

BONDING AND STRUCTURE.

Atoms combine with others to complete their octet. They do so by either transferring of electron or sharing of electrons. Transfer of electrons results into ionic bond while sharing of electron results into covalent bond.

There are 5 types of bonds which include

1. Ionic bonds
2. Covalent bonds
3. Co-ordinate covalent relative bonds
4. Metallic bonds
5. Hydrogen bonds

Ionic bonds

An ionic bond is formed when (an electron is formed) when an electron is transferred from one atom to another it is also known as an electrovalent bond.

By losing an electron, an atom gains a positive charge and becomes an ion.

The two oppositely charged cation and anion attract each other with a very strong electrostatic forces thus ionic compounds have very high melting points.

Eg include Na^+Cl^- , $\text{Mg}^{2+}\text{Cl}^-$, $\text{Zn}^{2+}\text{O}^{2-}$

Properties of ionic compounds

- They exist as solid at room temperature
- They have very high melting point and boiling point
- They are good conductors of electricity in molten state or in solution.
- The distortion of the electron cloud of an anion is called polarization

Properties of covalent bonds

1. They are normally liquid or gas in room temperature
2. They have low boiling point and melting point
3. They are insoluble in polar solvents but soluble in non - polar solvents
4. They do not conduct electricity

Polarization and its effect on bonding

(a) Effect on covalent bonding

When a covalent bond is formed between two similar atoms, bonding electrons are shared equally. However this isn't true when a covalent bond is formed between two different atoms.

The more electronegative atom attracts bonding electrons towards itself thus creating electric dipoles within the molecule. The molecule is said to be polarized.

Eg a molecule of phosphorous tri-chloride (PCl_3) is because chlorine



electronegative than phosphorous likewise SO_2 , H_2O , NH_3 , HI and HCl .

However carbon tetra chloride and carbondioxide molecules are non polar because their bonds are symmetrically arranged which gives the molecules a dipole moment of zero. Covalent compounds which are polar have physical properties different from what is expected from true covalent compounds eg some of them conduct electricity.

(b) EFFECT OF POLARIZATION OF IONIC BONDS

When a cation approaches an ion during an ionic bond formation it tends to distort the electron cloud of anion towards itself. The electron then tends to be more or less shared hence

Factors affecting polarization

(a) Ionic radius

Polarization increases with decrease in ionic radius of the cation however it increases with increase in ionic radius of an anion.

This is because in cation, a decrease in ionic radius leads to an increase in charge density due to high charge density, electrostatic attraction of electrons by the cation increases thus a high polarizing power.

For anions, a large ionic radius implies that the outer most electrons are very far away from the nucleus. These electrons can therefore be easily polarized (attracted) by the cation.

Example

For the compounds NaCl , LiCl and KCl , melting point increases from lithium chloride (LiCl) to potassium chloride (KCl) in the order



Why?

Explanation

Ionic radii of the cations increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$. The higher the charge density the higher is the polarizing power of the cation. The higher the polarizing power of the cation, the higher is the degree of covalency in its compounds.

Therefore the covalent character of the above chlorides decreases in the order



The higher the covalent character the lower is the melting point



Similarly the melting point of Aluminium chloride is lower than that of Aluminium oxide. This is because the chloride ion has a bigger ionic radius than the oxide ion. The chloride ion is therefore more easily polarized than the oxide ion. Consequently Aluminium chloride has a greater covalent character than aluminium oxide.

(b) Ionic charge

Polarization increases with increase in ionic charge. This is because in ionic charge leads to an increase in charge density. Consequently, aluminium chloride has a lower melting point than calcium chloride due to a high charge of the Aluminium ion (Al^{3+}) compared to calcium ion (Ca^{2+}).

Question

Below are the melting points of some compounds

Compound	M.P (R)
Al_2O_3	2290
AlCl_3	451
CaO	2850
CaCl_2	1051

Explain why

- (a) The melting point of Aluminium chloride is much lower than that of calcium chloride.
- (b) Melting point of Aluminium chloride is lesser than of Aluminium oxide

Solution

- a. AlCl_3 a high ionic charge and hence increase in charge density this leads to a high polarizing power this leads to an increase in covalency character hence a low melting point.
- b. The chloride ion has a bigger ionic radius than the oxide ion and therefore the chloride ion is easily polarised than the oxide ion and hence increase in covalence character this leads to low melting points.

The diagonal relationship

Down any group of the periodic table, charge density and electro negativity reduce therefore polarizing power reduces down the group.

Across any period ionic charge increase but ionic radius reduces therefore polarizing

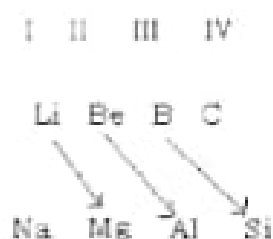
power increases across the period and also electronegativity i.e. charge density = $\frac{\text{charge}}{\text{radius}}$ increases.

Consequently an increase in polarizing power across the period is offset by a decrease in polarizing power down the group hence diagonal elements have similar polarizing power and electronegativity.

Similarity in polarizing power and electronegativity bring about similarity in chemical properties.

Consider part of the periodic table below.

I	II	III	IV
Li	Be	B	C
Na	Mg	Al	Si



From Lithium to beryllium polarizing power increases while from beryllium to magnesium polarizing power reduces.

The increase from Li to Be is offset by a decrease from beryllium to magnesium and therefore similar chemical properties.

Like wise Be and Al as well as Boron and Silicon have similar Chemistry (chemical properties) such elements are said to exhibit a diagonal relationship.

Diagonal relationship is defined as the relationship in which two elements diagonally opposite to each other in period 2 and 3 share similar chemical properties due to similarity in their polarizing power and electronegativity.

