

## ATOMIC STRUCTURE

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Atoms are composed of fundamental particles, the most important of which are the electrons, protons and neutrons. Protons and neutrons make up the nucleus of the atom. Hence these particles are collectively called the nucleons. Electrons equal to the number of protons revolve around the dense nucleus at a relatively large distance away from it.

**Atomic Number or Proton Number :** is the number of protons in the nucleus of the atom of an element.

**Mass Number or Nucleon Number :** is the total number of the protons and neutrons in the atom of an element.

Particle	Relative Mass	Relative charge	Charge /Coulombs	Mass/kg
Proton	1	+1	$+1.6 \times 10^{-19}$	$1.673 \times 10^{-27}$
Electron	1/1840	-1	$-1.6 \times 10^{-19}$	$9.11 \times 10^{-31}$
Neutron	1	0	0	$1.675 \times 10^{-27}$

**Isotopes:** are atoms having the same number of protons but different number of neutrons.

: are atoms having the same atomic number but different mass number.

Behaviour of sub-atomic particles in an electrical field.

Protons : attracted by the negatively charged plate.

Electrons: attracted by the positively charged plate.

The deviation is much greater than that of protons

Neutrons: are unaffected

### The Nuclear Atom

Geiger and Marsden experiment.

Geiger and Marsden bombarded thin foils of gold with collimated beams of  $\alpha$  particles and observed the subsequent path of the particles using a fluorescent zinc sulphide screen. Most of the particles passed through with little or no deviation indicating the atom to be mostly empty. A few of them however were deflected by large angles and some through almost  $180^\circ$ . This indicated the presence of a body larger in size, mass and charge than the  $\alpha$  particle. From the number and angles of deflection Rutherford deduced that almost all the mass of the atom must be concentrated into a tiny dense nucleus. He also calculated that the nucleus carried a positive charge approximately equal to half the relative atomic mass. He proposed that electrons equal to the number of positive charges were rotating round the nucleus further away from it, like the planets around the sun, the attraction between the electron and the nucleus being balanced by the centrifugal force.

### Electronic structure of atom

Rutherford's planetary model of the atom had two flaws.

1. It did not explain why the electrons do not fall into the nucleus ultimately as they would be expending energy during their motion. (Charged particles undergoing acceleration should emit energy. Electrons, being charged negatively while circling the nucleus are subjected to acceleration and hence should lose energy.).

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- 2 It also did not explain the formation of line emission spectrum by chemical substances on heating or when subjected to electric discharge.\* (The flame colours; Ordinary light gives a continuous spectrum).

In order to explain why electrons do not fall into the nucleus during their motion and the formation of discontinuous spectra Bohr used quantum theory along with two of his own assumptions.

He proposed that electrons revolved only in certain permissible orbits, each one possessing a definite amount of energy. As long as they moved in those permitted orbits, they did not lose energy and hence would not fall into the nucleus. This assumption explained the first flaw. When supplied with energy they absorbed certain definite amounts of energy and jumped to higher levels where they were said to be in an excited state. In the excited state, electrons are unstable and they come down to the ground state by releasing definite amounts of energy. The frequency of radiation emitted, he assumed, to be determined by the energy difference between the two energy levels. Thus each element emitted its own characteristic radiation.

By using the Planck's idea that energy is quantised and his assumption that energy exchange only takes place when they jump from one level to another he explained the formation of the discontinuous emission spectrum.

NOTE: The energy of the electronic levels is determined by  $-k/n^2$  where  $n$  is the number of the energy level (principal quantum number). Hence as the number of the energy level increases, the difference in energy between the levels decreases with the result that they come closer together and finally converge. At the convergence limit, electrons will be not under the field of attraction of the nucleus and thus the energy associated with the convergence limit would be the energy of ionisation of the element

### Uncertainty Principle - Heisenberg

It is now known that for very fast moving sub-atomic particles, both the position and velocity cannot be determined simultaneously. For example if an attempt is made to determine the exact position of an electron the light energy used to see would shift it away from the position.

We can refer only to the probability of finding an electron at a given position. Electron is now regarded as existing in a much more diffuse region. The region in space where the probability of finding an electron is maximum is called the orbital. Electrons are viewed as charge clouds and the region, which encloses almost all the charge cloud, is the orbital, The orbitals are of different shapes and are named s,p,d,f etc

It can be shown from quantum mechanics that for the principal quantum number  $n$ , the number of sub-levels will be  $n$ , the number of orbitals will be  $n^2$  and the maximum number of electrons that can be accommodated is  $2n^2$

The solutions also reveal that each orbital can hold only a maximum of two electrons, one spinning clockwise and the other anticlockwise, so that the magnetic field produced by one would be nullified by the other.

