increase in number of lone pairs.

- The decrease in the size of bond angle as the number of lone pair increases is due to increase in repulsion of lone pair-bonding pair electrons compared to the repulsion of bonding pair-bonding pair of electrons (as we will see later in the VSEPR theory).

Relationship between electron pair and molecular geometric shape

Molecular geometric shape of a molecular or ion can be directly deduced from its type of hybridisation. For example:

- Since the type of hybridisation of B in BF_3 is sp^2(trigonal planar hybridisation) its electron pair geometric shape will be automatically trigonal planar (with bond angle of 120°).

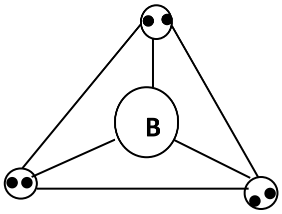


Figure: Electron pair geometric shape for BF_3

On another hand, molecular geometric shape is deduced from the electron pair geometric shape after eliminating non-bonded electron pairs.

- For example, in BF_3 case, all electron pairs where bonded and therefore nothing will be eliminated to get its corresponding molecular geometric shape.

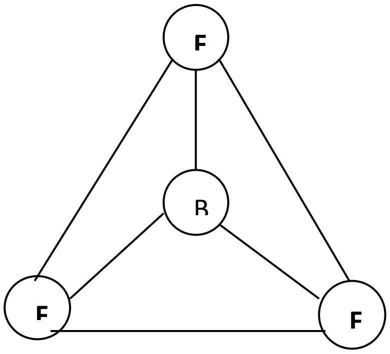


Figure: molecular geometric shape of BF_3

So the reader should understand that:

- In absence of lone pair, no line is eliminated from electron pair geometric shape and hence.

$$\textbf{Electron pair geometric shape} = \textbf{molecular geometric shape}$$

That is the case where there is no lone pair, what could happen in presence of lone pair?

In presence of lone pair, two things occur:

- Firstly some lines will not appear in the molecular geometric shape (compared to those present in the corresponding electron pair geometric shape) as result of the elimination of unbonded electron pair(s) from electron pair geometric shape. Remember that molecular geometric shape consider bonded electron pairs only.
- Secondly the bond angle will be distorted because bonded and non-bonded electron pairs exert different repulsion. This means that **in presence of lone pair the molecule can no longer be symmetrical it become asymmetrical** (also spelled unsymmetrical)

To have better understanding of the above two things consider shapes of SO_2.

- S in SO_2 is sp^2 hybridised and therefore its electron pair geometric shape will be trigonal planar as shown below (intentionally I'm going to use O in place of two dots(..) representing bonded electron pair to distinguish it from unbounded electron pair which will be represented by using the two dots as usual).

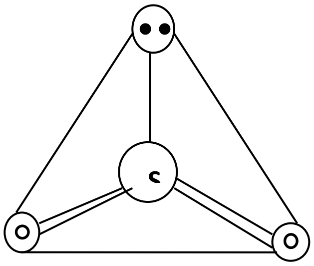


Figure: electron pair geometric shape of SO_2

- After eliminating the lone pair in the above electron pair geometric shape, molecular geometric shape is obtained which is bent-shape as shown below.

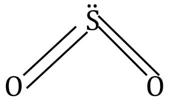


Figure: molecular geometric shape of SO_2

In the above case of the molecular shape, the bond angle is no longer 120° because lone pair and the bonded electrons exert different repulsion (in fact it is slightly less than 120° because lone pair exert stronger repulsion than bonded electrons as we will see later in the VSEPR theory).

So in absence of lone pair:

Electron pair geometric shape ≠ Molecular geometric shape

Be aware of this fact!

In geometry of covalent molecule, we are always more interested to understand the arrangement of atoms around central atom and therefore when you are asked just to give "the shape" of the molecule, always give **molecular geometric shape** and **not** electron pair geometric shape.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

VSEPR theory is helpful in understanding the modifications which are observed in the shape of molecule as result of presence of lone pair (s) in the molecule.

- It gives **qualitative** explanation on bond angles observed in covalent molecules (and some ions).

The VERPR theory was formulated by two scientists: **Sedgwick** and **Powell** and hence the theory is also known as **Sedgwick –Powell theory**.

Assumptions of valence shell electron pair repulsion (VSEPR) theory:

Assumption 1: Bonding orbitals tend to remain as widely separated from another as possible (so as to minimise repulsion between them).

Assumption 2: Lone pair orbitals exert a greater repulsion than bonding pair orbitals.

Assumption 3: Repulsion is increased by increase in electronegativity of the central atom.

According to VSEPR theory, repulsion between electron pairs is according to the following order:

Lone pair versus lone pair repulsion> lone pair versus bonding pair repulsion> bonding pair versus bonding pair repulsion.

- So the electron pairs will tend to arrange themselves around the central atom in such a way that there are fewest lone pair-lone pair interactions possible.

VSEPR theory explains arrangement of all electron pairs (bonded and unbonded) around the central atom and hence the term **VSEPR shape** for electron pair geometric shape.

- *Areas of high electron density such as bonds (single, double or triple) and lone pair of electrons are known as* **electron domains.**

So in simple terms ***VSEPR means that all electron bonding domains and electron non bonding domains around a central atom need to be positioned as far apart as possible in three-dimensional space.***

Don't over-expect!

VSEPR theory does not give **quantitative** explanation on bond angle.

- It cannot be used to predict the size of bond angle- never! It can only be used to explain observations made on size of bond angles; that is the reasons behind those sizes.
- However you may use the following rough estimation that every single **lone pair decreases the bond angle** by 2.5° from the expected bond angle in absence of lone pair. (But this is not always true; it may be just useful in the memorisation of some bond angle!) The rules hold more in absence of $\pi - \text{bond}$. In presence of π-bond the decrease in bond angle due to stronger repulsion of lone pair becomes smaller because π-bind exert stronger repulsion than sigma bond.

In absence of lone pair, bond angle of various geometric shapes is as follows;

Linear	180°	Trigonal planar	120°
Tetrahedral	109.5°	Trigonal bipyramidal	120° and 90°
Octahedral	90°		

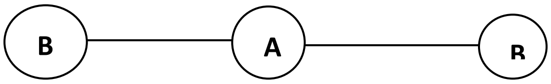
SHAPES OF MOLECULES AND IONS CATEGORISED ACCORDING TO THEIR TYPE OF HYBRIDISATION

1: sp-hybridisation

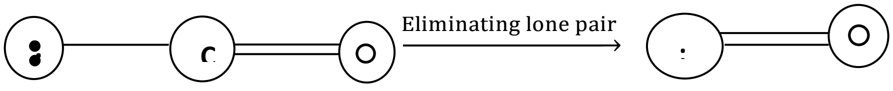
- Molecules with this hybridisation are **linear shaped**.
- If **A** stands for central atom, **B** for bonded electron pairs(or bonded atoms) and **E** for unbounded electron pair(lone pair) there are following possibilities of general form of molecules with sp-hybridisation:

i) $\mathbf{AB_2}$ for example $BeCl_2$

- Here both electron pair and molecular geometric shapes will be linear with bond angle of 180°



ii) **ABE** for example CO (By taking C as central atom) C in CO is double bonded to O with single lone pair it $(:C=O)$, therefore its shapes will be as follows: (Note: I will always use respective bonded atoms' symbol instead of two dots, **..**, to differentiate bonded electron pair from lone pair).



Electron pair geometric shape **Molecular geometric shape**

2: sp^2 – hybridisaition

- This type of hybridisation gives molecules (in absence of lone pair) with **trigonal planar shape**.
- Molecules with this type of hybridisation may take one of the following general forms:

i) $\mathbf{AB_3}$ for example BF_3

- Here both electron pair and molecular geometric shapes will be **trigonal planar** with **bond angle of 120°**.
- Molecules with this form are **symmetrical** (as each bonded electron pair exert the same strength of repulsion to each other) and hence are **non-polar** regardless to the nature of bonds present in the molecule.

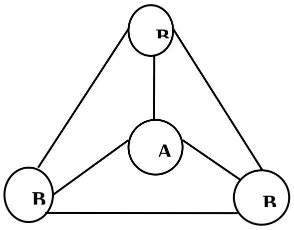
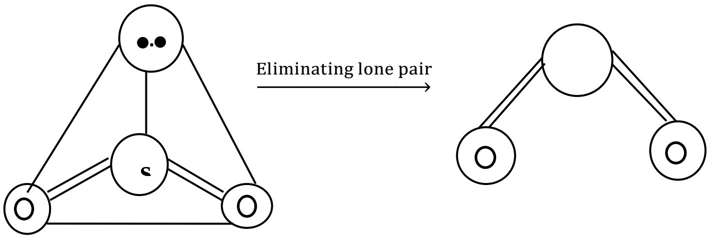


Figure: Electron pair and molecular geometric shape of AB_3

ii) $\mathbf{AB_2E}$ for example SO_2

- Here the molecular shape is changed into **bent** (**V** or **angular**) **shape.**



Electron pair geometric shape of SO_2

Molecular shape of SO_2

The reader should understand that:

Bond angle in SO_2 is 119° and not 117° as one could expect because the π-bond in SO_2 structure exert strong repulsion (stronger than sigma bond but slightly less than lone pair) and therefore there some degree of avoiding $\pi -$ bond repulsion as it avoid $\pi -$ bond - lone pair repulsion and hence the bond angle become closer to the ideal 120° (the expected bond angle in absence of lone pair)

- Another reason is the size of sulphur. Sulphur being large in size (accompanied with lower electronegativity), its pair of electrons are farther apart and hence smaller effect of the lone pair repulsion.

3: sp^3 Hybridisation

- This type of hybridisation (in absence of lone pair) gives **tetrahedral shaped** molecules:

- Molecules with this type of hybridisation may take one of the following forms:

i) $\mathbf{AB_4}$ for example CH_4

- As usual both electron pair and molecular geometric shape in this case are **tetrahedral** with **bond angle of 109.5°** .
- Again molecules with this general form are **symmetrical** and therefore **non-polar** regardless to the nature of their bonds (whether are polar or not).

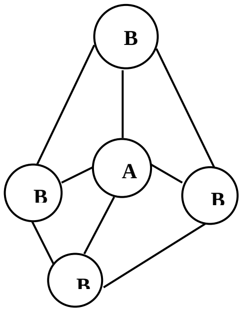
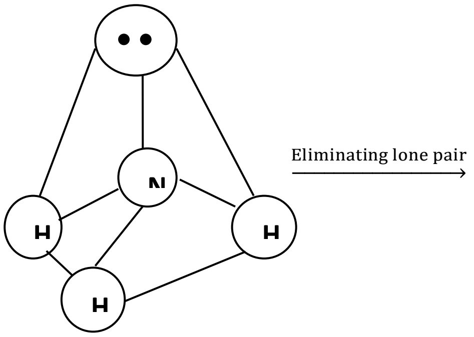


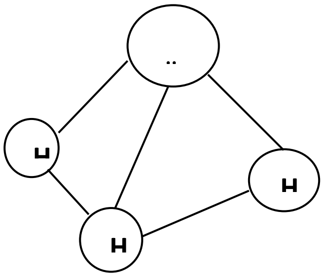
Figure: electron pair and molecular geometric shape of AB_4

ii) $\mathbf{AB_3E}$ for example NH_3.

- Here the molecular shape is **trigonal pyramidal** (or simply **pyramid** or **distorted tetrahedral**) with bond angle of about **107°** (**109.5° – 2.5°**).



Electron pair geometric shape of NH_3



Molecular shape of NH_3

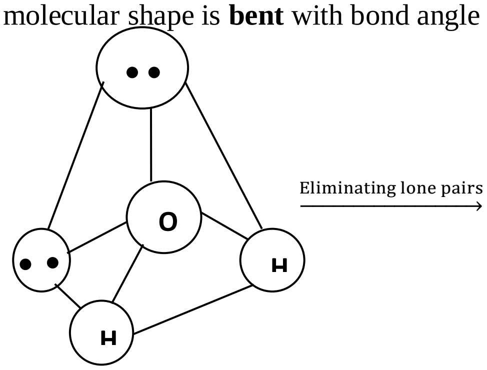
Another example of molecules (or ions) in general form of AB_3E is H_3O^+. NH_3 and H_3O^+ are **isoelectronic**.

Definition of isoelectronic species:

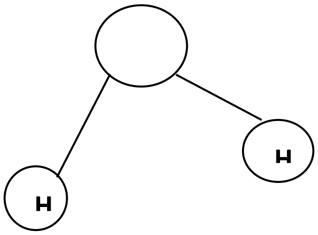
Are atoms, molecules or ions with exactly the same number and arrangement or electrons.

iii) **AB_2E_2** for example H_2O

In this case, the molecular shape is **bent** with bond angle of **104.5°** $(\mathbf{109.5^\circ} - (\mathbf{2 \times 2.5^\circ}))$



Electron pair geometric shape of H_2O



Molecular shape of H_2O

More examples

sp^3d hybridisation

- In absence of lone pair, this type of hybridisation give **trigonal bipyramidal shaped** molecules.

- Species with this type of hybridisation may take one of the following forms:

i) **AB_5** for example PCl_5.

- The shapes (of both molecular and electron pair geometry) of molecules in this form is **trigonal bipyramidal**.
- They are **symmetrical** and therefore **non-polar**.

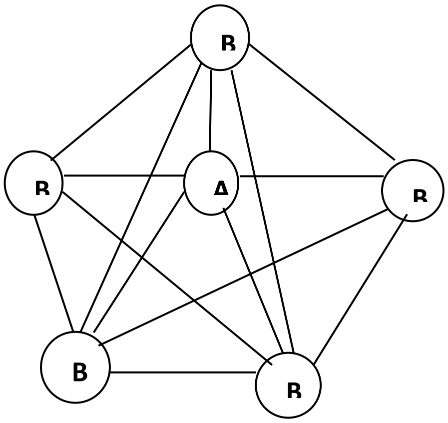
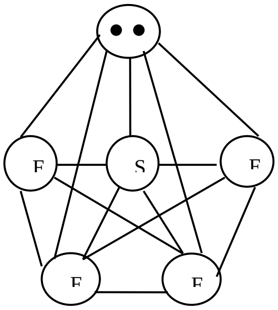


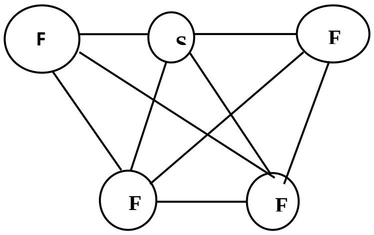
Figure: electron pair and molecular geometric shape for AB_5

ii) $\mathbf{AB_4E}$ for example SF_4.