Because of the diagonal relationship, the chemistry of magnesium and Lithium is similar in the following ways.

1. Both lithium and magnesium combine directly with nitrogen to form nitrides other alkali metals do not react with nitrogen.
2. Both lithium and magnesium form normal oxides only i.e. Li_2O and MgO . Other metals form normal oxides and also peroxides e.g. Na_2O_2 .
3. Carbonates and hydroxides of magnesium and Lithium decompose on heating.

and are sparingly soluble. Carbonate of other alkali metals are soluble and do not decompose heating.

4. Nitrate of Lithium and Magnesium decompose on heating i.e. form an oxide, nitrogen dioxide and oxygen. Nitrates of other Alkali metals only form a nitrate and oxygen on heating.
5. Hydroxides of Lithium and Magnesium are not deliquescent.
6. Hydrogen carbonates of Li and Mg only exist in solution
7. Their fluorides are soluble in organic solvents
8. Both magnesium and Lithium form carbides when heated in carbon.

Exercise

State properties in which the chemistry of the following element is similar.

- (a) Beryllium and Aluminium
- (b) Boron and silicon

Solution

Beryllium and Aluminium

Both metals are made passive by nitric acid

Both metals react with NaOH to evolve H_2

Both oxides and hydroxides of beryllium and aluminium are amphoteric.

The chlorides are covalent polymeric solids when anhydrous ($BeCl_2$), and ($AlCl_3$), which readily dissolve in organic solvents they are readily hydrolyzed by water, with the evolution of hydrogen chloride.

Beryllium carbide, Be_2C , aluminium carbide Al_4C_3 give methane on treatment with water, unlike the ionic carbides of the group.

2 metals, they are therefore referred to as methides.

Similar complexes of beryllium and aluminium have similar stabilities eg BeF_4^{2-} and AlF_6^{3-} .

The shape is in agreement with the simple theory of electron pair repulsion.

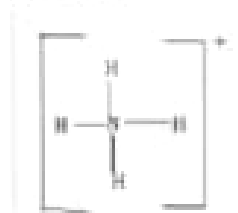
COORDINATE BOND (DATIVE BOND)

This is a covalent bond in which only one atom or group of atoms provides a pair of electrons being shared. The donor atom must have at least one lone pair of electrons i.e. a pair of electrons not being used for bonding.

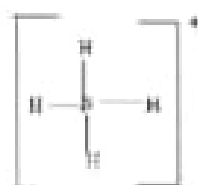
The acceptor atom must have atleast a vacant orbital.

Examples

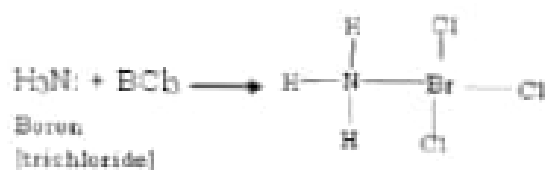
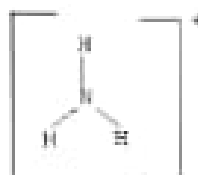
Ammonia



Adaptive bond is represented by an arrow pointing from the donor atom



Or



METALLIC BOND

In metallic bonding, each metal atom pools (loses) its valency electrons forming metal cations which are attracted together by the lost electrons. This results in a strong metallic bonds.

The lost electrons are delocalized and free to move through out the entire metal



structure thus metals conduct electricity and heat.

When atoms approach each other, their outer shell orbitals overlap forming molecular orbitals.

Because of a larger number of outer shell orbitals, many molecular orbits are formed which are non degenerate ie they are at different energy levels.

When light is shown on a metal, electrons absorb energy and transitions occur from lower energy molecular orbitals to higher energy molecular orbitals.

When electrons return to lower energy molecular orbitals.

When electrons return to lower energy molecular orbitals they emit energy in form of light. This explains why metals appear shiny.

Intermolecular forces

Covalent bonds have directional properties ie they are polar thus intermolecular forces exist between opposite poles of covalent molecules. The magnitude of intermolecular forces will determine whether the molecules are bond into solid state, liquid state a gaseous state.

Common intermolecular forces among covalent molecules include

Dipole-Dipole interactions, vander waal's forces and hydrogen bonds, hydrogen bonds are strongest among the intermolecule forces.

Intermolecular forces are generally weak compared to other bonds like covalent bonds or ionic bonds.

(i) Dipole-Dipole interactions

In solid state, polar molecules arrange themselves in such a way that opposite charges are adjacent to each other. This results into dipole-dipole attractions between the molecules.

Consequently ionic compounds dissolve in polar solvents because the energy required to break up the ionic crystal lattice is re-copued (recovered) by the energy released when dipole-dipole interactions occur between polar solvent molecules and ions of the ionic compound.

Vander waals forces

These are sometimes called molecular bonds, they are forces of attraction between electrical dipoles of different molecules. These forces exist in non – poor molecules eg

mobile gas molecules, hydrogen gas molecule. This is when non – polar molecules approaches each other, temporally dipole, moments are created between the moles. The opposite dipoles attract each other creating vander waal's forces.

Magnitude of vander waal's forces increase with increasing molecular mass and this explains why melting point an boiling point of alkanes increase with increase in molecular mass eg lower members are gases while higher alkanes are either liquids or solids at room temperature.

Hydrogen bonds

A hydrogen bond is dipole- dipole attraction between a hydrogen atom attached to a strongly electrongly to a strong electronegative atom and other electronegative atom in another molecule.