The most important orbitals are the s and the p. The electron probability distribution for an s orbital is spherically symmetric.\* In other words, the s orbital has a spherical shape. Each energy level has just one s orbital holding two electrons one spinning clockwise and the other anticlockwise. The p orbital has a dumb-bell shape with electron charge density of zero at the nodal plane.\* p orbitals are three in number in each energy level, except the first, orientated right angles to each other along the main axes, x, y and z. Since each orbital holds a maximum of two the p sub-level holds a maximum of 6 electrons

d orbitals come in a group of five orbitals so that the d sub-level can accommodate a maximum of ten electrons while f orbitals come in groups of seven and hold a maximum of 14 electrons

## ELECTRONIC CONFIGURATION OF ATOMS

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The electrons are distributed in the orbitals of the various sub-levels, in the different energy levels of the atom. The order in which they fill up the sub-levels is governed by stability. When electrons fill up the orbitals having the least energy they attain maximum stability. The increasing order of their relative energies is solely not dependent on the principal quantum number. It is also partly dependent on the shape of the orbitals. As nuclear charge increases, the energy of all the orbitals decreases as they are drawn closer to the nucleus. The spherical s orbitals are pulled in by the nucleus more strongly than the p orbitals, which in turn are attracted more strongly than the d orbitals. Hence the energy of the s orbitals decreases more rapidly than p orbitals which decreases more than d orbitals. The increasing order can be readily worked out from the following sequence.\*

The electronic structure of an element is deduced by the successive addition of electrons applying the following principle

**Aufbau Principle:** Electrons enter the orbital that is available with the lowest energy. The orbitals are arranged in the order of increasing energy and the electrons are added until the proper number of electrons for the element has been accommodated

**Pauli's Exclusion Principle:** No orbital can accommodate more than two electrons.

**Hund's Rule of Maximum Multiplicity:** When there are a number of orbitals of equal energy, electrons first fill them up singly and then get paired. By filling up singly, mutual repulsion between electrons is avoided and thereby maximum stability is achieved

When there are number of orbitals of equal energy special stability is associated with completely filled and half-filled configurations. Due to this  $d^9s^2$  and  $d^4s^2$  configurations are not found. They change into  $d^{10}s^1$  and  $d^5s^1$  configurations respectively to acquire greater stability\*

Note: Though the s orbital is at lower energy level than the d of the penultimate shell after the filling of the d sub-level, the order changes. The d electrons because of the shape of the d orbital penetrate into the region of space between the nucleus and the s probability zone and repel the s electrons and push them to higher energy level.

Before filling:  $1s \ 2s \ 2p \ 3s \ 3p \ 4s \ 3d$

After filling:  $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^2 \ 3d^x \ 4s^2$

Thus the electronic configuration of iron is  $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^2 \ 3d^6 \ 4s^2$  and not  $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^2 \ 4s^2 \ 3d^6$

## PERIODIC TABLE

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The modern Periodic Table is obtained by arranging the elements in the order of increasing atomic number such that elements with similar electronic configuration lie in vertical groups. Thus elements with electronic configuration ending up as  $ns^1$  are put in one Group while those that end up as  $ns^2$  are put in another Group.

The elements that fill up the s orbital of the highest energy level are said to belong to the s block. The elements that similarly fill up the p orbitals of the highest energy are said to belong to the p block. Thus there are two columns in the s block and six columns in the p block. The elements that fill up the d sub-level of the penultimate shell are called the d block elements.. Those that fill up the f sub-level are referred to as the f-block elements.

Elements, which form at least one ion with the incomplete d sub-level, are called transition elements. There are eight such elements in each series of the d block elements. The number of the Period gives the highest principal quantum number of the element. i.e. the value of n of the outermost electronic shell of the element

### Electronic configuration of ions

Metallic elements, belonging to Groups I, II and III form positively charged ions by losing electrons in their outermost shell, so that the ions may be iso-electronic with the preceding noble gas.