- In this form, the molecular shape is **unsymmetrical tetrahedral** (or **see-saw shape**)



$\xrightarrow{\text{Eliminating lone pair}}$

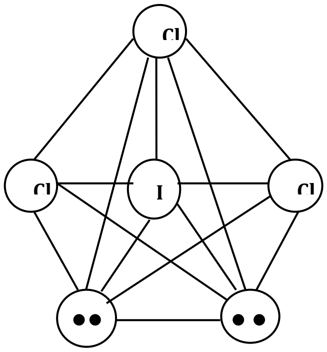


Electron pair geometric shape of SF_4

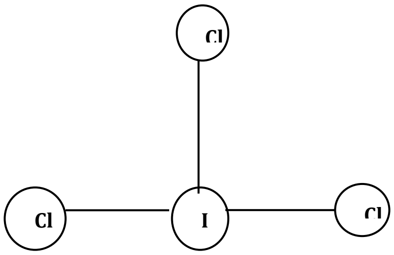
Molecular geometric shape of SF_4

iii) $\mathbf{AB_3E_2}$ for example ICl_3.

- In this case, the molecular shape is **T-shape**.



$\xrightarrow{\text{Eliminating lone pairs}}$

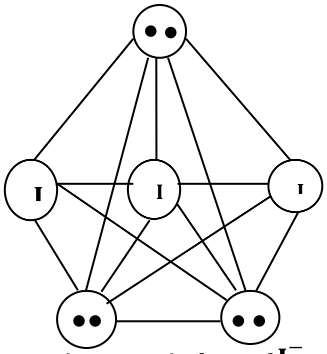


Electron pair geometric shape of ICl_3

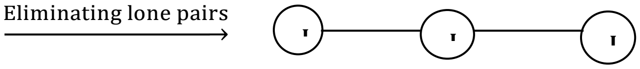
Molecular shape of ICl_3

iv) $\mathbf{AB_2E_3}$ for example I_3^-

- In this case, the molecular shape is **linear**.



Electron pair geometric shape of I_3^-



Molecular shape of I_3^-

sp^3d^2 hybridisation

- This type of hybridisation gives **octahedral shaped** molecules in absence of lone pair.

- Species with this type of hybridisation may take one of the following forms:

i) **AB_6** for example SF_6

- The shape of molecules in this form is **octahedral.**
- They are **symmetrical** and therefore **non-polar**.

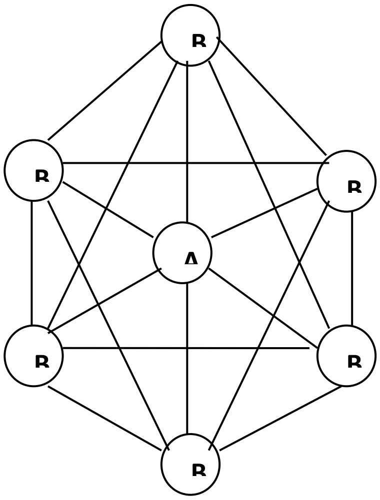
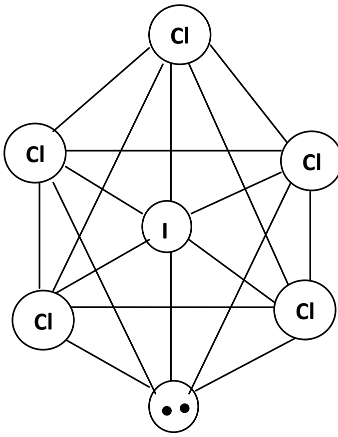


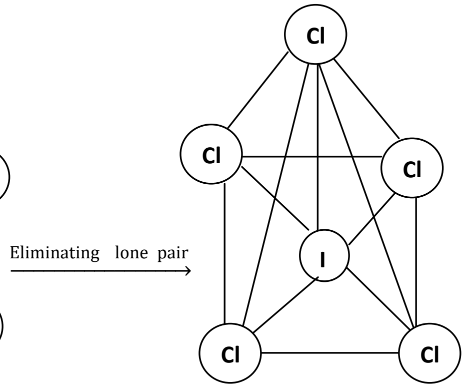
Figure: Electron pair geometric shape of AB_6

ii) **AB_5E** for example ICl_5

- In this form, the molecular shape is **square pyramid.**



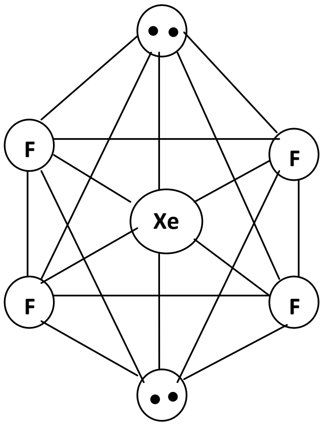
Electron pair geometric shape ICl$_5$



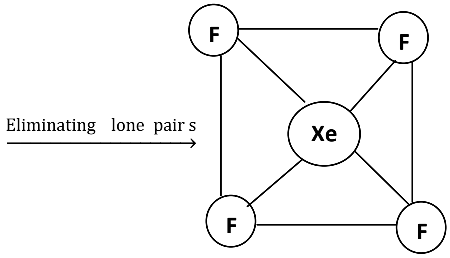
Molecular shape of ICl$_5$

iii) $\mathbf{AB_4E_2}$ for example XeF_4

In this forms, the molecular shape is **square planar.**



Electron pair geometric shape of XeF_4



Molecular shape of XeF_4

Example

Arrange the following molecules in order of increasing of their bond angles:

$$CH_{4,} H_2O, NH_3$$

Solution: CH_4 has no lone pair

H_2O has two lone pairs

NH_3 has one lone pair

Thus $\underset{\text{Increase in bond angle}}{\xrightarrow{H_2O, NH_3, CH_4}}$

DIGGING DEEPER EXERCISE 8

Question 1

Arrange the following entities in order of increasing bond angle between a non-central atom, the central atom and a non –central atom: carbonate ion, carbon tetrachloride molecule, water molecule and hydrogen cyanide molecule.

Question 2

On the basis of Sidgwick -Powell theory, describe and explain the shape of BF_3.

Question 3

On the basis of VSEPR theory, describe and explain the shape of nitrosyl chloride$(NOCl)$ molecule.

Question 4

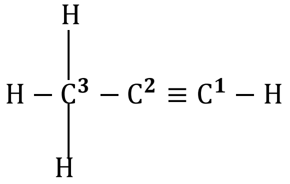
Using VSEPR model, predict molecular geometry (molecular shape) and electron geometry of the following:

a. CO_3^{2-}
b. ICl_2^-
c. NF_3
d. $SiCl_3^-$

Question 5

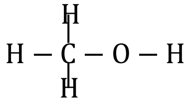
Predict the approximate value for the bond angles for each carbon indicated in the following compounds:

a)



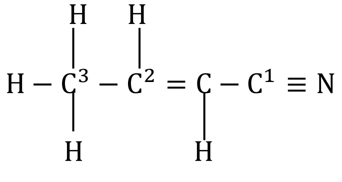
$H-\overset{H}{\underset{H}{C^3}}-C^2\equiv C^1-H$

b)



$H-\overset{H}{\underset{H}{C}}-O-H$

Question 6
Consider the following molecule



$H-\overset{H}{\underset{H}{C^3}}-\overset{H}{C^2}=\underset{H}{C}-C^1\equiv N$

For each of the marked carbons

i. Give type of hybridisation
ii. Predict the molecular geometry and electron geometry around each marked carbon.
iii. Predict the bond angles

Question 7

Use VSEPR theory to predict the shape of the following molecules:

a) BrF_5 b) HCN c) SCl_2

Question 8

Predict the approximate bond angle in the following:

a) $SiCl_2$ b) IF_4^- c) SCl_4

Question 9

CCl_4 is a perfect tetrahedron, but PCl_4^- is distorted tetrahedron. Explain.

Question 10

Arrange the following species in order of decreasing bond angle:

NH_2^-, NH_3, NH_4^+

Give reason(s) for your arrangement.

Chapter 9

INTERMOLECULAR FORCES

INTRODUCTION

Intermolecular forces of attraction *are electrostatic forces of attraction holding different molecules together*.

- This is the one which determine most of physical properties of pure substances or mixtures.

Strength of intermolecular force of attraction is the one which determine physical state of substances.

- Solid substances are said to have strong intermolecular forces of attraction.
- Liquid substances are said to have weak intermolecular forces of attraction.
- Gaseous substances are said to have no intermolecular forces of attraction.

When physical state of a substance is changed, a kind of force in the substance which is altered is the intermolecular forces of attraction.

- For example to change the physical state of the substance from solid to liquid and then liquid to gas, the following change occurs:

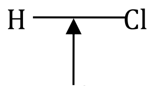
$$\text{Solid} \xrightarrow{\text{weakening intermolecular forces}(\textbf{melting})} \text{Liquid} \xrightarrow{\text{Eliminating intermolecular force}(\textbf{boiling})} \text{Gas}$$

Generally in most cases, physical change occurs as result of altering intermolecular forces of attraction.

Intermolecular forces versus interatomic forces

As we had studied before, **interatomic forces** *are electrostatic force of attraction holding atoms in a molecule (or a crystal) together.*

- They are actually **chemical bonds** in the molecule. For example a molecule of HCl, the bond (in this case covalent bond) which hold H and Cl atom together is what we call interatomic forces and hence the **terms chemical bond** and **interatomic forces** may be used interchangeably.



Chemical bond (inter atomic forces holding H and Cl in HCl molecule)

- Another way of explaining this is that, interatomic forces are electrostatic force of attraction occurring within the same molecule and hence the term **intramolecular forces** (**of attraction**) as the alternative term for **interatomic forces** (**of attraction**).
- Interatomic forces are also known as **primary bonds**

On another hand **intermolecular forces** (also known as **secondary bonds**) occur between different molecules. To have good understanding of this let us return to our example of HCl.

- In HCl, one may consider HCl being polar due to high electronegativity of Cl compared to H.Thus there is slight positive charge and negative charge on H and Cl respectively.

$$H^{\delta+}Cl^{\delta-}$$

- The one may consider that, in presence of different molecules of HCl, there will be electrostatic force of attraction between opposite partial charges of different molecules and therefore resulting to intermolecular forces of attraction.

$$- - -\mathrm{H}^{\delta+}\!\!-\!\!-\!\!-\!\!-\mathrm{Cl}^{\delta-} - - - \mathrm{H}^{\delta+}\!\!-\!\!-\!\!-\mathrm{Cl}^{\delta-} - - - \mathrm{H}^{\delta+}\!\!-\!\!-\!\!-\mathrm{Cl}^{\delta} - - -$$

Where: —— (full line) stand for interatomic forces (in this case covalent chemical bonds).

− − − (dotted line) stands for intermolecular forces.

When HCl undergoes physical change, say liquid HCl is boiled to gaseous HCl, intermolecular forces of attraction (− − − and not ——which are chemical bonds) are broken to form individual un-interacted molecules of HCl. For example if 2n molecules of HCl interacted to form liquid molecules of HCl; after boiling 2n individual un-interacted molecules of HCl will formed.

$$\mathbf{n}\ \mathrm{H}^{\delta+}\!\!-\!\!-\!\!-\!\!-\mathrm{Cl}^{\delta-} - - - \mathrm{H}^{\delta+}\!\!-\!\!-\!\!-\mathrm{Cl}^{\delta-} \xrightarrow{\text{Boiling}} \mathbf{2n}\mathrm{H}\!\!-\!\!-\!\!-\mathrm{Cl}$$

Liquid (There is intermolecular forces) **Gas (There is no intermolecular forces)**

In the above example, chemical composition of HCl remain unchanged as the chemical bond (covalent bond) in $\mathrm{H}-\mathrm{Cl}$ remain unaltered in the boiling process. And this is the general fact that in the physical change only intermolecular forces are changed and not interatomic forces (chemical bonds). *That is all about physical change, what about chemical change?*

Returning to our example of HCl; now considers the thermal decomposition of HCl into $\mathrm{H_2}$ and $\mathrm{Cl_2}$ which is the chemical change.

- In this case to make H and Cl unbonded, we have to break the chemical bond (interatomic force) between the two atoms.

$$2\ \mathrm{H}\!\!-\!\!-\!\!-\mathrm{Cl} \xrightarrow[\text{Heating}]{} \mathrm{H_2} + \mathrm{Cl_2}$$

(There are inter atomic forces between H and Cl) **(No interatomic forces between H and Cl)**

- And hence as the rule: interatomic forces (chemical bonds or intramolecular forces) are always broken during the chemical reaction.

Interesting fact to understand!

In most cases, interatomic forces are stronger than intermolecular forces of attraction and this explain why physical changes always occur in preference to chemical change.

- To have good understanding of all possibilities (of physical and chemical changes) consider hypothetical compound AB (l) which is formed from hypothetical elements $\mathrm{A_2(g)}$ and $\mathrm{B_2(g)}$.
- Assume liquid AB boil at certain temperature say $\mathrm{T_1}$ while decompose at another temperature say $\mathrm{T_2}$.
- If intermolecular forces of attraction between molecules of AB are weaker than interatomic forces between atom A and B in AB (as usual), then the boiling temperature $(\mathrm{T_1})$ will be lower than decomposition temperature $(\mathrm{T_2})$ and hence boiling of AB occurs before its decomposition.

Therefore in this case it becomes possible to get gaseous AB. That is about a usual case, what is about unusual case?

- If intermolecular forces between molecules of AB are stronger than interatomic forces between atoms A and B in AB, the boiling temperature (T_1) will be higher than decomposition temperature (T_2) and hence decomposition of AB will occur before its boiling. In this case it will be impossible to get gaseous AB. Any attempt to boil AB will result to $A_2(g)$ and $B_2(g)$ and not $AB(g)$!
- The occurrence of chemical change in preference to physical change is more common in melting of some substances like **thermosetting plastics** which tend to decompose before melting to liquid.

After that interesting discussion, let us summarise differences between interatomic forces and intermolecular forces.

INTERATOMIC FORCES		INTERMOLECULAR FORCES	
01	Force between atoms	01	Force between molecules
02	Strong force	02	Relatively weak force
03	Very short distances between atoms	03	Larger distance (between molecules)
04	Occurs within the same molecule	04	Occurs between different molecules
05	Affect chemical properties.	05	Affect physical properties

Evidences of presence of intermolecular forces of attraction

Every substance possesses some intermolecular forces of attraction. Even substances which we consider them as gases, they have some intermolecular forces; that is why they can be liquefied (at very low temperature and high pressure) by strengthening those intermolecular forces. Below are some evidences of presence of intermolecular forces:

- **Presence of different physical states of matter** (as explained earlier).
- **Imperfection of gases, i.e. no gas is perfect or ideal** (this is explained in a **physical chemistry book of the Ngaiza's series**).
- **Characteristic of the solution whether is ideal or not** (this is also explained in the **physical chemistry book of the Ngaiza's series**).