NOTE

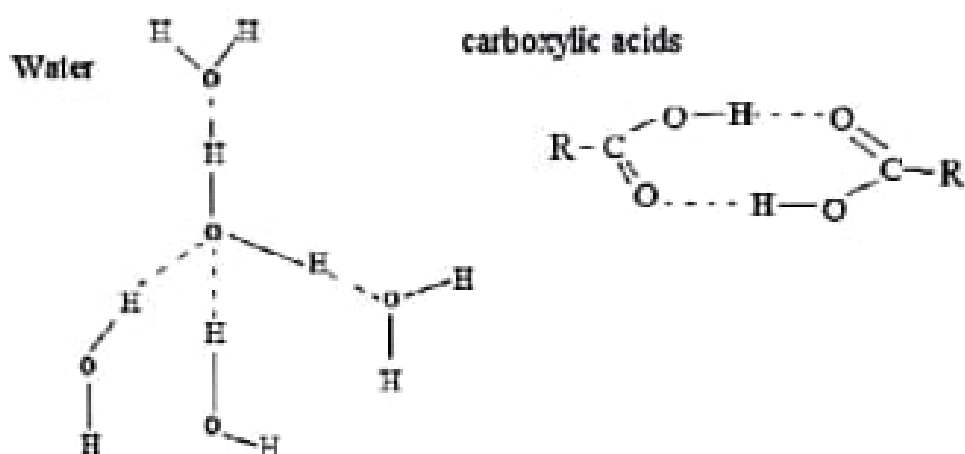
Highly electronegative atoms that can easily induce hydrogen bonds include fluorine, oxygen and nitrogen. Therefore molecules kin which a hydrogen atom is attached to one of these electronegative atoms normally contain hydrogen bonds eg HF, HN_3 and H_2O .

Hydrogen bonds are stronger than other intermolecular forces thus compounds having hydrogen bonds are characterized by unexpected physical properties eg melting point, boiling, density etc.

Dehydrogen bond is represented by a dotted line as shown in the compounds below.

Hydrogen fluoride $\text{H}^{\delta+} - \text{F}^{\delta-} \cdots \text{H}^{\delta+} - \text{F}^{\delta-} \cdots \text{H}^{\delta+} - \text{F}^{\delta-}$

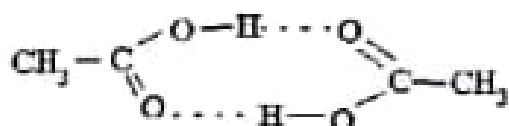




Effects of hydrogen bonding on physical properties of some compounds.

1. Ice floats of water
2. The formula mass of ethanoic acid as determined by freezing point depression method in benzene is twice the theoretical formular mass. This is because ethanoic acid associates in benzene through bonding to form dimmers.

Ethanoic acid



Question

Explain the following observations

Boiling points of hydrides of groups (vii) increase in the order $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$

The fluorine atom is highly electronegative thus hydrogen fluoride molecules are held by strong hydrogen bonds. This gives hydrogen fluoride an abnormally high boiling point.

The rest of the hydrides (HCl , HBr , HI) are held by weak vander waals forces.

Magnitude of vander waals forces increase with increasing the order to that of $\text{HCl} < \text{HBr} < \text{HI}$. The higher the molecular mass, the higher is the magnitude of vander-waal forces and the higher is the boiling point.

Ice floats on water

In ice, each oxygen atom is tetrahedrally bonded to four hydrogen atoms through covalent bonding and hydrogen bonding. This gives ice an extremely open tetrahedral



structure thus a low density.

When ice melts the water molecules are in constant motion the hydrogen bonds in water therefore progressively form and break over and over again. This enables close packing of water molecule thus water has a high density than ice.

Boiling points of alcohols are higher than those of alkanes of approximately the same molecular mass.

Alcohols are held by strong hydrogen bonds while alkane molecules are held by weaker vander-waals forces.

Intermolecular forces in alcohols therefore are stronger than those in alkanes thus alcohol require more energy for these forces to be broken such that alcohol can boil.

Evidence for existence of hydrogen bonds

Existence of hydrogen bonds can be confirmed by comparing properties of some compounds with similar compounds. These include.

- a. Ice has a lower density than water
- b. Boiling points of alcohol and carboxylic acids are higher than those of alkanes of approximately the same molecular mass.
- c. Amines have higher boiling points than alkanes of approximately the same molecular mass.
- d. Molecular masses of carboxylic acids determined by cryoscopic method in organic solvents are observed to be twice the theoretical molecular masses. This is because carboxylic acid dimerise through hydrogen bonding when placed in organic solvents.
- e. Ammonia, water and hydrogen fluoride have higher boiling points than other hydrides of group vi and vii respectively.
- f. 2-hydroxy benzoic acid has a lower boiling point than for hydroxy benzoic acid.

Similarly 2 nitro phenol has a lower boiling point than 4-nitrophenol.

Questions

Define the term hydrogen bond?

Give the term hydrogen bond?

Give example, discuss the effects of hydrogen bonds on physical properties of some compounds



Explain why ice has a lower density than water

Bonding and structure

- Bonding
- Electrovalent (ionic) bonding
- Coordinate bonding
- Vanderwaals bonding
- Hydrogen bonding

Structures

- ❖ Structure of simple molecular Cpds
- ❖ Structure of oxo anions
- ❖ Structures of ionic Cpds
- ❖ Structure of macro molecular covalent Cpds
- ❖ Metallic structures
- ❖ Structure of diamond and graphite

Bonding

Atoms of different elements or same elements combine to acquire stable electronic structures similar to those of noble gases which have full outer quantum shells such noble gases include: Helium, Neon, Argon, Krypton, Xenon.