Non-metallic elements belonging to Groups V,VI and VII form negative ions by accepting electrons so that they achieve the noble gas configuration

When d block elements form ions electrons are lost first from the outermost s orbital and then from the penultimate d sub- level

- Show on a labeled sketch the shapes and spatial distributions of all the orbital of principal quantum number 2.
  - Using s, p, d notation, write the electronic structure of (i) iron (ii) chromium (iii) copper
  - Represent the electronic configuration of the atoms of the elements in (b) using boxes to represent the orbitals
  - Write down the electronic configuration of (i) sulphide (ii) iron (II) (iii) iron (III) (iv) chromium(II)
- Write down the electronic configuration of the following and determine the number of unpaired electrons in each of them (a) phosphorus (b) chromium (c) oxygen (d) iron
- The first, second, third and fourth ionisation energies of an element E are 740,1500,7700 and 10500  $\text{kJ mol}^{-1}$  respectively. Assign the Group in the Periodic Table to which E belongs.
- The first ionisation energies of five successive elements A,B,C,D and E in the Periodic Table are 1400.1310, 1680, 2080 and 494  $\text{kJ mol}^{-1}$ . State the Group in the Periodic Table to which the elements A, B, C, D and E belong, giving your reasons
- The first ionisation energies, in  $\text{kJ mol}^{-1}$  of Group II and Group III elements are given below.

Group II	Be: 900	Mg: 736	Ca: 590	Sr: 548	Ba: 502
Group III	B: 799	Al: 577	Ga: 577	In: 558	Tl: 589

- Explain why the first ionisation energies decrease in magnitude on descending Group II.
- Explain why the first ionisation energy of aluminium is less than that of magnesium.
- Explain why the first ionisation energies of aluminium and gallium are equal
- Suggest why the first ionisation energy of thallium, Tl, is greater than that of barium.
- Suggest why the first ionisation of thallium is greater than that of indium.



## IONIZATION ENERGY

Ionization energy is the energy required to remove one mole of (the most loosely held) electrons from one mole of gaseous atoms under standard conditions. This is more specifically referred to as the first ionization energy.



Ionization energy is the energy imparted to the electron so that it can be removed completely from the nuclear attraction. After an electron had been removed the rest of them would be strongly attracted by the nucleus as the nuclear charge remains the same while the number of electrons that are being pulled in is less. Hence more energy is required to remove the second electron. Thus 2<sup>nd</sup> I.E is greater than the 1<sup>st</sup> I.E

Second ionization energy may be defined as the energy required to remove one mole of electrons from one mole of singly charge positive ions in the gaseous state.



The consecutive values of ionization energies would be related as follows:

$$I_1 < I_2 < I_3 < I_4 < I_5 \dots\dots$$

Successive ionization energies do not increase uniformly. Large amounts of energy are required to disrupt a completed sub-level and extra large amounts of energy are required to disrupt a noble gas configuration. The successive ionization energies of sodium illustrate the change clearly.

$I_1$	$I_2$	$I_3$	$I_4$	$I_5$	$I_6$	$I_7$	$I_8$	$I_9$	$I_{10}$	$I_{11}$
500	4600	6900	9500	13,400	16,600	20,100	25,500	28,900	141,000	158,000

A plot of  $\lg I$  against the number of electrons removed would reveal the steep changes in the variation of the values as noble gas configurations are disrupted.\*\*

Factors influencing the ionization energy of elements.

- |                  |                                       |
|------------------|---------------------------------------|
| 1 Nuclear charge | 3 Nature of the sub-level             |
| 2 Atomic radius  | 4 Stability of certain configuration. |

**Nuclear charge:** As nuclear charge increases, the attractive force would increase and hence more energy would be needed to overcome the increasing nuclear attraction.

**Atomic radius:** As the atomic radius increases the outermost electron would be further away from the nucleus experiencing a weaker attractive force. Hence the value decreases with increasing size.

**Nature of sub-level:** The s orbital is spherical in shape and the p orbital is dumb-bell shaped. The electrons in the s orbital are closer to the nucleus than the electrons of the p orbital of the same shell. Hence s electrons are more firmly held. The removal of s electron is hence comparatively more difficult than a p electron of the same shell as p electrons are slightly further from the nucleus and also experience the shielding effect of the s electrons

**Stability of certain configurations:** Completely filled sub-levels are more stable than others requiring large amounts of energy for their disruption. This additional stability is associated with half-filled sub-levels also.  
Stability of completely filled sub-level > stability of half-filled sub-level > stability of other configurations.