TYPES OF INTERMOLECULAR FORCES OF ATTRACTION

Types in pure substances:

A pure substance may be an **element** or **compound**. Whereas an element may be:

- Metal
- Giant non-metal (e.g. carbon or silicon)
- Simple non-metal (e.g. oxygen or iodine)
- Metalloid (boron, silicon, germanium, arsenic and tellurium) or
- Noble gas

And the compound may be:

- Ionic
- Giant covalent (e.g. silicon dioxide or silicon carbide)
- Simple covalent (e.g. water or ammonia)

Collectively:

- Metals, giant non-metals (and some metalloids like silicon), ionic compounds and giant covalent compounds are **substances with complex structures** and therefore have very strong physical properties.
- Simple non-metals, noble gases and simple covalent compounds are **substances with simple structures** and therefore have weak physical properties.
- Types of intermolecular force in substances with complex structures are:
    i) Metallic bonds (in metallic structure)
    ii) Ionic bonds or ion-ion interaction (in ionic compounds)
    iii) Giant covalent bonds(in giant covalent network structures of giant non-metals, some metalloids and giant covalent compounds)

Be aware of this fact:

The three above are very strong intermolecular forces and are actually **chemical bonds.**

- Those forces act as both interatomic forces as well as intermolecular forces and hence they determine both physical and chemical properties of the substances (unlike in the common observation explained earlier which will be witnessed in the weak intermolecular forces of substances with simple structures).

Types of intermolecular forces in substances with simple structure are:

i) Permanent dipole-dipole interactions or forces
ii) Induced or temporary dipole-dipole interactions (or forces)
iii) Hydrogen bonds

Be aware of this difference:

- Here the three types above are **weak intermolecular forces** between simple molecules and are not chemical bonds in reality!
- Instead sometimes are referred as **physical bonds** (they have effect only on physical properties and not chemical properties).The term intermolecular forces were commonly used for these weak forces.

Putting all weak intermolecular forces together!

Intermolecular forces between simple molecules are collectively known as Van der Waals forces.

So by definition:

Van der Waals forces *are the weak electrostatic force of attraction between opposite dipoles in two different molecules.*

- However commonly the term is used for induced dipole-dipole forces (to differentiate it from dipole-dipole forces and hydrogen bonds).

Combining all types of intermolecular forces in pure substances!

This gives the following types of intermolecular forces:

i) Metallic bonds
ii) Ionic bonds
iii) Giant covalent bonds
iv) Permanent dipole-dipole forces
v) Temporary dipole-induced dipole forces
vi) Hydrogen bonds

Metallic bonds

Metallic structure are generally visualised as solid consisting of fixed cations held in place by mutual attractions for a sea of valence electrons.

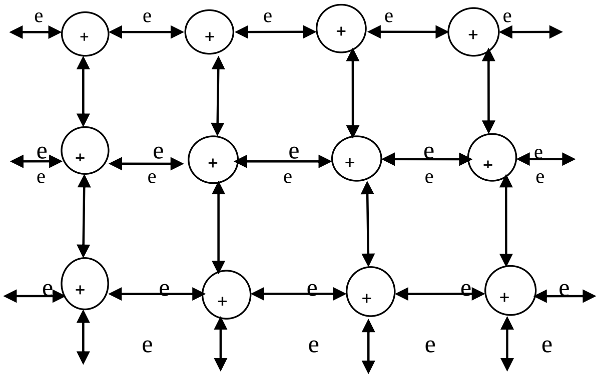


Figure: Two dimensional representation of metallic bond in the metal lattice

- When the metal is melted by heating, the metal lattice is broken.

  The metallic bonds are very strong intermolecular forces and this explains why generally metals are solid with high melting and boiling point. Metals with strong metallic bond have high melting point which make them to be hard while metals with weak metallic bond have low melting point which make them to be soft.

- Also metals with strong metallic bond have high boiling point and density.

Example 1

Magnesium is the hard metal while sodium is soft. Explain

Solution

Magnesium has stronger metallic bond as result of its smaller metallic radius and greater number of valence electrons (Mg has two valence electrons while Na has one), and hence the metal has higher melting point.

Example 2

Between Lithium and potassium which one has higher melting point? Give reasons(s) for your choice.

Solution

Lithium has higher melting point.

Reason

Li being on the top of group I has smaller metallic (atomic) radius leading to its stronger metallic bond and hence the metal has higher melting point.

Ionic bonds

Ionic bonds or **ion-ion interactions** *is the electrostatic force of attraction between cation (positively charge ions) and anions (negatively charge ions) in ionic compound.*

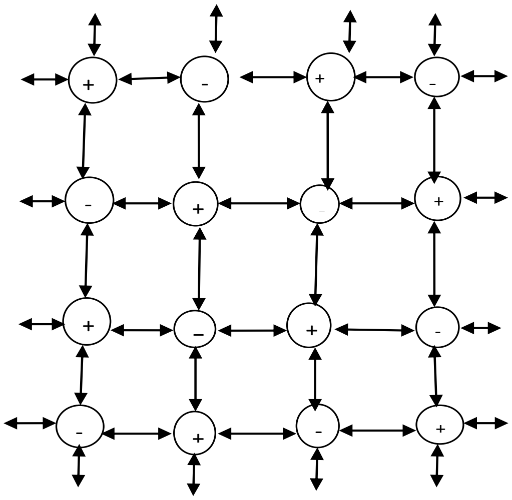


Figure: two dimensional representation ion-ion interactions in ionic lattice

- When the ionic compound is melted by heating, ionic lattice is broken as result of weakening the electrostatic force of attraction in ion-ion interactions.
- The ion-ion interactions in ionic bonds are very strong and explain why ionic compounds have very strong physical properties like:
  - Having high melting point
  - Having high boiling point
  - Being solids etc

Giant covalent bond

Giant covalent bond *is the force holding a lot of non-metallic (or metalloid) atoms in the giant covalent structure.*

- It may occur in elements or compounds.

Conditions which favour the formation of giant covalent bond in the elements are:

- Presence of four valence electrons in atoms of the element (This gives the possibility of forming network of covalent bond with stable octet structure).
- Small size of atoms of the element (This enables the formation of strong covalent bond).

Note: The same conditions apply for the formation of giant covalent compounds.

So the formation of giant covalent bond is common in group IVA elements (which have four valence electrons).

- And among group IVA elements themselves, carbon (more specific in its allotropic form of diamond) has greatest ability to form giant covalent bond because it has smallest atomic size in the group.
- The ability of carbon to form strongest giant covalent bond explains why diamond is the hardest natural substance.

Basically the formation of giant covalent bonds is well witnessed in carbon and silicon.

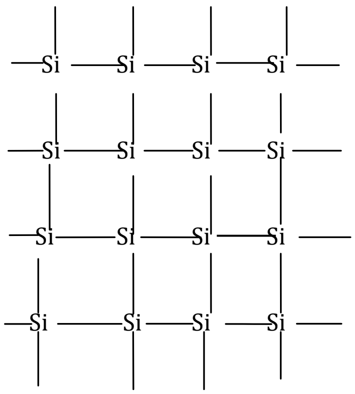


Figure: two dimensional representation of giant covalent bonds in silicon

A good example of giant covalent bond network structure of compounds is in SiO_2 as shown in the figure below (Another example is silicon carbide (SiC).

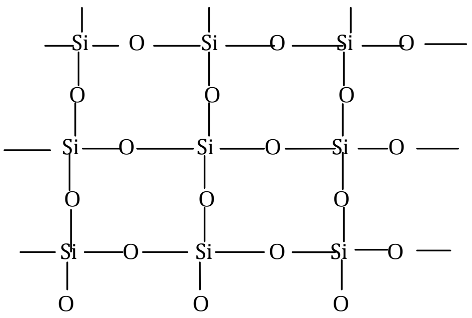


Figure: two dimensional representations of giant covalent bonds in silicon (iv) oxide

Two important things to note in the formation of giant forces in SiO_2:

- Each isolated molecule of silicon (iv) oxide (silicon dioxide) has two single bonds $(Si - O)$ which is equivalent to four valence electrons in silicon (Each covalent bond consist of pair of electrons). Adding with fact that, silicon has relatively small size, the formation of giant covalent bonds is assured in the SiO_2.
- The size of Si is not too small to enable the formation of double bond (pi bond) with oxygen, if this would occur, there would be 8 valence electron about Si and therefore SiO_2 could not form giant covalent bonds .
- The formation of double bond as barrier for the formation of giant covalent bond is witnessed in $CO_2(O = C = O)$ where there are 8 valence electrons about carbon and hence CO_2 cannot form giant covalent bonds like CO_2 (remember: carbon has smaller atomic size than silicon and therefore has greater ability to form pi bond).

Substances with giant covalent bonds (giant forces):

- **Have very high melting and boiling point.** (Very high temperature is needed in the process of breaking very strong giant covalent bonds).
- **Are very hard** (It is very difficult to break the giant forces).
- **Are highly insoluble** in water and most of common solvent. (There is no attraction between the solvent and substance which will release enough heat to break the giant covalent bonds).

Permanent dipole-dipole forces

Permanent dipole-dipole forces (also written as **permanent dipole-permanent dipole** or simply **dipole-dipole forces**) occur between polar molecules.

- The larger the net dipole moment of the molecule the greater the dipole-dipole forces between molecules.

Permanent dipole-dipole forces were discovered by a Dutch physicist, Keesom hence the term **Keesom forces** for permanent dipole-dipole forces.

By definition:

Dipole-dipole forces *are the intermolecular forces of attraction between oppositely charged ends of a polar covalent molecule.*

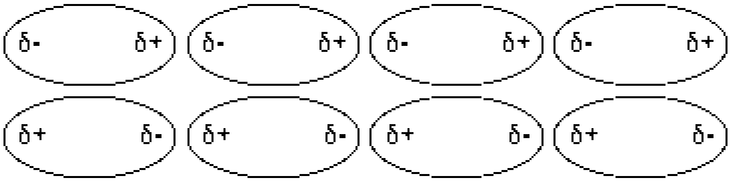


Figure: dipole-dipole forces

Don't forget that:

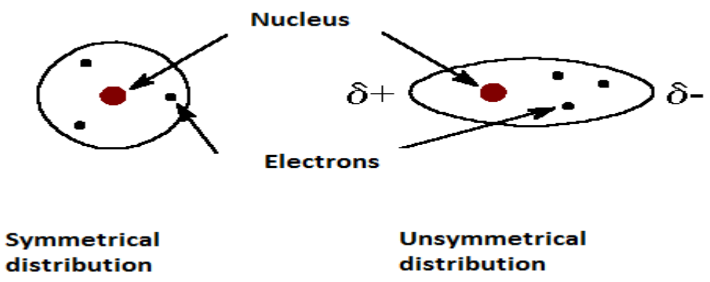
The polarity of a molecule depends on both the shape and the polarity of the bonds.

- If there are no polar bonds, the molecule will be non-polar regardless to its shape.
- If there are polar bonds, but the shape is symmetrical, the molecule will be non-polar because the dipole moment will be cancelled by symmetry.
- If there are polar bond, and the molecule is unsymmetrical the molecule will be polar (there will be a positive pole and a negative pole and the whole molecule will act as a **dipole**).

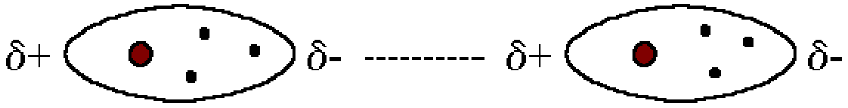
Temporary dipole-dipole forces

In non-polar molecules the net dipole moment is zero. However many non-polar molecular substances including atomic noble gases can be liquefied at low temperature and high pressure. The non-polar bromine is a liquid and iodine is even a solid at room temperature. Hence there must be considerable forces of attraction which keeps non-polar molecules or even atoms together. *Where are these forces coming from?* Don't worry, below is the explanation of it!

- The electrons in a molecule or an atom are in continuous motion. At any particular moment, the electron charge cloud around the nucleus will not be perfectly symmetrical.



- As result the molecule acquires more negative charge on one side of the molecule than another side and hence it possesses an instant dipole. This temporary dipole will induce dipole in neighbouring molecules (because electrons repel one another). As result, the positive end of the neighbour molecule or atom will be pointing towards a negative of the original dipole thus leading to the electrostatic force of attraction between them.

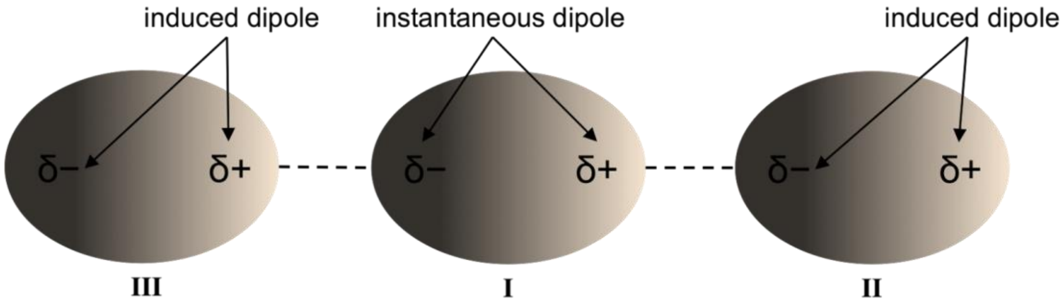


The forces explained above are what we call **temporary** (or **instantaneous**) **dipole-dipole forces** (also written as **temporary dipole-temporary dipole forces**).

- Since the forces are initiated by instantaneous (or temporary) dipole and thereafter inducing dipole to another non-polar molecule or uncharged atom, they are also known as **instantaneous** (or **temporary**) **dipole-induced dipole forces**.
- They are also termed as **induced dipole-induced dipole forces**; **transitory forces** or more common are known as **dispersion forces**.
- They were discovered by German physicist Fritz **London** and hence the term **London dispersion forces** or simply **London forces** for the dispersion forces.

By definition:

London forces *are forces of attraction between induced dipoles.*



London dispersion forces are good explanation for presence of intermolecular forces in non-polar covalent molecules and uncharged atoms like noble gases.

The reader should be aware of this!