The atoms combine in two types of bonding ionic bonding or covalent bonding ionic bonding or covalent bonding.

Atoms of the same metal come together through metallic bonding.

Vanderwaals bonding, coordinate bonding and hydrogen bonding come as a result of covalent bonding has taken place.

Electrovalent bonding

Electrovalent bonding is the type of bonding which there is transfer of electrons from outer most shells of the metal atoms to outer most shells of non – metal atom. The metal atom lose electrons and become cations while non metal atom, gain electron and become anions.

After the ions are formed, they are strongly attracted to each other through electrostatic forces of attraction which constitute ionic bond and the energy required to break the,

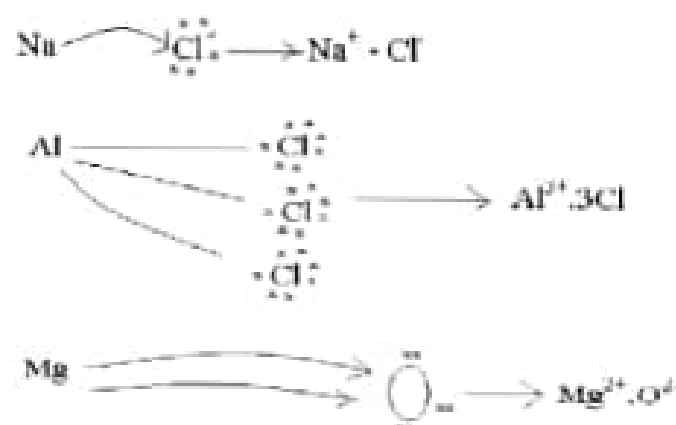
ionic bonds, is called lattice energy and its magnitude depends on two factors ie ionic radius and ionic charge. If ions of opposite charge have small ionic radii they approach each other strongly ie electrostatic force of attraction between the ions is high and this leads to high lattice energy.

If the ions of opposite charge have high charge density eg X^{2+} & Y^{2-} or X^{3+} & Y^{3-} they approach each other strongly with a very high electrostatic force of attraction and thus the ionic bonds will be very strong leading to high lattice energy.

Therefore lattice energy can be defined in two ways.

Lattice energy it is the enthalpy change or heat change that occurs when 1 mole of a crystal ionic solid is broken down to form free gaseous ions or it is the enthalpy change or heat change that occurs when one mole of ionic crystal lattice is formed from its constituent gaseous ions. This is an exothermic process heat given out.

Eg



Properties of Ionic Compounds

- ❖ They are crystalline solids at room temperature
- ❖ They conduct electricity either in molten state or in aqueous state.
- ❖ They are soluble in polar solvent such as water but insoluble in organic solvents such as benzene, ethanol, carbon disulphide
- ❖ They have very high melting points and very high boiling points

Note

Some ionic compounds may acquire covalent character particularly those formed from small cations eg Lithium chloride and Aluminium chloride possess some covalent character and

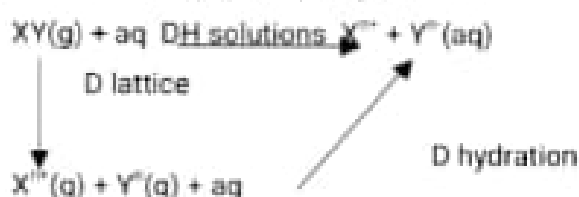


therefore can easily dissolve in organic solvents such as ethanol, benzene etc

This is because Li^+ and Al^{3+} have very small ionic radii and this makes them to have very high charge density and very high polarizing power and this leads to formation of covalent compounds with low melting point and boiling point.

When an ionic cpd is dissolved in water there are three energy terms involved.

- ❖ Enthalpy of solution
- ❖ Enthalpy of lattice
- ❖ Enthalpy of hydration



Covalent bonding

This is the type of bonding that takes place when non metal ions combine they can be of the same element or different elements. This type of bonding involves sharing of electrons and each atom contributes the same number of electrons for sharing.

They can share either a part of electrons or two or three pairs

When a pair of electrons is shared a single covalent bond is formed. When two pairs of electrons are shared a double covalent bond is formed and when three pairs of electron are shared then a triple covalent of electrons constitute a covalent bond is formed.

Note: Each pair of electrons constitute a covalent bond.

Show how the bonding takes place in the following C'pds.

Note: each pair of electrons constitute a covalent bond.

Show how the bonding takes place in the following C'pds

(a) Chlorine gas Cl_2



Carbondioxide



Ammonia gas



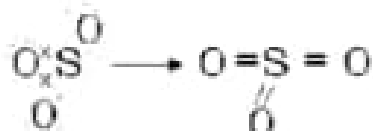
Sulphur dioxide gas



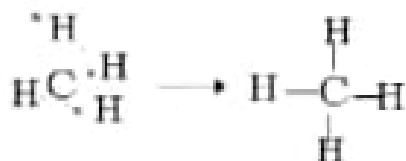
Nitrogen gas N_2



Sulphur trioxide gas



Methane gas



Water



Properties of covalent C'pds

Covalent cpds are mainly gases and volatile liquids with low melting points and boiling points except silicon (iv) oxide which has again a covalent structure and it is a solid with high melting point and high boiling.

Covalent C'pds are non conduction of electricity ie they are non electrolytes except some gases which dissolve in water to form some ions and are able to conduct electricity. Such gases include HCl, Cl_2 , NH_3 , SO_2 , CO_2 .

Equations



Most of the covalent Cpds consist of discrete molecules

Most covalent Cpds are insoluble in water but soluble in organic solvents eg CCl₄ is insoluble in water but very soluble in ether.