A graph of the first ionization energy of the elements plotted against the atomic number illustrates the factors clearly.

Along a Period as electrons are being added on to the same shell, the magnitude of the ionization energy increases due to the increase in the nuclear charge. This is clearly seen in the first Period. in Period 2 and 3 this trend is seen with breaks in Group III and Group V

The sharp decrease from Group 0 to Group I, is because of the increase in the atomic radius due to the addition of the extra shell, the increasing radius outweighing the effect of the increasing nuclear charge.

The electrons of the inner shells repel the outermost electron and also shield the outermost electron from the effect of the nuclear charge. Hence as the number of inner shells increases the attraction felt on the outermost electron decreases, decreasing the energy.

The ionization energy of Group III elements is less than that of Group II elements. This is because in Group III the electron is removed from the p sub-level whereas in Group II it is removed from the s orbital. Less energy is sufficient to remove the singly filled p electron than the firmly held s electron due to

The special stability associated with the completely filled s sub-level.

The closer proximity of the s electrons than the p electrons.

The ionization energy of VI elements is less than that Group V. In Group VI the electron that is being removed is experiencing inter-electronic repulsion and hence requires less energy. Further the half-filled sub-level in Group V is fairly stable and requires more energy to remove

- Sketch graphs, with ionisation energy on the vertical axis, to illustrate the following:
  - The first ionisation energy of the noble gases He, Ne, Ar, etc plotted against atomic number.
  - The first ionisation energies for a series of elements, consecutive in atomic number and beginning with a noble gas and going through a 'short period'.
  - The successive ionisation energies (1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, etc) of the element magnesium, plotted against the number of electrons removed.
  - The first ionisation energy of the alkali metals, Li, Na, K, etc. plotted against atomic number.
  - The first ionisation energies for a series of elements, consecutive in atomic number and beginning with a noble gas and going through a 'long period'.
  - The first ionisation energies for a series of elements, consecutive in atomic number and beginning with a halogen.
  - The successive ionisation energies (1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, etc) for an element with the outermost configuration  $ns^2 np^2$ , plotted against the number of electrons removed
- The first, second, third and fourth ionisation energies of an element E are 740, 1500, 7700 and 10500  $\text{kJ mol}^{-1}$  respectively. Assign the Group in the Periodic Table to which E belongs.
- The first ionisation energies of five successive elements A, B, C, D and E in the Periodic Table are 1400, 1310, 1680, 2080 and 494  $\text{kJ mol}^{-1}$ . State the Group in the Periodic Table to which the elements A, B, C, D and E belong, giving your reasons.

### Electron affinity

Electron affinity of an element is the energy change that occurs when one mole of its gaseous atoms gains a mole of electrons under standard conditions.



Most first electron affinities are exothermic. This is because energy is released when the electron comes under the attraction of the nucleus. (Bond formation is exothermic.) However when an electron is added to an atom with a full or exactly half-full outer shell the electron affinity is low or endothermic as these configurations are comparatively more stable.

Element	Na	Mg	Al	Si	P	S	Cl
E.A/ $\text{kJ mol}^{-1}$	-20	+67	-30	-135	-60	-200	-364

The subsequent electron affinities are always endothermic since the initial repulsion between the negatively charged ion and the incoming electron outweighs the energy released when the electron comes under the attraction of the nucleus.



## CHEMICAL BONDING

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The electronic configuration of noble gases is very stable and normally elements react in order to attain the stable octet configuration either by losing gaining or sharing the electrons. Depending on the manner they attain the noble gas configuration different types of bonds are formed.

### Electrovalent bonding or ionic bonding

When an element that has comparatively low ionization energy and an element with a relatively high electron affinity combine, electrons are transferred from the former to the latter so that the ions formed are iso-electronic with the noble gases. The strong electrostatic attraction that prevails between the oppositely charged ions is referred to as the ionic bond.

The compounds formed of ionic bonds do not contain individual molecules, but are formed of an infinite assembly of ions. The ions due to their mutual attraction arrange themselves in a regular pattern. Thus they are always crystalline solids at room temperature. The electrical force binding them being very strong, they are non-volatile with high melting and boiling points. Because they are comprised of ions they conduct electricity in the molten or aqueous state, once the ions are made mobile. In the solid state they do not conduct electricity. Generally ionic compounds are soluble in polar solvents like water. In aqueous solutions the rate of reactions of ionic compounds is very fast-almost instantaneous.