All covalent molecules and uncharged atoms have dispersion forces regardless of whether they have other form of intermolecular forces or not.

- Polar covalent molecules which have either dipole-dipole forces or hydrogen bonding are just an additional to the dispersion forces they already have.
- For non-polar covalent molecules these forces are the only intermolecular forces.

So among the three Van der Waals forces (permanent dipole-dipole, dispersion forces and hydrogen bonds), dispersion forces is more common and therefore the **term Van der Waals forces is commonly used to imply the dispersion forces**. For the same reason dispersion forces is also termed as **Van der Waals dispersion forces**.

Factors affecting strength of Van der Waals dispersion forces

There are two main factors which affect the strength of Van der Waals dispersion forces which are

i) Number of electrons

- Greater number of electrons in the molecule or atom means greater possibility of forming temporary dipole as there is **more movement of electrons** in the molecule (atom) of many electrons than in the molecule(or atom)with fewer of them.

ii) Surface area

- A molecule (or atom) with **greater surface area over which electrons can move** has greater possibility of forming temporary dipoles and hence stronger Van der Waals dispersion forces.

Combining the two factors

All the two factors (number of electrons and surface area) increase simultaneously with the increase in molecular weight (or atomic weight for atom).

- **Molecule with greater molecular weight or atom with greater atomic weight has greater number of electrons and larger surface area as well.**

So in other words we can conclude that:

- **Van der Waals dispersion forces increases with an increase in the molecular weight.**

Extra factor for organic compounds

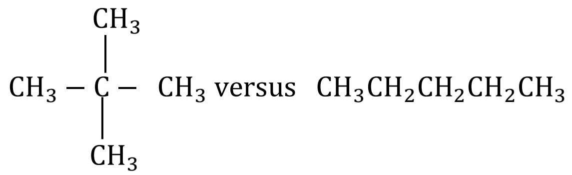
There is another factor which has small effect on the strength of Van der Waals dispersion forces in the organic compounds. The factor is **the shape of organic molecule**.

- This is because even isomers (have the same molecular formula and therefore the same molecular weight) of an organic compound are found to have slight difference in their boiling point.
- With two organic compounds of the same molecular formula as well as the same molecular weight, the more branched isomer has slightly weaker Van der dispersion forces due to the following reasons:

  i) The more branched carbon chain has smaller surface area because it is more spherical in shape

  ii) The more branched carbon chain has poor package of carbon atoms in space leading to poor package of carbon chains because the branched chains are more loosely packed (It is easier to have very close or more compact packing between adjacent carbon chains which are unbranched than branched ones). Remember that for Van der Waals forces to be strong the molecules must be as close as possible.

For example:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 \text{ versus } CH_3CH_2CH_2CH_2CH_3$$

- Although both have the same molecular weight with the same molecular formula of (C_5H_{12}) the former (which is more branched) has lower boiling point which means has weaker Van der Waals dispersion forces.

Don't get confused!

- The fact does not hold if the two organic compounds have different molecular formula and therefore different molecular weight.
- The compound with greater molecular weight has stronger Van der Waals dispersion forces regardless to whether is more branched or not.

London dispersion forces versus dipole-dipole forces

Sometimes you will meet with cases where there is a competition between London dispersion and dipole-dipole forces. For example HCl versus HI;

- Cl being more electronegative than I, is more negative polarised(and of course H in HCl is more positive polarised for the same reason) and therefore HCl has stronger dipole-dipole forces than HI. That is about dipole-dipole forces, *what about the dispersion forces?*
- HI having greater molecular weight has stronger London dispersion forces than HCl. *Have you seen the contradiction?* That is the compound (HCl) which has stronger dipole-dipole forces, has weaker London dispersion forces! Now the question is ***between*** HCl ***and*** HI ***which one has overall stronger intermolecular forces?***

To answer that contradicting question, we must look for some useful experimental observation like their boiling point.

- Since boiling point of $HI(-34°C)$ is greater than that of $HCl(-85°C)$, HI have stronger intermolecular forces. This means the London dispersion forces has won the battle over dipole-dipole forces.

And that fact does not hold just for HCl and HI only, it is general rule that: **Effect of London dispersion forces is stronger than the effect of dipole-dipole forces.**

WARNING!

The reader should take this warning very seriously because there is very common misconception here!

- Don't be misled by most of authors who mention that dipole-dipole forces are stronger than the dispersion forces. That is totally misconception!

Now you may ask yourself this little challenging question. If wherever there is dipole-dipole forces there is also London dispersion forces and always the dispersion forces outweighs dipole-dipole forces, what is the use of the later? Don't worry; here is the clear explanation of it!

- Dipole-dipole forces are not worthless despite the fact that the dispersion force outweighs it in the competition!
- Its effect comes into account when comparing strength of intermolecular forces in the compound with similar dispersion forces.
- For example CH_3F (Molecular weight $= 34$) has similar strength of the dispersion forces to CH_3CH_3(Molecular weight $= 30$) but boiling point of the former (-78.3°C) is higher than that of the later (-88.5°C) suggesting that CH_3F has stronger intermolecular forces of attraction than CH_3CH_3.This is because in additional to the dispersion forces (which have similar strength in both compound) CH_3F has dipole-dipole forces(due to presence of polar bond, $C^{\sigma+} - F^{\sigma-}$) where CH_3CH_3 has only the dispersion forces.

- To make things clearer we may conclude that:

  If two compounds (polar and non-polar) have similar molecular weight (their molecular weight does not differ much) then the polar covalent compound will possess stronger intermolecular forces of attraction because it has dipole-dipole forces in additional to the London dispersion forces which both have.

BUT

If the non-polar covalent compound has much greater molecular weight will possess stronger intermolecular forces although has no dipole-dipole forces.

- To put more evidence to the point, consider the experimental values of boiling point of some alkanes and fluoroalkanes shown in the table below:

Fluoroalkane	B.pt (°C)	Alkane	B.pt (°C)
$CH_3F(Mwt = 34)$	-78.3	CH_3CH_3 $(Mwt = 30)$	-88.5
CH_3CH_2F $(Mwt = 48)$	-37.1	CH_3CH_2 CH_3 $(Mwt = 44)$	-42

Two things to note from above table:

- In each pair of fluoroalkane (polar covalent compound) and alkane (non polar covalent compound) where the two have almost the same molecular weight and therefore the similar strength of dispersion forces, fluoroalkane has slight higher boiling point (surprisingly this fact has also an exceptional for bigger molecule and its explanation is beyond the scope of this book!).
- Although $CH_3CH_2CH_3$ is non-polar has higher boiling point than CH_3F (polar) due to its much greater molecular weight and therefore stronger dispersion forces. This also justify that the dispersion forces has greater effect than dipole-dipole as explained earlier.

Two final sentences to conclude about comparison of strength between dipole-dipole force and dispersion forces:

- *The contribution made to the total Van der Waals forces by dipole-dipole forces is usually small.*
- *The contribution made to the total Van der Waals forces by dispersion forces is very large by far.*

Hydrogen bonds

Since hydrogen is very small, its positive pole is highly concentrated and therefore has very large ability of attracting the negative pole (partially negatively charged atom) of neighbor molecule.

- This effect is observed when there is large electronegativity difference between hydrogen and another covalent bonded atom.

Dipole-dipole interaction (forces) experienced when hydrogen atom (H) is bonded to nitrogen (N), oxygen (O) or fluorine (F) are exceptionally strong.

These very strong interactions are known as **hydrogen bonds**. It is the special case of dipole-dipole forces whereby the positive pole is hydrogen.

By definition:

Hydrogen bonding *is the special type of intermolecular forces between the partially positively charged hydrogen atom in a polar bond and lone pair (non-bonding electron) on a nearby small electronegative ion or atom mainly* F, O *or* N.

- It can also simply be defined as *the electrostatic force of attraction between partial positively charged hydrogen atom and lone pair of neighbour atom.*

Conditions which favour formation of hydrogen bonding

(i) Hydrogen atom must be bonded to highly electronegative atom usually fluorine, oxygen or nitrogen.
(ii) The electronegative atom, to which the hydrogen bonds must possess at least one lone pair of electrons.

Factors affecting strength of hydrogen bond

There are two main factors which determine strength of hydrogen bond. These are:

i) Electronegativity difference between hydrogen atom and strong electronegative atom bonded to it.

- If the electronegative atom bonded to the hydrogen atom is stronger electronegative, then the hydrogen atom will be more positively charge. This will lead to greater attraction between the positive hydrogen and lone pair of the strong electronegative atom of the neighbour molecule and hence stronger hydrogen bonding .That is **larger electronegativity difference means stronger hydrogen bonding.**

ii) Number of hydrogen bonds which can be formed per molecule.

- Greater number of hydrogen bonds a compound can form per its molecule means stronger hydrogen bonding.
- On another hand number of hydrogen bonds depends on the number of lone pair and number of hydrogen atoms bonded to the atom with lone pair (atom with high electronegativity).

- If a molecule has strong electronegative atom with **greater number of lone pairs accompanied with greater number of hydrogen atoms**, then there will be stronger hydrogen bonding.

To have better understanding of the above two factors consider the following comparison of strength of hydrogen bonding.

First comparison: H_2O versus NH_3

- H_2O has two lone pairs on oxygen accompanied with two hydrogen atoms bonded to the oxygen atom. That means **H_2O can form two hydrogen bonds per molecule**.
- Although NH_3 has three hydrogen atoms bonded to a nitrogen atom, has only one lone pair on the nitrogen atom. So there is no enough lone pairs to satisfy all hydrogen atoms and hence NH_3 **can form only one hydrogen bond per molecule.**

Conclusion on the comparison:

Since H_2O can form two hydrogen bonds per molecule while NH_3 can form only one hydrogen bond per molecule, there is stronger hydrogen bonding existing between molecules of H_2O than that existing between molecules of NH_3.

Second comparison: H_2O versus HF

- H_2O can form two hydrogen bonds per molecules as we have seen earlier.
- Although HF has three lone pairs on a fluorine atom, has only one hydrogen atom on the fluorine atom. So number of lone pair does not match with number of hydrogen atoms and therefore **HF can form only one hydrogen bond per molecule.**

Conclusion……………..!

Since H_2O can form greater number of hydrogen bonds (two hydrogen bonds) per molecule than HF (which form only one hydrogen bond per molecule), molecules of H_2O experience stronger intermolecular hydrogen bonding than molecules of HF.

Third comparison: HF versus NH_3

- As we have seen earlier, both HF and NH_3 can form only one hydrogen bond per molecule.
- But since F is more electronegative than N, there is larger electronegativity difference between H and F than between H and N and hence molecules of HF experience stronger hydrogen bonding than molecules of NH_3.

It is worth to understand this factor too!

Another factor which affects strength of hydrogen bond is the atomic size of the atom with lone pair. The atom with lone pair must be very small in size for the hydrogen bonding to be strong. *In large atom, lone pairs are too diffuse (take large area) to be attracted by partial positively hydrogen and hence weaker hydrogen bonding.*

DIFFERENCES BETWEEN HYDROGEN BOND AND COVALENT BOND

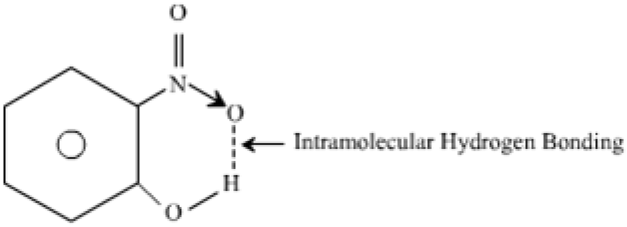
COVALENT BOND		HYDROGEN BOND	
01	It is interatomic (or intramolecular force) in nature	01	It is intermolecular forces in nature
02	Has shorter bond length	02	Greater bond length
03	Is stronger	03	Is weaker compared to covalent bond
04	Determine chemical properties	04	Has greater influence on physical properties
05	Not necessary for hydrogen atom to be involved	05	Must involve hydrogen atom

TYPES OF HYDROGEN BONDS

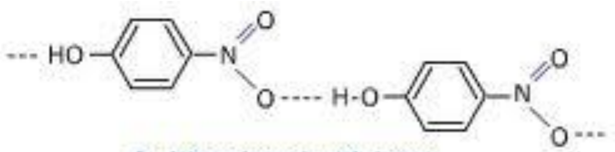
There are two types of hydrogen bonds which are

(i) Intramolecular hydrogen bond
(ii) Intermolecular hydrogen bond

Intramolecular hydrogen bond: In this, hydrogen bond occurs within a molecule, that is, between atom and neighbour electronegative atom in the same molecule. A good example of a compound whose molecules exhibit intramolecular hydrogen bonding is o-nitrophenol as illustrated below:



Intermolecular hydrogen bond: In this, hydrogen bond occurs between different molecules. A good example of a compound whose molecules exhibit intermolecular hydrogen bonding is p-nitrophenol as illustrated below:



P- Nitrophenol with inter molecular hydrogen bonding

EFFECTS OF HYDROGEN BONDS

Hydrogen bonding plays an important role in determining structure and physical properties of molecules containing it. Hydrogen bonds are responsible for:

- High melting and boiling point of compounds
- High solubility of compounds in water

- Dimerisation of molecules
- Floating of ice over water

High melting and boiling points

Usually the melting and boiling point of covalent compounds increase with the increase in molecular mass due to an increase of Van der Waals dispersion forces.

- However **compared to the London dispersion forces (Van der Waals dispersion forces), hydrogen bonds are stronger intermolecular forces of attraction.**
- Presence of hydrogen bonding explain why some compounds of lower molecular weight (and therefore weaker London dispersion forces) have unexpectedly higher melting and boiling points than their relative molecular masses would lead. Example ammonia(NH_3), water (H_2O) and hydrogen fluoride (HF) have higher boiling point than their molecular masses would lead to expect owing to hydrogen bonding.

With given two compounds of the same molecular mass but differing in the types of hydrogen bonds they posses, the compound with intermolecular hydrogen bond has higher boiling point because **in intermolecular hydrogen bonding there is greater association between molecules.**

Example 3

H_2O is liquid while H_2S is gas at room temperature although the molecular weight of H_2S is greater than that of H_2O. Explain

Solution

There is strong hydrogen bonding existing between water molecules as result of higher electronegativity of oxygen than that of sulphur thus making boiling point of water which is above the room temperature higher than that of H_2O which is below.

Example 4

HF is liquid at room temperature while other hydrogen halides are gases. Explain

Solution

F being on the top of halogen group has highest electronegativity so there is strong hydrogen bonding existing between HF molecules while in other hydrogen halides there is a weaker intermolecular force of attraction which is Van der Waals force of attraction and hence boiling point of HF become higher (above the room temperature).