Coordinate bonding

Coordinate bond is a type of covalent bond in which the shared pair of electrons is provided by only one of the bonded atoms. One atom is the donor and the other is the acceptor.

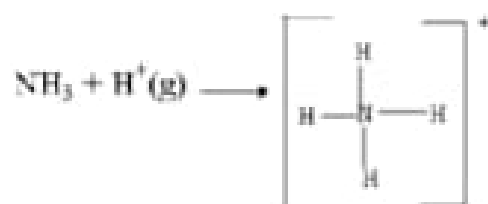
A coordinate bond is sometimes called a dative bond. Once a dative bond is formed it has the same characteristics as a covalent bond.

A coordinate bond is differentiated from a normal covalent bond where electrons are shared from both atoms and where they are going.

For an atom to act as a donor, it must have at least one pair of unshared electrons (a lone pair of electrons).

The acceptor atom should lack a pair of electrons. Cpds or ions which exhibit coordinate bonding are as follows.

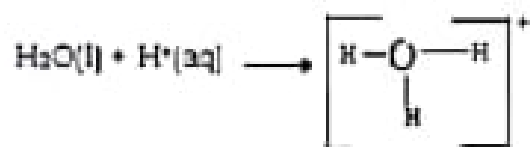
(a) Ammonium ion



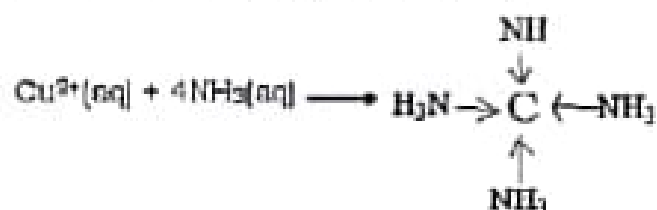
(b) Ammonium boron chloride H₃N.BCl₂



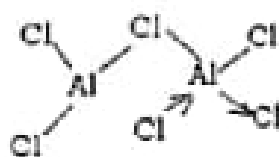
(c) Hydroxonium ion (H_3O^+)



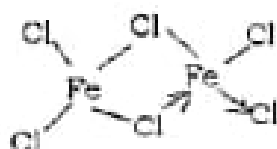
(d) Tetra amine copper (II) ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$



(e) Aluminium chloride in the vapour phase has a formula Al_2Cl_6 which is a dimer of AlCl_3 through coordinate bonds.



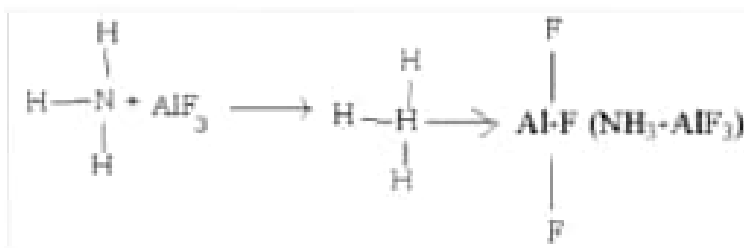
Iron (III) chloride in vapour phase a formula FeCl_6 which is dimer of FeCl_3 through coordinate bonding.



Beryllium chloride in the vapour phase has a formula Be_2Cl_4 which is a dimer of BeCl_2 through coordinate bonding.



Ammonium aluminium fluorid (NH_4AlF_6)



Nitrogen Chloride (NO₂)



Shapes of simple covalent molecules and ions

The shapes of simple covalent molecules or ions are predicted by a theory called valence shell electron pair repulsion theory which was advanced by sidy wick and powell (VSEPR theory).

The theory is based on the following principles

The arrangement of the electron pairs around the central atom in a molecule or ion depends on the number of electron pairs of the central atoms

The stable structure adopted by a molecule or ion is the one which the electron pairs around the central atom are distributed so as to minimize the repulsion and hence to minimize the energy of the molecule or ion.

Any lone pair of electrons on the central atom will occupy the top position and will repel the bond pairs more greatly and can influence the geometry of the molecule.

Note: lone pair of electrons is a pair of electrons which do not take part in bonding.

A bond pair is a pair of electrons that form a single covalent bond.

According to the theory, repulsion decreases in the

- Order; lone pair – lone pair > lone pair – bond pair > pair-bond pair.
- Triple bond (X ≡ Y) > double bond (X = Y) > single bond (X-Y)
- The repulsion decreases with the decrease in the electro negativity of the central atom. This affects the bond angles.

Steps to follow when working out the shape of the molecule or ion

- Write the electronic configuration of the central atom in terms of SPDF notation
- Determine the number of electrons in the outer most quantum shell



iii. Determine the number of bond pairs and ion pairs of electrons in the central atom

iv. Write the formula of the C'pd in the form AX_nE_n where

A-Central atom

X- Ligands (surrounding atoms)

M - number of ligands

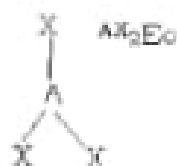
E- Ion pair of electrons

n - Number of ion pairs of electrons

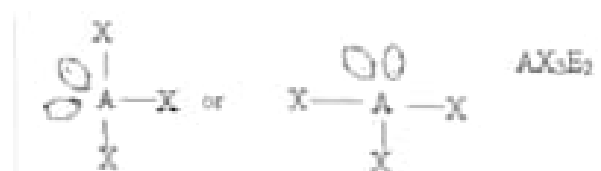
The molecule or ion can adopt any of the follow shapes / structures

Linear structure $X-A-X^{AX}_2E_0$

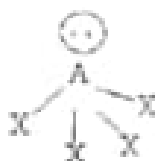
Triagonal planor (triangular) structure



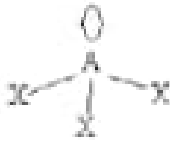
T - shaped structure



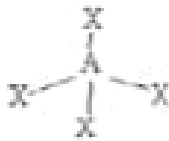
Sea saw (AX_4E_1)