Ionic compounds are hard. However they are brittle. With a slight deforming force it is possible to slightly displace one layer of ions relative to the next and thereby bring ions of similar charge next to each other. Similar ions repel each other forcing apart the two portions of the crystal.

### Covalent bonding

Atoms, which require high amounts of energy to obtain the noble gas configuration either by losing or by gaining electrons, do so by sharing. This is brought about by the atomic orbitals of each atom overlapping with each other, coalescing and forming a molecular orbital. Only singly filled orbitals take part in such bonding, so that the resultant molecular orbital has only two electrons. In the molecular orbital the two electrons circulate around and are attracted to two nuclei of the two bonded atoms. This increased negative charge in the centre holds the two positively charged nuclei together, thus forming the bond. e.g.  $\text{PCl}_3$   $\text{CS}_2$   $\text{N}_2$

Depending on the number of electrons involved, the bonding is classified as single double and triple.

Covalent bonding produces mainly simple or individual molecules. The inter-molecular forces in them are the weak van der Waal's forces and hence at room temperature they are generally gases or liquids. i.e. molecules are mobile. Thus covalent compounds have low melting and boiling points and are volatile. They do not conduct electricity in the molten state. Covalent compounds dissolve readily in organic solvents and as a rule they react together slowly.

If covalent bonding forms continuously a giant molecule can result. Such macromolecules have high melting and boiling points as throughout the entire structure a network of covalent bonds links the atoms. e.g. diamond, silica, graphite

### Dative bonding or Co-ordinate bonding

This is also a covalent bonding but the bonding electrons instead of coming from both atoms, are provided by only one of them. The atoms providing the two electrons for the bond is referred to as the **donor** and the other atom that receives the electron is referred to as the **acceptor** or **recipient**. In order to donate the electrons the donor should have an unshared or lone pair of electrons and the acceptor a vacant orbital.

In ammonia the nitrogen atom has a lone pair of electrons. The H ion has a vacant orbital. The nitrogen atom donates one of the electrons from its lone pair to the vacant orbital of the H ion and then shares with it forming the ammonium ion\*\*.

When boron forms boron trifluoride it does not attain the noble gas configuration. The boron in BF has a vacant orbital and is able to form a dative bond with ammonia.

Examples of dative bonding:  $\text{Al}_2\text{Cl}_6$ ,  $\text{C} = \text{O}$ ,  $\text{H}_3\text{O}^+$ , complexes formed by d-block elements.

### Metallic bonding

The special properties associated with metals like malleability, ductility, electrical and thermal conductivity are explained on the basis of a different type of bonding called the metallic bonding

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In metals the valence electrons of each atom are assumed to overlap with all the neighbouring atoms. Due to this electrons are not localized between just two atoms but are delocalised among all the atoms of the crystal. Thus the valence electrons become mobile. As a result at one moment some atoms would gain electrons, some others lose and at the next moment the situation is reversed. The metal crystal hence can be considered to be made up of a lattice of positive ions in a sea of electrons and the attraction between the positive ions and the sea/cloud of electrons constitutes the metallic bond. The valence electrons moving in orbitals around the positive ions, enveloping the whole lattice act like glue binding the positive ions. The strength of the metallic bond depends on the number of electrons involved in the bonding.

### Electronegativity

Electronegativity is the ability of an atom to attract electrons. Electronegativity depends on the charge per unit area of the atom. Thus electronegativity  $\propto$  nuclear charge

$$\propto \frac{1}{\text{atomic radius}}$$

Along a Period from left to right electronegativity would increase owing to the increase in nuclear charge and simultaneous decrease in atomic radius. Down a group electronegativity decreases because the effect of the increasing atomic size is greater than that of the increasing nuclear charge. The most electronegative element is fluorine and in each Period the halogen. Pauling has devised a scale of relative electronegativities for all elements assigning an arbitrary figure of 4 to fluorine. These numbers give a measure of the tendency of the element to draw electrons to itself.

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0

When electronegativities of elements that combine are similar covalent bonds are formed. As the difference increases ionic character increases.