Example 5

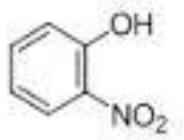
F_2 is gas while HF liquid. Explain

Solution

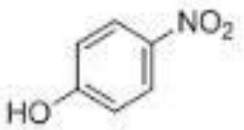
In HF, there is stronger intermolecular force of attraction which is hydrogen bonding while F_2 being non-polar covalent molecule has van-der-waals force of attraction and hence boiling point of F_2 become lower

Example 6

p-nitrophenol has higher boiling point than o-nitrophenol, explain.



o-nitrophenol



p-nitrophenol

Solution

The first compound has higher boiling point because possess intermolecular hydrogen bonding between its molecules which allows more association than intramolecular hydrogen bonding which exists in another given compound.

High solubility of a compound in water

Being polar molecules, compounds with hydrogen bond have high solubility in water which is polar solvent.

- This is due to ability of the compounds to undergo hydrogen bonding with water molecules (water itself possess very strong hydrogen bonds between its molecules). Example of ammonia (NH_3) which has hydrogen bond, has very high solubility in water (actually ammonia is the most soluble substance in water, 1cm^3 of water dissolves 800cm^3 of ammonia!)

Also compounds with intermolecular hydrogen bonding are more easily associated with water through hydrogen bonding than related compounds with intramolecular hydrogen bonding hence they (compounds with intermolecular hydrogen bonding) become more soluble in water .

- This explains why p-nitrophenol is more soluble in water than o-nitrophenol.

Example 7

Ammonia has unexpectedly high solubility in water. Explain.

Solution

Ammonia is capable of forming very strong hydrogen bonding with water molecules thus making its solubility in water very high.

Dimerisation of molecules

Hydrogen bonding may lead to association between molecules thus playing an important role in determination of structure of the compound.

Dimerisation *is the association between two smaller molecules to give a single larger molecule*. The larger molecule is known as a **dimer**.

When ethanoic acid is placed in a solvent with no hydrogen bonding the measured molecular mass of the acid is about 120g/mol which is twice the expected molar mass of 60g/mol thus suggesting the molecular formula of the acid to be $(CH_3COOH)_2$ ***and not simply*** CH_3COOH***, why?***

- This is simply because; in solvent with no hydrogen bonding two molecules of ethanoic acid associate together to form dimer as illustrated in the next page:

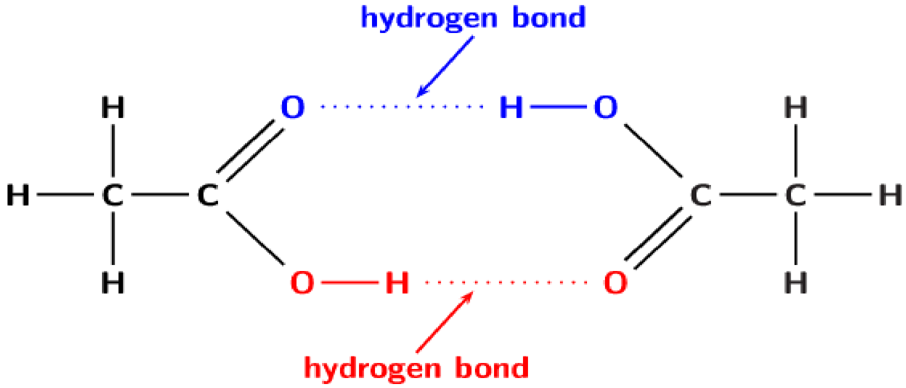


Figure: Dimerisation of ethanoic acid

Why dimerisation is possible in ethanoic acid?

This is due to the fact that: there is very strong hydrogen bonding existing between molecules of ethanoic acid which is result of presence of two positions of making hydrogen bonding leading to two clear strong hydrogen bonds between two molecules of the acid.

Floating of ice in water

Intermolecular hydrogen bonding exists in both liquid water and ice (solid water).

- In the liquid state, water molecules are in constant motion whereby intermolecular hydrogen bonds are continuously broken and reformed. As result, the arrangement of water molecules in the liquid state is random.
- In the solid state (ice), there is no molecular motion. The molecules are arranged in such a way that maximum number of hydrogen bonds between water molecules is obtained. What is the effect of this? As result an open structure is created where by water molecules are stretched by the hydrogen bonds from different direction to extra interstitial spaces making ice to occupy greater volume as well as lower density compared to liquid water and hence ice floats on liquid water.

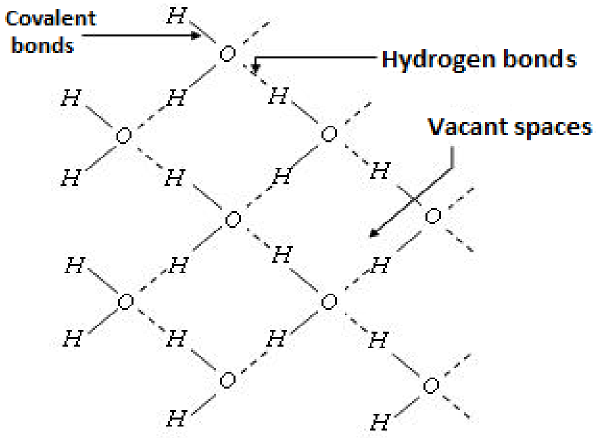


Figure: Structure of ice

Very important thing to note from the structure of ice!

In the above structure; each oxygen has **four bonds**; **two** covalent bonds (in full lines) and **two** hydrogen bonds (in dotted lines). *What does this mean?*

- This implies that all two lone pairs of water in oxygen have participated in the hydrogen bonding and of course technically are no longer lone pairs, are 'bonded' pair of electrons (remember hydrogen bonds in ice are very strong that is why it is solid) and this explain why bond angle in ice (solid water) is 109° and not 104.5° like in liquid water. In ice there is negligible effect of repulsion of lone pairs, even 'lone pairs' of water in oxygen act as bonded pair in very strong hydrogen bonding and hence all four pair of electrons are regarded as bonded pairs arranging themselves as far as possible in the tetrahedral structure to minimise repulsion between them.

Interesting fact: Without hydrogen bonding there would be no aquatic life in Polar Regions!

Have you ever thought about life of aquatic organism in the Polar Regions where temperature is below* 0°C*?

The temperature in Polar Regions is below freezing point of water. You may wonder how fish and other aquatic organisms survive in these extremely adverse conditions?! The secret of their survival lies on the presence of hydrogen bonding! But……. how?

- *Due to hydrogen bonding, ice floats in liquid water.*
- *This floating ice cover the liquid water and therefore preventing complete solidification of water in lakes and oceans which are found in the polar region. The ice actually act as a 'blanket' to prevent underlying water in lakes and oceans in polar regions from becoming solid through freezing and hence making possible for fish and other aquatic organisms to survive in polar regions.*
- *Without hydrogen bonding all water in polar region would freeze and no one would enjoy the beauty of aquatic organisms there! Their life would be impossible!*

Let us read another interesting story and continue enjoying chemistry! Chemistry for the life enjoyment!

Interesting fact: Hydrogen bond sank the Titanic!

Have you ever heard about Titanic accident? *The accident which is considered as most famous ocean liner disaster in history! The marine accident which killed more than 1500 people! If you are at bad luck side of not ever hearing of this sad story, here is the single sentence summary of it.*

The sinking of Titanic ship occurred in North Atlantic Ocean due to collision between the ship and iceberg which resulted to huge opening in the ship.

But the interesting fact is that, without hydrogen bonds the sinking of titanic would be impossible! How hydrogen bonds sank the Titanic? The following two 'dots' provide the answer.

- *Firstly,* ***is the hydrogen bonds which made ice to float over water and therefore iceberg formed in the cold ocean water*** *(the titanic hitted the iceberg).*

- *Also* ***because water molecules stick together by hydrogen bond (it would be volatile, it would be an advantage in preventing the accident), the water was able to flow into the ship, flood it and finally sink the Titanic***.

That is chemistry! Enjoy it!

Intermolecular forces in the mixture of substances

When two substances are mixed together, the kind of intermolecular forces in the mixture will depend on the type of intermolecular forces in the pure components before mixing.

- For example; if HCl is mixed with HI there are following possibilities of intermolecular forces:

First possibility:

Two molecules of HCl may interact (as in pure HCl) by dipole-dipole forces

$$H^{\delta+}\!-\!Cl^{\delta-}\ \underset{\downarrow}{---}\ H^{\delta+}\!-\!Cl^{\delta-}$$

Dipole-dipole forces between two molecules of HCl in the mixture.

Second possibility:

Two molecules of HI may interact (as in pure HI) by dipole-dipole forces.

$$H^{\delta+}\!-\!I^{\delta-}\ \underset{\downarrow}{----}\ H^{\delta+}\!-\!I^{\delta-}$$

Dipole-dipole force between two molecules of HI in the mixture

Third possibility:

One molecule of HCl may interact with one molecule of HCl by dipole-dipole forces in the following ways:

i) H pole of HI may interact with chlorine pole of HCl

$$H^{\delta+}\!-\!Cl^{\delta-}\ \underset{\downarrow}{-----}\ H^{\delta+}\!-\!I^{\delta-}$$

Dipole-dipole forces between H pole of HI and Cl pole of HCl

ii) H pole of HCl may interact with iodine pole of HI

$$H^{\delta+}\!-\!I^{\delta-}\ \underset{\downarrow}{-----}\ H^{\delta+}\!-\!Cl^{\delta-}$$

Dipole-dipole forces between H pole of HCl and I pole of HI

Note: when we are talking about intermolecular forces in this section, our intention will be the third possibility although in reality any one of the three possibilities may occur.

- Below are some types of intermolecular forces in the mixture.

i) Dipole-induced dipole forces

This type of intermolecular force occurs when a molecule with a dipole induces a dipole in a non-polar molecule.

- It is formed when polar covalent compound is mixed with non-polar covalent compound or uncharged atoms (or molecules). A good example of this is when chloroform, $CHCl_3$ (polar) is mixed with carbon tetrachloride, CCl_4 (non-polar).

- Dipole-induced dipole forces were discovered by Debye hence the term **Debye forces** for dipole-induced dipole forces.

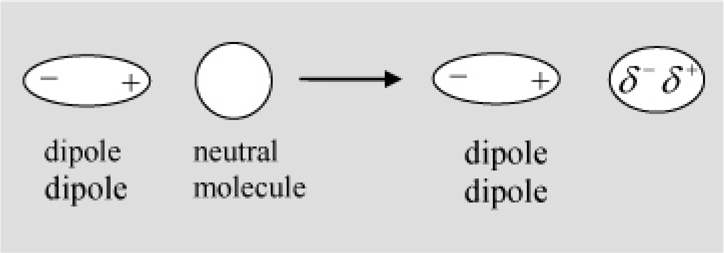


Figure: Formation of dipole-induced dipole forces

ii) Ion –induced dipole forces

These forces exist between ions and non-polar molecules.

- The ion induces a dipole in the non-polar molecule leading to weak instantaneous force which holds the compounds together.
- A real practical example of ion-induced dipole forces is the force found in haemoglobin which is the molecule that carries oxygen around your body. Haemoglobin has Fe^{3+} ions which are responsible for inducing dipole to oxygen,O_2(non polar molecule)and therefore O_2 is attracted to these ions by ion-induced dipole forces.

Combining dipole-induced dipole forces and ion-induced dipole forces:

These types of forces are collectively known as **induced-dipole forces.**

- **Induced-dipole forces** *result when an ion or a dipole induces a dipole in an atom or a molecule with no dipole*.

iii) Ion-dipole forces

This types of intermolecular force exists between an ion and **dipole** (polar molecule) and hence the term **ion –dipole forces**.

- When ionic compound like NaCl mixed with a polar covalent compound like H_2O the following things occur:
  - A positive ion (Na^+) of the ionic compound $(NaCl)$ will be attracted to the negative pole $\left(O^{\delta-}\right)$ of the polar molecule(H_2O).
  - A negative ion (Cl^-) of the ionic compound $(NaCl)$ will be attracted to the positive pole $\left(H^{\delta+}\right)$ of the polar molecule(H_2O).

These intermolecular forces (ion-dipole forces) weaken the ionic bonds between cations and anions of the ionic compound and hence **ionic compounds like NaCl appears to dissolve in polar solvent like water** (see figure below).

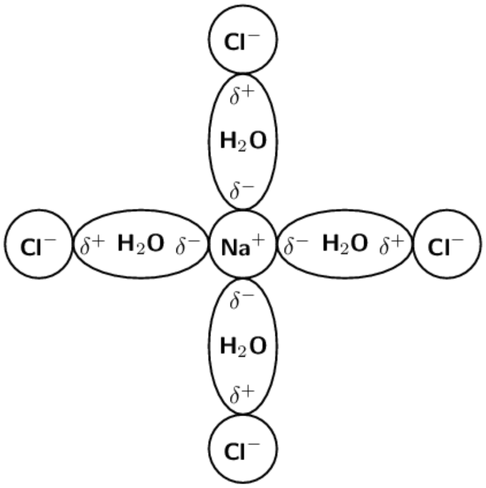


Figure: ion-dipole forces in sodium chloride solution

iv) Dipole-dipole forces

When one dipole (polar) molecule comes into contact with dipole molecule, the positive pole of one molecule will be attracted to the negative pole of the other, and these two molecules will be held together in this way by dipole forces.

- Mixture of HCl and HI (or SO_2 and HCl etc) is the good example of the mixture whose components are held together by dipole-dipole forces.

Presences of dipole-dipole forces explain why polar substance dissolves in the polar solvent or why two polar substances are expected to be miscible.

To generalise the solubility of substances with respect to their intermolecular forces:

Generally;

Principle of dissolving so as to make solution say that; *"like dissolve like"*

- Thus according to the principle; polar compounds dissolve in polar solvents but are insoluble in non-polar solvents while non-polar compound tend to dissolve in non-polar solvents but are insoluble in polar solvents.

Alternatively in terms of miscible and immiscible mixture, it can be stated as;

Polar + Polar = Miscible mixture

Polar + Non-polar = Immiscible mixture

Non-polar + Non-polar = Miscible mixture

Where '+' means 'and' in this case and '=' means 'forms' as usual.

The most common polar solvent is water while most of **organic solvents** like benzene and ether are non-polar.

Note:

Types of intermolecular forces do not end here. On your own you may derive other types of intermolecular forces in the mixture if you understand type of the intermolecular forces present in the pure components as done in the above examples.

DIGGING DEEPER EXERCISE 9

Question 1

Can non polar molecules such as CH_4 participate in hydrogen bond? Why or why not?