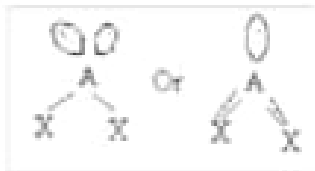
Pyramidal (AX_3E_1)



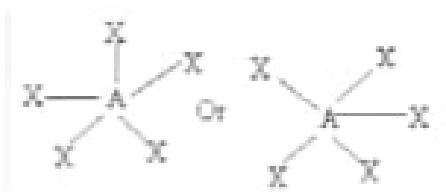
Tetra hedral (AX_4E_1)



V- Shaped structure AX_2E_2 or AX_3E_1



Trigonal bipyramidal (AX_5E_0)

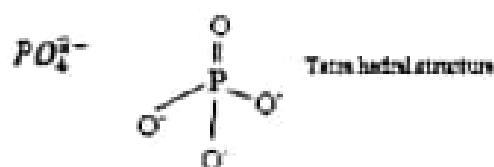
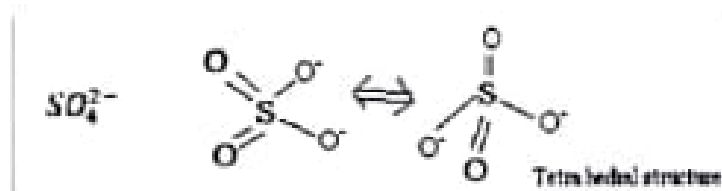
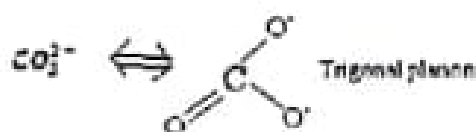


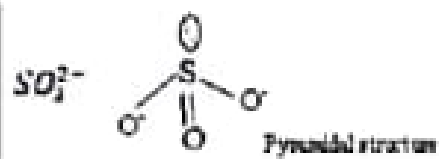
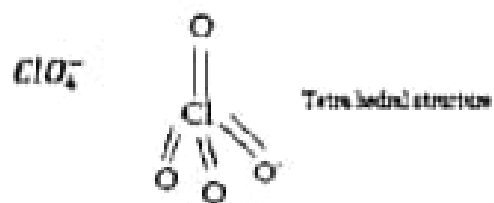
Note

1. When a central atom has atleast alone pair of electrons, the molecule can adopt any of the following shapes or structures.
 - ❖ v-shaped structure
 - ❖ T- shaped
 - ❖ Pyramidal
 - ❖ Sea-saw

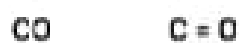


- When a central atom has no lone pair of electrons then the molecule can adopt any of the structures.
 - Linear
 - Trigonal planar
 - Tetrahedral
 - Trigonal bipyramidal
- Oxygen atom forms a double bond with the central atom except when the oxygen has a charge of negative that is when it forms a single bond with the central atom
- An oxo anion (XO_m^{n-}) shows that m oxygen atoms with negative charge and thus forms single bonds with the central atom and the rest of the oxygen atoms form double bonds with the central atom eg

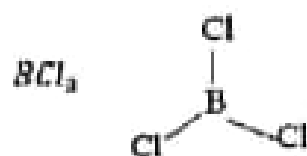


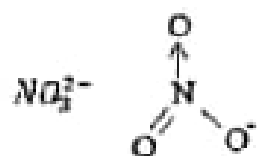


Linear structure

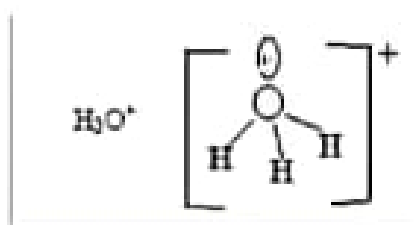
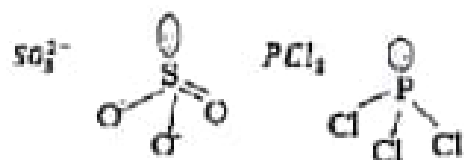
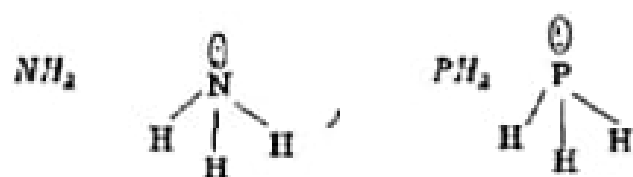


Trigonal planar structure AX_3E_0

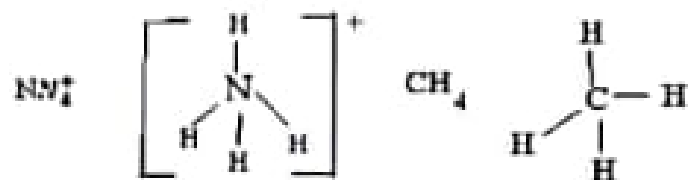


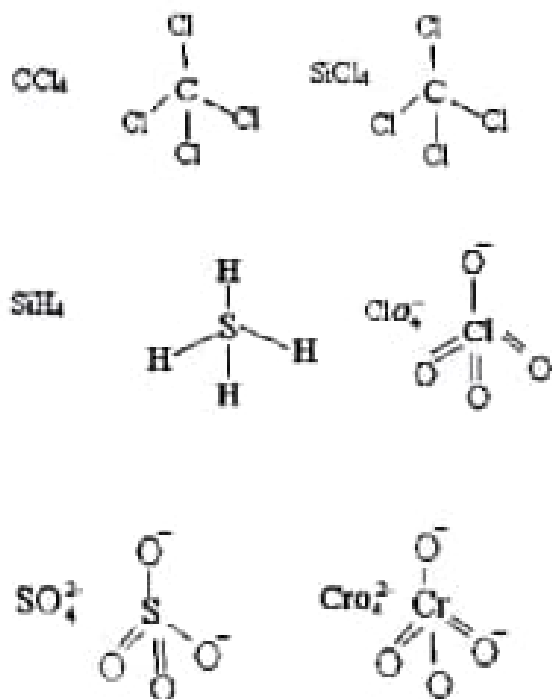


Pyramidal structure (AX₃E₁)