## INTERMOLECULAR FORCES

Forces of attraction and repulsion existing between molecules are referred to as intermolecular forces. The inter-molecular forces determine the physical properties of substances like melting and boiling point, density, viscosity and volatility. They are weak compared with intra-molecular forces (forces that hold the atoms together in molecules) like the covalent bonding. However in some cases they are strong enough to bring about appreciable changes in the physical properties of the substances. All forces are electrical and vary with the structure of the molecule.

### Dipole –dipole attractions

When atoms of different elements are involved in covalent bonding, true sharing does not take place, due to the difference in electronegativity. The more electronegative atom would draw the electron closer to itself imparting it a slight negative charge and a corresponding positive charge to the other. Thus there would be an electron displacement towards the more electronegative atom. This displacement of electron cloud towards the more electronegative atom without being shared is referred to as polarization and the resulting molecule is referred to as *an electric dipole or a polar molecule*.

Polar molecules have a slight ionic character. The intermolecular attraction between such dipoles is referred to as dipole-dipole attraction. Polar molecules are attracted by electric field. Thus a jet of water from a burette is attracted and its path altered by an electric field while non-polar liquids like tetrachloromethane are not affected. (Note: Whether the field is positive or negative polar molecules are always attracted.)

The difference in charge is only a fraction of the charge of an electron but the difference leads to the existence of dipole moment.\*

### Transient dipole-transient dipole attractions (London forces)

In covalent bonds formed between atoms of equal electronegativity, though electrons are equally shared. Still there is a fluctuating charge separation in the molecule. This is because, due to the motion of the electrons, the centre of density of the positive nuclei and the centre of density of the negative charges of the electrons do not continuously coincide. At one moment the charge cloud will be denser on one side and on the next moment on the other side. This condition gives rise to a slight, fluctuating charge separation in the molecule and consequently instantaneous dipoles/transient dipoles are formed. As a result of this, molecules, which approach each other closely enough with proper orientation, tend to adhere. Therefore even simple molecules such as helium or hydrogen have some tendency to adhere. Such weak attractive forces are referred to as London forces

The strength of the London forces increases as the number of electrons increases. Hence as the number and complexity of the atoms in the molecule increases these forces increase in strength. London forces are operative only when the molecules approach each other very closely. Hence they are appreciable only in liquids and solids. In gases at room temperature and pressure the forces are not very effective.

- The weak intermolecular attractions between permanent dipoles, transient dipoles and induced dipoles are nowadays jointly referred to as van der Waal's forces
- The attraction between permanent dipoles is stronger than the attraction between transient dipoles. However if the number of electrons is high the transient dipole-transient dipole attractions can be stronger than attractions between permanent dipoles.
- When the number of electrons are equal the strength increases as the surface area exposed increases
- The boiling points of the halogens are in the order  $F_2 < Cl_2 < Br_2 < I_2$  because the number of electrons increases.
- The boiling points of the alkanes are in the order  $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10} < C_5H_{12}$  for the same reason

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**Hydrogen bond**

Hydrogen bond is a strong dipole- dipole attraction. This inter-molecular force arises when hydrogen is joined to the most electronegative elements like fluorine, oxygen or nitrogen. Hydrogen bond may be defined as an electrostatic attraction formed between a hydrogen atom attached to a strongly electronegative atom and a second strongly electronegative atom having a lone pair of electrons

Hydrogen atom is unique in that it has a single electron surrounding the nucleus. When that electron is bonded to atoms like fluorine, oxygen or nitrogen the electron is drawn away from the hydrogen atom and almost a bare nucleus is exposed. This is able to approach another more electro-negative atom having a lone pair of electrons and attract it strongly to form a bond.

Hydrogen bond alters appreciably the physical properties of substances. The compounds having hydrogen bond have abnormally high melting and boiling points compared to compounds of similar molar masses but without hydrogen bonding. Also they possess comparatively high values for the enthalpy of vapourisation, enthalpy of fusion, specific heat capacity, viscosity and surface tension.