Question 2

Using your knowledge of the properties of water, explain the quote *"Hydrogen bonds sank the Titanic"*

Question 3

a) Explain why sodium has a lower melting point than magnesium
b) By referring to their structure and bonding, explain why magnesium oxide has higher melting point than sulfur dioxide.

Question 4

Why KHF_2 exists while $KHCl_2$ does not?

Question 5

Explain why the bond angles in ice are 109° and not 104° like in liquid water?

Question 6

Carbon dioxide is a gas whereas silicon dioxide is a solid of high melting point. Explain.

Question 7

Butane,$CH_3CH_2CH_2CH_3$, has higher boiling point than $2-\text{methylpropane}$, $CH(CH_3)_3$. Explain.

Question 8

Explain why CO_2 has lower solubility in water?

Question 9

Ethanoic acid,$C_2H_4O_2$, in the gas phase just above its boiling point has an apparent molar mass of 120g/mol. Explain

Question 10

State and explain with reasoning the relative solubility of $PbCl_2$ and $PbCl_4$ in water.

Question 11

Arrange the following compounds in order of their boiling point.

HF, HCl, HBr, HF

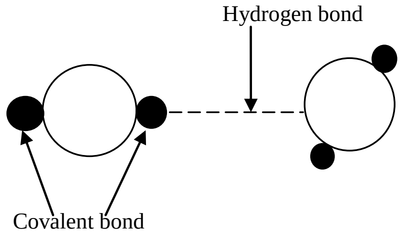
Question 12

Which of the following pairs of substance is likely to have higher boiling point? Give reason for your choice.

i. Na and K
ii. C and Si
iii. Ne and Ar
iv. NH_3 and PH_3
v. NaCl and HCl
vi. F_2 and Cl_2

Question 13

Consider the following representation of two water molecules in the liquid state



a. What bonds are broken when water boils? Are these intermolecular or intramolecular bonds?
b. What bonds are broken when water is electrolyzed? Are these intermolecular or intramolecular bonds?

Question 14

Arrange the following compounds according to increasing solubility in water, least soluble first

a. CH_3COOH
b. CH_3CH_3
c. $CH_3CH_2OCH_2CH_3$

Question 15

Explain why argon and fluorine have similar boiling point?

Question 16

What kind of intermolecular forces must be broken or overcome in order to:

a) Melt diamond
b) Sublime solid iodine
c) Melt table salt
d) Boil liquid ammonia
e) Melt solid neon
f) Melt iron

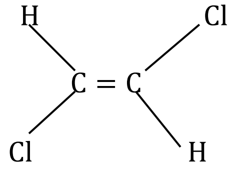
Question 17

Although CH_3CH_2Cl and $CH_3CH_2CH_2CH_3$ do not differ much in their molecular weights, the boiling point of the former is much higher than that of the later. Explain

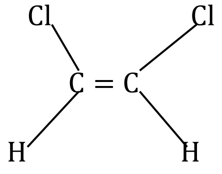
Question 18

Predict whether the following molecules are polar or non-polar

a)



b)



c) SO_2 d) NF_3 e) PF_5

Question 19

Which substance would most likely dissolve in water; CO_2 or CHF_3 why?

Question 20

Which intermolecular forces exist in each of the following?

i. Water
ii. Carbon tetrachloride
iii. Ammonia
iv. Helium

EXAMINATION QUESTIONS FOR PART TWO

Question 1

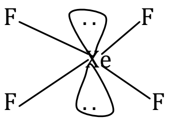
a) The shape of the molecule BCl_3 and that of unstable molecule CCl_2 are shown below:

i) Why is each bond angle exactly 120° in BCl_3?

ii) Predict the bond angle in CCl_2 and explain why this angle is different from that in BCl_3.

b) Give the name which describes the shape of molecules having bond angles of $109° 28'(109.5°)$. Give an example of one such molecule.

c) The shape of the XeF_4 molecule is shown below:



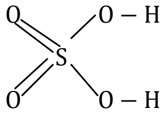
i) State the bond angle in XeF_4

ii) Suggest why lone pairs of electrons are opposite to each other in the molecule.

iii) Name the shape of this molecule, given that the shape describes the positions of the Xe and F atoms only

Question 2

a) Sulphuric acid is a liquid that can be represented by formula drawn below.



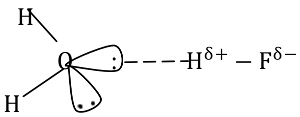
Given that electronegativity value for hydrogen, sulphur and oxygen are 2.1, 2.5 and 3.5 respectively; clearly indicated the polarity of each bond present in the formula given.

a) Name type of hybridisation and molecular shape of the sulphuric acid molecule.

b) Suggest the strongest type of intermolecular force present in pure sulphuric acid. Briefly explain how this type of intermolecular force arises.

Question 3

The diagram below show how a water molecule interacts with hydrogen fluoride molecule.



a) What is the value of the bond angle in a single molecule of water?

b) Explain your answer to part (a) by using the concept of electron pair repulsion

c) Name the type of interaction between a water molecule and hydrogen fluoride molecule shown in the diagram above.
d) Explain the origin of the δ^+charge shown on the hydrogen atom in the diagram.
e) When water interacts with hydrogen fluoride, the value of bond angle in water change slightly. Predict how the angle is different from that in a single molecule of water and explain your answer.

Question 4

Ethene, C_2H_4 and hydrazine, N_2H_4, are hydrides of elements which are adjacent in the periodic table. Data about ethene and hydrazine are given in the table below.

	C_2H_4	N_2H_4
Melting point/°C	-169	+2
Boiling point/°C	-104	+114
Solubility in water	Insoluble	High
Solubility in ethanol	High	High

a) Ethene and hydrazine have a similar arrangement of atoms but differently shape molecules.
   i. What is the $H-C-H$ bond angle in ethene?
   ii. What is the $H-N-H$ bond angle in hydrazine?
   iii. State and explain whether hydrazine is polar or non-polar
b) The melting and boiling points of hydrazine are much higher than those of ethene. Suggest reasons for these differences in term of the intermolecular forces each compound possesses.
c) Explain, with the aid of diagram showing lone pair of electrons and dipoles, why hydrazine is very soluble in ethanol.

Question 5

a.
   i) How ions are held together in the solid sodium metal
   ii) How ions are held together in solid sodium chloride
b. The melting point of sodium chloride is much higher than that of sodium metal. What can be deduced from this information?

Question 6

Name type of hybridisation and molecular shape of
i) NH_4^+
ii) CH_4
What is the relationship between the two?

Question 7

The water molecule is polar, how does this offer experimental proof that the molecule cannot be linear?

Question 8

Give reasons for the following observations;

i. The boiling point of water, ethanol and ethoxyethane (diethyl ether) are in the reverse order of their relative molecular masses unlike those of their analogous sulphur compounds H_2S, C_2H_5SH and $C_2H_5SC_2H_5$.
ii. Aluminium fluoride has much higher melting point than aluminium chloride.

Question 9

Arrange the following bonds according to polarity.

$H-H, O-H, Cl-H, S-H, F-H, N-H$

Question 10

Explain the following observation:

- i. PCl_5 is more reactive than PCl_3.
- ii. $AlCl_3$ is covalent while AlF_3 is ionic.

Question 11

Give the name of a geometrical structure and one example of the molecule/compound formed from the following hybridised atomic orbitals.

- i. sp^3 hybridised orbital
- ii. sp^2 hybridised orbital
- iii. sp^3d^2 hybridised orbital

Question 12

a. Given the meaning of the following:

- i. Lone pair of electrons
- ii. Dative bond
- iii. Sigma bond

b. By using modern molecular theory complete the table on the following molecules.

Molecule	**Geometrical structure**	**Name of the structure**	**hybridisation**
CO_2			
CH_2O			
PH_3			

Question 13

a. State the bond angle in NH_3 and BF_3 and state the name of the shape of each molecule.
b. Explain why NH_3 has polar molecules where as molecules of BF_3 are non-polar.
c. Polar molecules of NH_3 form hydrogen bonds. Draw diagram to show this hydrogen bonding.
d. Explain why the $H-N-H$ bond angle in NH_3 is less than that in NH_4^+

Question 14

The boiling points of water, hydrogen chloride and argon are shown in the table below.

Substance	H_2O	HCl	Ar
Boiling point /°C	100	−85	−186
Total number of electrons	10	18	18

a. H_2O , HCl, Ar all have Van der Waals forces. Outline how Van-der-Waals force arise between molecules.
b. Liquid H_2O has additional intermolecular forces
  - i) What are these forces?
  - ii) Explain with the aid of diagram, how these forces arise between molecules of H_2O.
c. Liquid HCl also has additional intermolecular forces. What are these forces.
d. Explain the variation in boiling point shown in the above table.

Question 15

a. The table below shows boiling points of fluorine, fluoromethane (CH_3F) and hydrogen fluoride.

Compound	F_2	CH_3F	HF
Boiling point/K	85	194	293

Name the strongest type of intermolecular force present in;-

i. Liquid F_2
ii. Liquid CH_3F
iii. Liquid HF
iv. Explain how the strongest type of intermolecular force in liquid HF arises

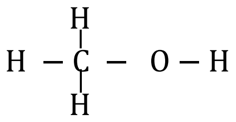
b. The table below shows the boiling points of some other hydrogen halides.

Compound	HCl	HBr	HI
Boiling point/K	188	206	238

i. Explain the trend in the boiling points of the hydrogen halides from HCl to HI.
ii. Give one reason why the boiling point of HF is higher than that of all the other hydrogen halides.

c.

i. Methanol has the structure



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$$

Explain why $O-H$ bond in a methanol molecule is polar?

ii. The boiling point of methanol is$+65$°C, the boiling point of oxygen is -183°C. Methanol and oxygen each has M_r value of 32. Explain why the boiling point of methanol is much higher than that oxygen.

Question 16

a. Below are elements of group VI A their atomic numbers and symbols.

Element	Atomic number	Symbol
Oxygen	8	O
Sulphur	16	S
Selenium	34	Se
Tellurium	52	Te

i. Give full electronic distribution in selenium

ii. Can sulphur form S=S? Give reason(s) to support your answer.

iii. The hydrides of group VIA elements are H_2O, H_2S, H_2Se and H_2Te. Arrange the hydrides in order of increasing their boiling point starting with the least volatile giving clear reasons for your arrangement.

b.

i. Suggest why the strength of the $C-H$ bond in CH_4 is greater than that of the $Si-H$ bond in SiH_4. State the relationship if any, between the strength of covalent bond in CH_4 and the boiling temperature of CH_4 and hence state which one (CH_4 or SiH_4) has greater boiling point.

c. State the type of hybridisation shown by the nitrogen atoms in:

i. N_2

ii. N_2H_2

iii. N_2H_4

Question 17

a. Consider shape of the molecule of BCl_3 and that of unstable molecule CCl_2

i. Why is each bond angle exactly $120°$ in BCl_3?

ii. Predict the bond angle in CCl_2 and explain why this angle is different from that in BCl_3?

b. When considering electron pair repulsions in molecules, why does a lone pair of electrons repel more strongly than a bonding pair?

c. Co-ordinate bonding can be described as **dative covalency**.

i. In the above context, what is the meaning of each of terms **covalency** and **dative**?

ii. Write an equation for a reaction in which a coordinate bond is formed

d. Arrange the following elements in order of increasing their melting points giving clear reason(s) for your trend.

Neon, Sodium, Magnesium, Aluminium and silicon.

Question 18

a. For each of the following species, identify type of hybridisation of an element in the bracket, **name** electron pair geometric shape, molecular geometric shape and bond angle.

   - i. X_eF_4 (Xe)
   - ii. H_2SO_4 (S)
   - iii. I_3^- (I)

b.

   - i. Predict and explain the polarity of the bonds within BF_3 and NF_3.
   - ii. State whether BF_3 and NF_3 are polar molecules. Explain your answer.

Question 19

(a) Briefly explain Sidgwick -Powell theory

(b) What type of intermolecular force is found between:

   - (i) F_2 and Cl_2
   - (ii) Two water molecules

c) Although sodium and potassium are metals, they can never be used in construction of bridges; explain.

Question 20

Starting with the shortest one, arrange the following bonds in order of their bond length

i. $CH_2 \overset{\overset{(1)}{\downarrow}}{=} CH \overset{\overset{(2)}{\downarrow}}{-} CH_2 \overset{\overset{(3)}{\downarrow}}{-} CH_3$

ii. $CH \overset{\overset{(1)}{\downarrow}}{\equiv} C \overset{\overset{(2)}{\downarrow}}{-} CH \overset{\overset{(3)}{\downarrow}}{=} CH_2$

iii. $CH_2 \overset{\overset{(1)}{\downarrow}}{=} C \overset{\overset{(2)}{\downarrow}}{=} CH \overset{\overset{(3)}{\downarrow}}{-} CH_3$

iv. $CH_2 \overset{\overset{(1)}{\downarrow}}{=} C \overset{\overset{(2)}{\downarrow}}{=} C \overset{\overset{(3)}{\downarrow}}{=} CH \overset{\overset{(4)}{\downarrow}}{-} C \overset{\overset{(5)}{\downarrow}}{\equiv} CH$

ANSWERS TO DIGGING DEEPER EXERCISES

Exercise 6

Question 1

The two bonded oxygen atoms having equal electro negativity, the nucleus of each oxygen exert an equal pull on the shared electrons and hence the bond become non polar.

Question 2

a) Covalent
b) Ionic
c) Be being smaller in size than Ba, has greater polarising power and hence there is a greater degree of polarisation in $BeCl_2$ than in $BaCl_2$.

Question 3

i) Non-zero
ii) Zero
iii) Non-zero
iv) Non-zero
v) Non-zero

Question 4

- In copper, stress applied on a metallic lattice causes sliding of layers of cations without breaking the metallic structure because the sea of electrons(delocalised electrons) are still holding the cations together and hence copper become ductile.
- In $CuSO_4$, stress applied on the ionic lattice with regular pattern causes sliding of layers resulting in ions of similar charge coming together leading to the repulsion that shatters the ionic structure and hence $CuSO_4$ become brittle.

Question 5

Na Metal conducts electricity by movement of its delocalised valence electrons in the solid state while NaCl conducts electicity by movement of ions which are Na^+ and Cl^- in molten state or aqueous

Question 6

Refer to the text.

Question 7

Covalently bonded compounds do not conduct electricity, regardless of the state they are in. This is because electrons are being shared during the bond, not donated or accepted. Because there is no transfer of electrons, there are no ions. Ions are what conduct electricity and thus, without ions, the compounds cannot conduct electricity. Also, covalent compounds are uncharged molecules with the electrons held tightly together. This also means there are no free electrons, or charged ions, to conduct electricity.

The exception to this rule is when a covalent compound reacts with water. When this occurs, ions are formed and the compound is able to conduct electricity

Question 8

Ionic compounds are said to be brittle. This is because of the arrangement of the ionic lattice. This arrangement is specific to alternate positive and negative ions and keep similar charges far apart. When it is altered, the like charges will become close to each other and will repel each other. This repulsion shatters the lattice causing the compound to break.

Question 9

Presence of delocalised electrons in a metal makes it to be malleable and ductile. While in the case of NaCl electrons are held tightly in respective ions in ionic bond thus making the ionic compound (NaCl) brittle.

Question 10

No. Molecules of SiO_2 are held together by network of giant covalent bonds and hence SiO_2 will be brittle rather than ductile.

Question 11

The delocalised electrons of aluminum metal allow it to conduct heat while quartz which is actually SiO_2 has network of giant covalent bonds in which electrons are tightly held in the bonds and hence they cannot transfer heat well.

Question 12
When two F atoms are covalent bonded to F_2, all of their atomic orbitals are full occupied with electrons and hence there is no possibility of forming third covalent bond so as to form F_3.
Question 13

Ionic Compounds	Covalent Compounds
Usually solid at room temperature	Usually liquid or gas at room temperature
High melting and boiling points	Low melting points
Soluble in water	Insoluble in water
Conducts electricity	Do not conduct electricity
Undergo fast reactions	Undergo slow reactions

Question 14

HBr (Because Br is more electronegative than I, the $H - Br$ is more polar that the $H - I$ bond).

Question 15
Yes. The dipole points towards the side with the two oxygen atoms because oxygen is more electronegative than sulphur.

Question 16

The molecule must be symmetrical. This means the polar bonds must be oriented in equal and opposite directions. In this way, there will be no net dipole overall. For example in CO_2, the $C = O$ bond are each polar, but they point towards each end of the linear arrangement and therefore the overall molecule is non polar.

Question 17

CO , NCl_3, and SF_2 .

Question 18

- It is no hundred percent electrovalent because electronegativity of H and Cl do not differ much and thus the covalent bond formation become more favourable.
- However Cl being more electronegative has greater ability of attracting covalent bonded electrons leading to the formation of partial positive charge and partial negative charge on hydrogen and chlorine respectively and hence the compound become partially ionic.

Exercise 7

Question 1

a) sp^3d^2 hybridisation
(Hint: there are five sigma bonds and one lone pair making a total of 6 pairs of electron in 6 hybrids orbital of about I).

b) sp^2 hybrisation
(Hint: with structure,$HO - \ddot{N} = O$ there are 2 sigma bond and 1 lone pair about and therefore making a total of three sp^2 hybrid orbitals in N)
c) C_1: sp^2 hybridisation
C_2: sp^3 hybridisation
(Hint: first carbon in acetic acid $CH_3 - \overset{\overset{O}{||}}{C} - OH$ is the carbon in $COOH$ group and the carbon has 3 sigma bonds and hence three sp^2 hybrid orbitals in it. The second carbon has four sigma bonds and hence it is sp^3 hybridised).
d) sp^3 hybridisation
(Hint: Each oxygen atom in hydrogen peroxide,$H - O - O - H$, has two sigma bonds and two lone pair making a total of four sp^3 hybrid orbitals in O)
e) sp^2 hybridisation
f) sp hybridisation
Question 2

With outermost energy level of $n = 3$, phosphorus may undergo sp^3d hydridisation so as to form covalency of 5 and therefore forming PCl_5 while in nitrogen there are no d-orbitals in its outermost energy level of $n = 2$ to enable it to form five sp^3d hybrid orbitals.

Question 3

PCl_5 has higher energy electronic structure as it is formed through sp^3d hybrid orbitals (after excitation of electrons) compared to sp^3 hybrid orbitals used for formation of PCl_3 which do not involve excitation of electrons. This makes PCl_5 unstable and therefore more reactive.

Question 4

a) sp^3 hybridisation b) sp^2 hybridisation
c) sp^3d hybridisation d) sp^3d hybridisation
e) sp^3 hybridisation

Question 5

sp^3d and sp^3d^2 (Because elements in the second period have outermost energy level of n=2 which has no d sublevel to enable such hybridisation).

Exercise 8

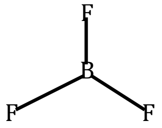
Question 1

$$H_2O\ (104.5°) < CCl_4 (109.5°) < CO_3^{2-} (120°) < HCN\ (180°)$$

- H_2O and CCl_4 are sp^3-hybridised so their electron pair geometric shape is tetrahedral
  - CCl_4 having lone pair its bond angle is the tetrahedral angle which is $109.5°$
  - H_2O having 2 lone pairs its angle is decreased to $104.5° (109.5° - (2 \times 2.5°)$, keeping in mind that each lone pair decrease the bond angle by $2.5°)$
- The bond angle that would be observed if all electron pairs would be bonded electron pairs).
- CO_3^{2-} is sp^2 hybridised with no lone pair therefore its shape is trigonal planar with the bond angle of $120°$
- HCN is sp-hybridised and therefore its shape is linear with bond angle of 180°

Question 2

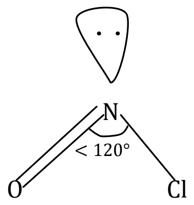
- There are 3 **bonded electron pair without any lone** pair around Boron (B).
  - To minimise repulsion, the three electron pairs are directed to the **corners of an equilateral triangle** in three dimension and hence BF_3 is **trigonal planar in shape** with an angle of $120°$.



Shape of BF_3

Question 3

- There are 2 bonded electron pair(double bond is counted as one electron pair) and 1 lone pair around oxygen (O)
  - To minimise repulsion, the three electron pairs are directed to the corner of triangle in three dimensions.
  - This makes the electron pair geometric shape of the molecule to be trigonal planar. However because lone pair exert greater repulsion than bonding pair of electrons the bond angle is slightly less than 120°.



Shape of NOCl

Question 4

a) Molecular geometry: Trigonal planar
Electron geometry: Trigonal planar
b) Molecular geometry: Linear
Electron geometry: Trigonal (triangular) pyramidal
c) Molecular geometry : Trigonal (triangular) pyramidal
Electron geometry: Tetrahedral
d) Molecular geometry : Trigonal planar
Electron geometry: Tetrahedral

Question 5

a) $C^1: 180°$: $C^2: 180°$: $C^3 : 109.5°$
Hint: C^1 is sp hybridised, C^2 is sp hybridised, C^3 is sp^3 hybridised
b) $109.5°$ (Hint: The carbon is sp^3 hybridised)

Question 6

i. C^1: sp hybridisation
C^2 : sp^2 hybridisation

C^3 : sp^3hybridisation

ii. C^1 : molecular geometry is linear, electron geometry is linear
C^2 : Molecular geometry is trigonal planar, electron geometry is trigonal planar

C^3 : Molecular geometry is tetrahedral, electron geometry is tetrahedral
iii. C^1: 180°
C^2: 120°
C^3: 109.5°

Question 7

a) Square pyramid b) Linear c) Bent

Question 8

a) 120° b) 90° c) 90° and 120°

Note:

In this question we were asked to give just an approximate value of the angle. So don't worry about small deviation due to presence of lone pair in (a) and (c).

Question 9

CCl_4 has four electrons pairs about the central C all of which are bonded and therefore they exert equal repulsion and whence tetrahedral shape results. On another hand presence of one lone pair which exerts greater repulsion than the four bonded electron pairs about P of PCl_4^- prevents the formation of tetrahedron for PCl_4^-.

Question 10

$$\xrightarrow[\text{Decrease in bond angle}]{NH_4^+ > NH_3 > NH_2^-}$$

Reason

NH_4^+ has tetrahedral shape with 109.5° bond angles. NH_3 has a trigonal pyramidal shape and the lone pair pushes the bonds together making the bond angle less than the tetrahedral angle (bond angle in NH_3 is 107°).NH_2^- has two lone pairs and these push the two bond pairs even closer together than in NH_3 molecule. (With two lone pairs, bond angle in NH_2^- is 104.5°).

Exercise 9

Question 1

Non polar molecules cannot form hydrogen bonds because there is no electronegativity difference between the atoms and hence no partial charges in the atoms.

Question 2

Hydrogen bonds sank the titanic in two ways:-

i) Hydrogen bonds caused ice to float in water and therefore the iceberg that was hitted by titanic was formed in the cold water.
ii) Hydrogen bonds caused water molecule to stick together and therefore were able to flow into the ship and whence sinking the titanic.

Question 3

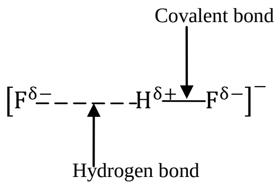
a) Sodium has weaker metallic bond due to:
- Its fewer valence electron (Na has only one valence electron while Mg has two)
- Its larger metallic radius.

Thus it is easier to weaken metallic bonds between Na atoms and hence it's lower melting point.

b) MgO being ionic has stronger intermolecular forces of ionic bonds in ion-ion interaction than Van der Waals forces existing between molecules of SO_2 which is covalent.

Question 4

F atom being smaller in size accompanied with higher electronegativity than Cl atom, can form very strong hydrogen bonding leading to the formation of HF_2^- in KHF_2 while Cl cannot form strong hydrogen bond so as to form HCl_2^-.



Question 5

In ice, each water molecule forms **two hydrogen bonds** with adjacent water molecule such that **each oxygen** atom is surrounded by **four hydrogen** bonded atoms. Thus in ice there are **four bonded electron pairs** without **any lone pair** around oxygen atom making its shape tetrahedral with bond angle of 109° unlike in liquid water where there are two lone pairs (unbounded electron pairs) decreasing the bond angle to 104°.

Question 6

CO_2 is a simple covalent molecule (where π-bond exists) whose molecules are held together by weak Van der Waals dispersion forces while SiO_2 is a giant molecule where single sigma bonds exists whose molecules are held together by very strong giant covalent bonds.

Question 7

Butane being unbranched has a stronger Van der Waals dispersion forces because:

- It has larger surface area than the branched $2-\text{methyl propane}$
- It chains have more compact packing than the branched $2-\text{methylpropane}$

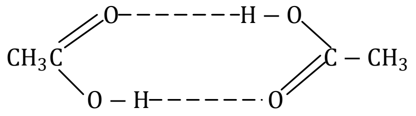
The two factors make butane to have stronger Van der Waals dispersion forces and hence higher boiling point than $2-\text{methyl propane}$ although the two compounds have the same molecular weight.

Question 8

Weaker intermolecular Van der Waals dispersion forces in CO_2 are not able to displace the stronger intermolecular hydrogen bonds in water for hydration and hence the CO_2 become almost insoluble in water.

Question 9

In the vapour phase two molecules of ethanoic acid associate through intermolecular hydrogen bonding to form a dimer.



Dimer of ethanoic acid with Mr. of 120g/mol

Question 10

- $PbCl_2$ being ionic (Pb^{2+} in $PbCl_2$ has lower charge and therefore has smaller polarising power making $PbCl_2$ to have lower degree of polarisation) can form strong **ion-dipole forces** with water molecules that result in the **release of energy** to break the giant ionic lattice structure of $PbCl_2$ for hydration to occur. This make$PbCl_2$ more soluble in water.
- $PbCl_4$ being covalent (Pb^{4+} in $PbCl_4$ has higher charge and greater polarising power and hence higher degree of polarisation in $PbCl_4$) has no favourable interaction with water molecules because the weak intermolecular Van der Waals forces in it are not able to displace the stronger intermolecular hydrogen bonds in water. This makes $PbCl_4$ insoluble in water.

Question 11

$$\xrightarrow[\text{Decrease in their boiling point}]{\text{HF} > HI > HBr > HCl}$$

Question 12

i. Na
Reason: Na has stronger metallic bond because has small metallic radius

ii. C
Reason: C form stronger giant covalent bond because has small atomic size

iii. Ar
Reason: Ar has a stronger Van der Waals dispersion forces because has greater atomic weight (Greater number of electrons and surface area)

iv. NH_3
Reason: NH_3 has stronger intermolecular hydrogen bond than intermolecular Van der Waals dispersion forces of PH_3.

v. NaCl
Reason: has stronger ion-ion forces (ion bond) than intermolecular Van der Waals dispersion force of HCl.

vi. Cl_2
Reason: Cl_2 has a stronger intermolecular Van der Waals dispersion forces because has greater molecular weight (which means greater surface area and greater number of electrons in Cl_2).

Question 13

a) Bond broken: Hydrogen bond
Bond kind: Intermolecular bond

b) Bond broken :Covalent bond
Bond kind: Intramolecular bond

(Remember: Boiling is **physical change** while electrolysis is the **chemical change)**

Question 14

CH_3CH_3, $CH_3CH_2OCH_2CH_3$, CH_3COOH

Question 15

Both Ar and F_2 being non-polar, their boiling point is determined by strength of Van der Waals dispersion forces. Since the two have the same electronic structure (Each has 18 electrons), they have the same strength of Van der Waals dispersion forces and hence similar boiling point.

Question 16

a) Giant covalent bond
b) London dispersion forces
c) Ion-ion forces (or ionic bonds)

d) Hydrogen bonds
e) London dispersion forces
f) Metallic bonds

Question 17

CH_3CH_2Cl is the polar molecule as the result of large electronegativity difference between carbon and chlorine thus there is electrostatic force of attraction between partial positive charge in carbon and partial negative charge in chlorine ($C^{\sigma+} - Cl^{\sigma-}$) unlike in $CH_3CH_2CH_3$ which is non-polar.

Question 18

a) Non polar
b) Polar
c) Polar
d) Polar
e) Non polar

Question 19

CHF_3 being polar is more likely to dissolve in water which is also polar solvent than CO_2 which is non-polar

Question 20

i. London dispersion forces and hydrogen bonds
ii. London dispersion forces
iii. London dispersion forces and hydrogen bonds
iv. London dispersion forces

SOLUTIONS TO EXAMINATION QUESTIONS

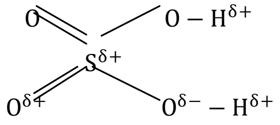
Question 1

a)
i. Electrons pairs around the central atom (B) are all bonded and therefore they repel equally.
ii. 117.5°
Reason: Lone pair exerts greater repulsion than bonded pairs of electrons.

b) Name of the shape: Tetrahedral, Example: CH_4
c)
i. 90°
ii. Lone pairs repel more strongly than bonded pairs of electrons.
iii. Square planar

Question 2

a)

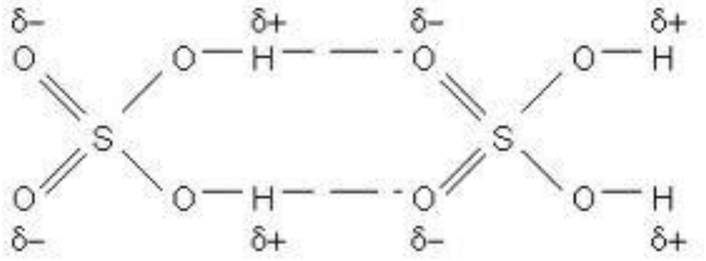


b) Type of hybridisation: sp^3 hybridisation

Molecular shape: Tetrahedral.

c) Hydrogen bond
Explanation:

It occurs as result of electrostatic attraction between partial positively charge hydrogen of one molecule and lone pair in partial negatively charge oxygen atom of the adjacent sulphuric acid molecule.



Where – – – – – stands for hydrogen bonding.

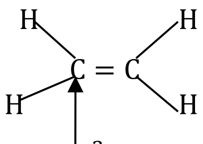
Question 3

a) 104.5°
b) Water molecule has two lone pairs (in its oxygen atom) which exert stronger repulsion than bonded electron pairs and therefore the bond angle become less than the expected tetrahedral angle of 109.5°
c) Intermolecular hydrogen bonding.
d) F atom being stronger electronegative, pull the shared electrons from H atom which is weaker electronegative.
(**Warning!** Don't talks about O atom because there is no δ^+ in H atom of H_2O in the given diagram and the question mention that the δ^+ charge shown on the hydrogen atom in the diagram).

e) Prediction: slight greater than 104.5°
Explanation: In presence of HF molecule, lone pairs in O of H_2O interact with $H^{\delta+}$ of HF through hydrogen bonding and therefore **they act like bonded electron pair** which always exert smaller repulsion.

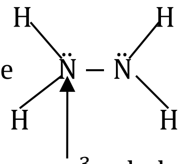
Question 4

a) Structure of ethene



sp^2 hybridised without lone pair

Structure of hydrazine



sp^3 − hybridised with 1 lone pair

Therefore:

i) Bond angle of $H - C - H$ is 120° (trigonal planar angle).
ii) Bond angle of $H - N - H$ is 107° (Due to presence of one lone pair the tetrahedral angle of 109.5° is reduced to 107°)

b) Hydrazine is **polar**

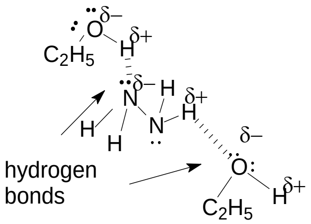
Explanation:

$N - H$ bond is polar and there is 1 lone pair around each sp^3-hybridised N making N_2H_4(hydrazine) trigonal bipyramidal about each N such that there is non-zero resultant of dipole moments and hence the hydrazine becomes polar.

c) More energy is required to overcome the stronger intermolecular hydrogen bonds in hydrazine than the weaker intermolecular Van der Waals dispersion forces in ethene and hence higher melting and boiling point of hydrazine.

d) Hydrazine molecules can form intermolecular hydrogen bonds with ethanol molecules and hence more it become very soluble

- The intermolecular hydrogen bonds between hydrazine and ethanol is illustrated in the diagram below:



Question 5

a.
i) By metallic bond which exist between sodium ions and delocalised valence electrons
ii) By ionic bond which act as the electrostatic force of attraction between sodium cations (Na^+) and chloride anions(Cl^-)

b. Ionic bonds (ion-ion forces) are stronger forces than metallic bonds

Question 6

i) sp^3 hybridisation, tetrahedral
ii) sp^3 hybridisation, tetrahedral

The two are i**soelectronic.**

Question 7

If H_2O were linear, then there would be no net dipole, and the molecule would be therefore non polar. Since it is polar, the two lone pairs must be on adjacent sides of the tetrahedral electron geometry, leaving the two bonds on adjacent sides. This results in a net dipole with the negative end near the oxygen atom, and the positive end near the two hydrogen atoms.

Question 8

i. For given first group of compounds boiling point is determined by the strength of hydrogen bonding which increases from ethoxyethane to water, where water has strongest hydrogen bonding and therefore highest boiling point. For the second group of compounds, boiling point is determined by Van-der Waals dispersion forces of attraction which increase with an increase in molecular weight; so H_2S having lowest molecular weight has lowest boiling while $C_2H_5SC_2H_5$ having highest molecular weight has highest boiling point.

ii. AlF_3 is more ionic in characters as result of its lower degree of polarisation brought by smaller polarisability of smaller sized F^-.

Question 9

$$\mathrm{H-H < S-H < Cl-H < N-H < O-H < F-H}$$

$$\xrightarrow[\text{Increase in bonds polarity}]{\hspace{6cm}}$$

Question 10

(i) PCl_5 has higher energy electronic structure and therefore less stable as it is formed by sp^3d hybridisation which has higher energy than sp^3 hybridisation which is used in forming PCl_3.

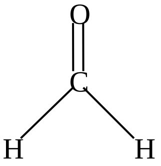
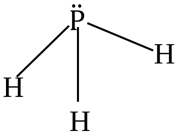
(ii) $AlCl_3$ has higher degree of polarisation as result of greater polarisability power of Cl^- which has larger size than F^- of AlF_3 and hence according to Fajan's rule, $AlCl_3$ becomes more covalent in characters.

Question 11

Refer to the text

Question 12

(b)

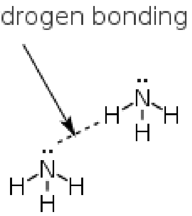
Molecule	**Geometrical structure**	**Name of the structure**	**hybridisation**
CO_2	$O=C=O$	Linear	sp hybridisation
CH_2O		Trigonal planar	sp^2 hybridisation
PH_3		Triangular pyramid	sp^3 hybridisation

Question 13

a) **Bond angles:**
107° in NH_3
120° in BF_3
Shape of molecules:
Triangular pyramid for NH_3
Trigonal planar for BF_3

b) Due to presence of lone pair in N, NH_3 is triangular pyramid shaped which is unsymmetrical structure while BF_3 having no lone pair has symmetrical structure in its trigonal planar shape and hence NF_3 is polar and BF_3 is non –polar.

c)

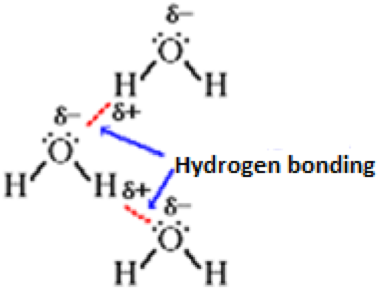


d) Due to presence of lone pair in N of NH_3 which exert stronger repulsion than bonding pair of electrons, $H - N - H$ bond angle is less than tetrahedral angle of NH_4^+ which has no lone pair.

Question 14

a) Hint: explain how London dispersion forces occur (Remember when you are asked just about "Van der Waals forces", the implication is always the London dispersion forces)

b)
   i. Hydrogen bond
   ii. Due to electronegativity difference between H and O (oxygen is more electronegative than H), the $O - H$ bond is polar with partial positive charge in the hydrogen atom. Thus the partial positively charged H of one molecule of H_2O attracts the lone pair of partial negatively charged oxygen atom of neighbour H_2O molecule and whence hydrogen bond is formed.



c) Dipole –dipole forces

d) On additional to Van der Waals dispersion forces, water molecules are held together by hydrogen bonds which are stronger intermolecular forces than dipole-dipole forces which present in HCl in the addition to the Van der Waals dispersion forces. That is why water has highest boiling point among the three. Argon has lowest boiling point because has Van der Waals dispersion forces only.

Question 15

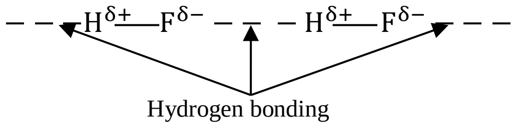
a)

i. London dispersion forces

ii. London dispersion forces

iii. Hydrogen bonds

iv. H being highly less electronegative than F is partially positively charged. This hydrogen positive pole of one HF molecule attracts lone pair of partially negatively charged F of the neighbour HF molecule resulting to the hydrogen bonding.



b)

i. The strongest type of intermolecular forces in the given hydrogen halides is Van der Waals (London) dispersion forces whose strength increases with an increase in the molecular weight

- HI having greatest molecular weight has strongest of Van der Waals dispersion forces and therefore highest boiling point while HCl having lowest molecular weight has weakest forces.

ii. There are very strong hydrogen bonds holding molecules of HF together.

c)

i. O being more electronegative than H has partial negative charge while H has partial positive charge making the bond polar.

ii. There are hydrogen bonds holding molecules of methanol together, those hydrogen bonds are stronger intermolecular forces than Van der Waals dispersion forces present in the oxygen.

Question 16

a)

i. It is more than easier for you (Don't forget to use boxes and arrow because you asked to give full electronic distribution)

ii. No

Reason:

Atomic size of sulphur (or size of p-orbitals in sulphur) is too large to enable side-way overlapping of atomic orbitals so as to form pi- bond in the double bond.

iii. H_2O, H_2Te, H_2Se, H_2S

Reason

- H_2O has hydrogen bonds which are stronger intermolecular forces than Van der Waals dispersion forces of other molecules.
- For the other molecules, H_2Te has greatest molecular weight and therefore strongest Van der Waals dispersion forces while H_2S has the least one.

b)

i.

- C **being smeller is size than Si** can form stronger covalent bond in $C-H$ than Si in $Si-H$.
- There is no relation between strength of covalent bond of CH_4 and its boiling point (because the covalent bond is the interatomic forces which has no effect on the physical properties like boiling).The boiling point of CH_4 and SiH_4 depends on the strength of Van der Waals dispersion intermolecular forces which increases with an increase in their molecular weight and hence SiH_4 has greater boiling point (because SiH_4 has greater molecular weight than CH_4).

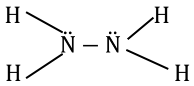
c)

i) $\ddot{N} \equiv \ddot{N}$

Type of hybridisation: sp hybridisation

ii) $H-\ddot{N}=\ddot{N}-H$

Type of hybridisation: sp^2 hybridisation



Types of hybridisation: sp^3 hybridisation

Question 17

a) (i) In BCl_3, all three pairs of electrons are bonded electrons which repel equally so they get as far as possible in trigonal planar arrangement with bond angle of $120°$ so as to minimise repulsion.
(ii) Predicted bond angle is about $118°$.
Explanation:
This is because in CCl_2 there is a lone pair in C which repels more than bonding pair of electrons making the bonds relatively closer than in BCl_3 where all pair of electrons are bonded.

b) Lone pair are more compact (very close) than bonding pair

c)
i) Covalency meaning: shared electron pair
Dative meaning: both electrons comes from one atom

$$\text{Neon} < sodium < Magnesium < Aluminium < Silicon$$

Reason:

- Neon has Van der Waals dispersion forces which are very weak intermolecular forces.
- Sodium, magnesium and aluminium have metallic bonds (which are stronger than Van der Waals dispersion forces of Neon).
  - With only one valence electron accompanied with large atomic size, sodium has weakest metallic bond while aluminium has strongest one.
- Silicon has giant covalent bonds which are stronger intermolecular forces than metallic bonds.

Question 18

a)

i. Type of hybridisation: sp^3d^2 hybridisation
Electron pair geometric shape: Octahedral
Molecular geometric shape: Square planar
Bond angle: $90°$

ii. Type of hybridisation: sp^3 hybridisation
Electron pair geometric shape: Tetrahedral
Molecular geometric shape: Tetrahedral
Bond angle: $109.5°$

iii. Types of hybridisation : sp^3d hybridisation
Electron pair geometric shape: Trigonal bipyramidal
Molecular geometric shape: Linear
Bond angle: 180°

b)

i.
$B - F$ is a polar bond, because F, is more electronegative than B;
$N - F$ is a polar bond, because F is more electronegative than N

ii.
- BF_3 is a non-polar molecule because of its symmetrical distribution of electron pairs in its trigonal planar shape makes it to have zero resultant of dipole moment.
- NF_3 is a polar molecule due to its unsymmetrical distribution of electron pair in its trigonal pyramidal shape as result of presence of lone pair. This makes NF_3 to have non-zero resultant of the dipole moment.

Question 19

(a) Refer to the text
(b) (i) London dispersion forces (or temporary dipoles-induced dipole forces) (ii) hydrogen bonds.
(c) The given metals have very weak metallic bond as result of their large metallic radii accompanied with only one valence electron in each thus making them soft accompanied with low density and high solubility in water and hence the metals become unsuitable for making bridges.

Question 20

The bond which involves hybridised orbitals with greater percentage of s-characters will be shorter than the bond with hybridised orbitals of smaller percentage of s- characters.

i.

1. Is the bond with $\mathrm{sp}^2-\mathrm{sp}^2$ carbon
2. Is the bond with $\mathrm{sp}^2-\mathrm{sp}^3$ carbons
3. Is the bond with $\mathrm{sp}^3-\mathrm{sp}^3$ carbons

Hence the order becomes:

$(1)<(2)<(3)$

ii.

1. Is the bond with $\mathrm{sp}-\mathrm{sp}$ hybridised carbons
2. Is the bond with $\mathrm{sp}-\mathrm{sp}^2$ hybridised carbons
3. Is the bond with $\mathrm{sp}^2-\mathrm{sp}^2$ hybridised carbons

Hence the order becomes:

$(1)<(2)<(3)$

iii.

1. Is the bond with $\mathrm{sp}^2-\mathrm{sp}$ hybridised carbons
2. Is the bond with $\mathrm{sp}-\mathrm{sp}^2$ hybridised carbons
3. Is the bond with $\mathrm{sp}^2-\mathrm{sp}^3$ hybridised carbons

Hence the order becomes:

$(1)=(2)<(3)$

iv.

1. Is the bond with $\mathrm{sp}^2-\mathrm{sp}$ hybridised carbons
2. Is the bond with $\mathrm{sp}-\mathrm{sp}$ hybridised carbons
3. Is the bond with $\mathrm{sp}-\mathrm{sp}^2$ hybridised carbons
4. Is the bond with $\mathrm{sp}^2-\mathrm{sp}$ hybridised carbons
5. Is the bond with $\mathrm{sp}-\mathrm{sp}$ hybridised carbons

Hence the order becomes:

$(2)=(5)<(1)=(3)=(4)$