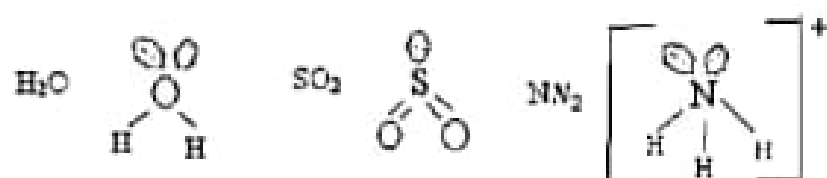


Tetrahedral structure (AX₄E₀)





V-Shaped structure

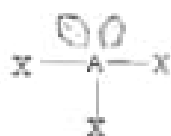


Trigonal bipyramidal (AX_5E_0)



T-Shaped structure (AX_3E_2)





Eg CCl_3



ICl_3



See-saw AX_4E_1



Eg SF_4 , Sulphur tetra fluoride



Effect of electro negativity of the central atom on the bond angle

Electro negativity can be defined as the ability of an atom to attract bond electron towards itself when combined in a C'pd.

Bond angle is the angle formed between two covalent bonds.



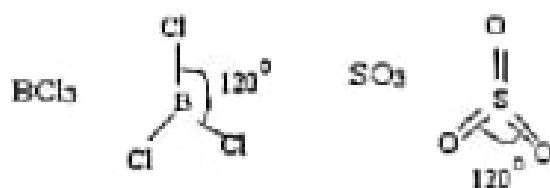
Linear structures have a bond



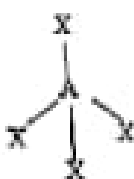
Trigonal planar structures have a bond angle of 120°



Eg



Tetrahedral structures are expected to have a bond angle of 90° but some time it is either less or greater than 90° due to the differences in the electro negativity of the central atom and the ligands eg



When the electro negativity of the central atom is high then there is a strong attraction of the bonding electrons towards itself and this results into a high concentration of bonding electrons around the central atom and this increases the repulsion between the bonding electron pairs and thus the bond angle is bigger than expected.

But if the electronegativity of the central atom is smaller than the ligands then the bonding electrons will be attracted towards the ligands and there will be a low



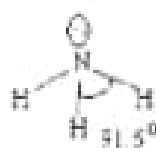
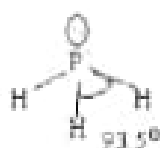
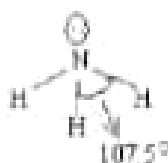
concentration of bonding electrons around the central atom and thus the repulsion between bond angle to be smaller.

The effect of electronegativity of the central atom on bond angles is much felt in pyramidal structures and V-shaped structures where there is atleast along pair of electrons on the central atom.

Considering the hydrides of group V and group VI

Group V: NH_3 , PH_3 , AsH_3 (pyramidal)

Group VI: H_2O , H_2S , SeH_2 (V-shaped structure)



The hydrides of gpV adopt a pyramidal structure because the central atom has a lone pair of electrons but the bond angle decreases from the hydride of nitrogen to the hydride of Arsenic. This is because the electronegativity of nitrogen is higher than that of phosphorous which in turn is higher than that of arsenic.

In ammonia there is a high conc of bonding electrons around the central atom making the repulsion greater and thus making the bond angle to be bigger.

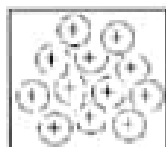
In phosphine (hydride of phosphorous) the electronegativity of phosphorous is smaller than that of nitrogen and there is a low concentration of bonding electrons around the phosphorous atom and the repulsion between bond pairs reduces making the bond angle to be smaller. NB the same explanation applies to the hydrides of group VI elements.

Metallic bonding

A metallic bond is a strong attraction between the metal ion and the delocalised electrons

In a metal structure positive ions of the metal are packed in a regular array with in a sea

of electrons liberated from the metal atoms.



The more the no. of valency electrons of the metal, the stronger the metallic bond.

Group I metals are very soft and can easily be cut with a knife because their metallic bond is weak because each atom contributes one electron to the metallic bond formation (charge cloud).

Group II metals are harder than group I metals and therefore their boiling and melting points are higher than those of group I metals.

This is because each atom of a group II metal contributes two electrons to the charge cloud and thus the metallic bond is stronger.

Transition metals are very hard e.g. iron, manganese, chromium etc. because their metallic bonds are very strong because they have many valency electrons contributed to the metallic bond.

Properties of metals

They are conductors of heat and electricity because of the delocalized electrons.

They have high luster (they have shiny surfaces).

They have high density.

They have high melting and boiling points.

They are malleable and ductile i.e. their metal ions can slide relative to one another when under stress without shattering.

Vander Waals forces

Vander Waals forces are the kind of attraction between polar covalent molecules or non-polar covalent molecules due to dipole-dipole interaction.

In polar covalent molecules and non-polar covalent molecules, Vander Waals' forces increase with increase in relative molecular mass.

Among the Group VII (halogens), the Vander Waals forces increase down the group due to the increase in relative molecular mass of the halogens; chlorine and fluorine are



gases at room temperature, bromine is a volatile liquid while iodine is a volatile solid which sublimes on warming.

The van der Waals forces become progressively stronger as one moves down the group and therefore the boiling points of the halogens increase down the group.

Among alkanes the van der Waals forces increase with increase in relative formula mass eg methane, ethane, propane and butane are gases at room temp, although their boiling points are different. From pentane to hexadecane are liquids at room temperature.

Those alkanes with 17 carbon atoms and above are solids (waxy solids)

In alcohols there are van der Waals forces existing in their molecules in addition to hydrogen bonds.

The boiling points of alcohols are higher than those of alkanes.

Branching in organic compounds both polar and non polar reduces van der Waals forces and the branched isomers have relatively lower boiling points than unbranched isomers.

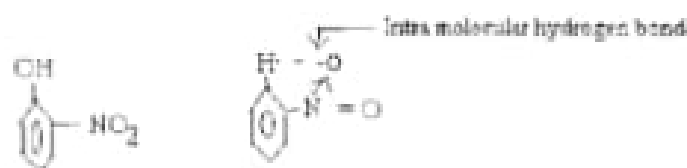
Hydrogen bonding

A hydrogen bond is a permanent dipole-dipole interaction (attraction) between a hydrogen atom in one molecule and a more electronegative atom in another molecule or the same molecule.

There are two types of hydrogen bonding:-

Intramolecular hydrogen bonding which exists in the same molecule and intermolecular hydrogen bonding which exists in different molecules.

2-nitrophenol is the best example where intramolecular hydrogen bonding takes place.



4-nitrophenol exhibits intermolecular hydrogen bonds



Intermolecular hydrogen bonding is stronger than intra molecular hydrogen bonding because there are many molecules involved in the hydrogen bond formation while intra molecular hydrogen bonding there is only one molecule.

The more electronegative atoms include oxygen, fluorine, sulphur and nitrogen.

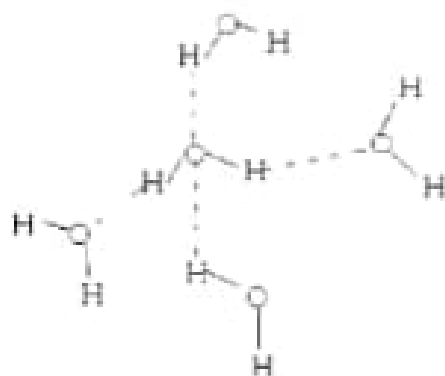
Effect of hydrogen bonding on the physical properties of some compounds (covalent)

Physical properties of some covalent c'pds such as solubility in water, melting and boiling points, density are affected by the presence of hydrogen bonds.

When a c'pd contains a more electronegative atom such as atom, its physical properties will be different from those of the group members eg the hydrogen of gpVI and gVII are generally gases at room temperature but water and hydrogen fluoride are liquids at room temp.

This is because water molecules associate together through strong hydrogen bonds and to break these bonds, more energy is needed and therefore water boils at 100°C but hydrogen sulphide its boiling point is -60°C .

Hydrogen sulphide molecules associate together through weak vander waal's forces which require less energy to break and therefore it is a gas at room temperature.



Similarly the boiling point of hydrogen fluoride is 20°C while that of hydrogen chloride is -80°C . this is because fluorine is more electronegative than chlorine and therefore hydrogen fluoride molecules associate through strong hydrogen bonds which require a lot of energy to break while hydrogen chloride molecules associate through weak vander waal's forces which require less energy to break and that is why HCl exists as a gas at room temperature while HF exists as a liquid at room temperature.



Ammonia (NH_3) and phosphine (PH_3) are hydrides of gpV elements and their boiling points are -35°C and -86°C respectively. The boiling point of ammonia is much higher than that of phosphine. This is because nitrogen atom is smaller and more electronegative than that of phosphorous ammonia molecule associate through stronger hydrogen bonds which requires more energy to break while PH_3 molecules associates through weak vander waals forces which require less energy to break.

Among the Hydrides of gpV, gpVI and gpVII elements water has the highest boiling point because it forms extensive hydrogen bonds and each water molecule forms 4 hydrogen bonds which require more energy to break.

When water is cooled up to 0°C it forms ice which is solid water because the hydrogen bonds are very strong at this temperature and they hold water molecules in their liquid positions and the ice formed is less dense than liquid water (it has a lower density than water) because the 4 hydrogen bonds around the water molecule will give ice a tetrahedral structure which is open and therefore will occupy more space/volume and with the same mass of the water the density reduces. But when the ice melts the hydrogen bonds are progressively broken and this facilitates the close plucking of the water molecules and there is a decrease in volume and therefore the density increases.

The table below shows the boiling points of the hydrides of group V, groupVI and group VII.

	Gp IV					GpV		
Hydride	CH_4	SiH_4	GeH_4	SnH_4	NH_3	AsH_3	SbH_3	PH_3
Bpt($^\circ\text{C}$)	-161	-112	-95	-52	-35	-56	-20	-86
Period No.	2	3	4	5	2	4	5	3

	Gp VI					GpVII		
Hydride	H_2O	H_2S	H_2	H_2Te	H_2	HCl	HBr	HI
Bpt($^\circ\text{C}$)	100	-60	40	-5	20	-80	-60	-35



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Question

- a. On the same axes, plot graphs of boiling points of the hydrides of gp IV, gpV, gp IV and gp VII against period number.
- b. Explain the shape of the graph.