Compound	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
m. pt./K	273	188	207	225

Compound	HF	HCl	HBr	HI
b.pt./°C	20	-85	-67	-39

The unexpectedly high values result from the association of the molecules due to hydrogen bonding. Hydrogen bonding accounts for the high solubility in water of compounds containing oxygen or nitrogen. (hydrophilic groups) Hydrogen bonding plays an important role in maintaining the structure of proteins, carbohydrates and nucleic acids. The double helix structure of DNA is maintained by hydrogen bonding. The value of hydrogen bonding vary between 12-40 kJ mol<sup>-1</sup>

- The extensive hydrogen bonding in water results from the presence of two hydrogen atoms and two lone pairs of electrons enabling a molecule to form up to four bonds or in an average of two bonds per molecule
- The hydrogen bonding in HF is stronger than in water but the boiling point is lower than water This is because the number of bonds formed per molecule is less than in water and also all the hydrogen bonds do not rupture during boiling. The vapour contains dimeric molecules H<sub>2</sub>F<sub>2</sub>

## SHAPES OF MOLECULES

The shape of many simple molecules and ions can be predicted on the basis of valency shell electron pair repulsion theory. (VSEPR theory) The basic principle behind the determination of the shape is that electron pairs, which may be considered as negative centres repel one another and hence try to be as far apart as possible. Thus the orbitals around the central atom tend to form the maximum angles with each other. For instance, when there are two electron pairs they would be at  $180^\circ$  to each other, and if there were three electron pairs they would be at  $120^\circ$  to each other.

The number of electron pairs determines the orientation of the orbitals in space but in describing the shape of the molecule only the position of the nuclei are considered. i.e the bonded electron pairs and not the lone pairs are considered.

- Give the shape of the following compounds:

$\text{BeCl}_2$ ,  $\text{BF}_3$ ,  $\text{CH}_4$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ ,  $\text{SCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SF}_4$ ,  $\text{ClF}_3$ ,  $\text{IF}_5$ ,  $\text{XeF}_4$ ,  $\text{Cl}_2\text{O}$ ,  $\text{BrF}_5$ ,

- Give the shape of the following ions:

$\text{ICl}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{AlF}_6^{3-}$ ,  $\text{PH}_4^+$ ,  $\text{CH}_3^-$ ,  $\text{CH}_3^+$ ,  $\text{ICl}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{NH}_2^-$ ,  $\text{H}_3\text{O}^+$ ,

When multiple bonds occur they act as one negative centre as they occupy only one position in space. Thus whether the bond is single, double or triple it is taken as one negative centre

$\text{CO}_2$ ,  $\text{HCN}$ ,  $\text{COCl}_2$ ,  $\text{POCl}_3$ ,  $\text{SOCl}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{SO}_2\text{Cl}_2$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$

All electron pairs are not identical. The lone pairs are concentrated closer to the nucleus of the central atom, than a bond pair. Hence the repulsion of the lone pair would be greater than that of the bond pair. The difference in the repulsion would cause a slight deviation in the bond angle though the basic shape would be unaltered.

In ammonia there are three bond pairs and one lone pair. The axes of the four orbitals would be arranged tetrahedrally but due to the increased repulsion of the lone pair the bonding pairs would be pushed closer. Thus the angle H-N-H is  $107^\circ$  and not  $109^\circ 28'$ .

In water the O atom has four pairs of electrons in its outer shell two of which are lone pairs. The four orbitals point towards the four corners of a tetrahedron, but the tetrahedron is more distorted than in ammonia due to the repulsion of two lone pairs and the bond angle is  $104.5^\circ$

Repulsion between orbitals is also affected by the electronegativity of the central atom. The more electronegative the central atom is, greater would be the electron displacement towards the central atom and greater would be the repulsion between bonded pairs. Consequently greater the electronegativity smaller would be the contraction caused, by the repulsion of the lone pair. Thus the contraction in water is much less than that in hydrogen sulphide due to the higher electronegativity of O.

1. An element Y forms an ion  $\text{YO}_3^-$  having a trigonal pyramidal structure. In what Group of the Periodic Table would you expect the element Y to be found?
2. Give the outermost electronic configuration of the element L, which forms an ion  $\text{LO}_3^-$  having a trigonal planar structure
3. An element X forms an ion  $\text{YO}_3^{2-}$  having a trigonal pyramidal structure. Assign the Group in the Periodic Table to which the element belongs.
4. Elements D and E form ions,  $\text{DCl}_4^+$  and  $\text{EF}_4^-$  respectively both having tetrahedral shape. Assign the Groups in the Periodic Table to which the elements D and E belong.
5. A complex ion of antimony  $[\text{SbF}_5]^n$  is square planar in shape. Calculate the value of n
6. Draw the shapes of the following molecules.  
 $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{NH}_3 \cdot \text{BF}_3$
7. Give the dot and cross diagrams of the following oxides of nitrogen and predict their shapes  
 $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ ,