IIT JEE CHEMICSTRY

Chemistry is one such subject which can assure you guaranteed marks in IIT JEE if you have prepared well. Most of the topics in chemistry are not very much twisted and get tested directly. For example most of the students do not pay much attention to topics like:- s, p, d blocks, transition elements, surface chemistry, coordination compounds, gaseous state, nuclear chemistry, chemical equilibrium and stereo-chemistry. These topics are not only easy but do get questions in IIT JEE Chemistry papers every year and hence are very scoring but still students do neglect them. Scoring in Chemistry is more about planning than about application and understanding of concepts. Certain topics like organic chemistry are pretty much like mathematics and physics as far as IIT JEE is concerned as it relies on testing of concepts and questions are always framed considering multiple concepts together. Unlike organic chemistry, inorganic chemistry is directly opposite as all questions asked are always direct and do not need much application. Topics like stoichiometry are always difficult to handle and need lot of in depth knowledge about reactions and mole concept.

Physical Chemistry

Physical Chemistry is the branch of chemistry which is quite like mathematics and physics in developing underlying principles of chemistry. It observes and explains the physical and chemical properties of matter. Physical chemistry at IIT JEE level starts from basics of mole concept, quantities at atomic level and covers energy, thermodynamics and kinetics which forms the basis of how reactions occur. Various topics covered in physical chemistry such as stoichiometry, chemical equilibrium, concentration of solutions, atomic structure, thermodynamics or chemical energetic form the backbone of chemistry at IIT JEE level and higher chemistry at graduate and post graduate level.

Physical chemistry has at least 30-40% weight-age in the IIT JEE chemistry paper and hence it is most important of the trio – physical, organic and inorganic chemistry.

Atomic Structure

Fundamental Practicles

Atoms are made up-essentially, of three fundamental particles, which differ in mass and electric charge as follows:

	Electron	**Proton**	**Neutron**
Symbol	e or e^-	p	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	-1	+1	0
Mass in kg	9.109534×10^{-31}	$1.6726485 \times 10^{-27}$	$1.6749543 \times 10^{-27}$
Mass in amu	5.4858026×10^{-4}	1.007276471	1.008665012
Actual charge/C	$1.6021892 \times 10^{-19}$	$1.6021892 \times 10^{-19}$	0

The atomic mass unit (amu) is 1/12th of the mass of an individual atom of $_6C^{12}$, i.e. 1.660565 ´ 10^{-27} kg. The neutron and proton have approximately equal masses of 1 amu and the electron is about 1836 times lighter; its mass can sometimes be neglected as an approximation. The electron and proton have equal, but opposite, electric charges; the neutron is not charged.

The existence of electrons in atoms was first suggested, by J.J. Thomson, as a result of experimental work on the conduction of electricity through gases at low pressures, which produces cathode rays and x-rays, and a study of radioactivity by Becquerel, the Curies and Rutherford.

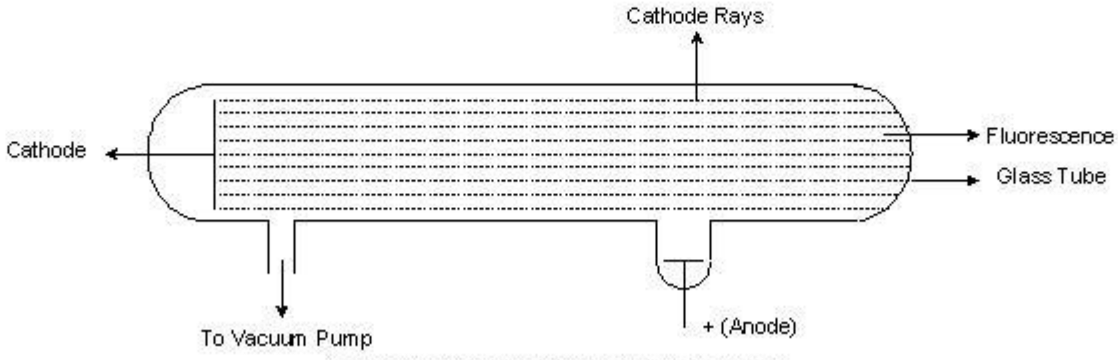
An atom is electrically neutral, and if it contains negatively charged electrons it must also contain some positively charged particles, and the supposition that they existed within atoms came about as a result of Rutherford's experiments in which he bombarded elements with the α - rays and α-rays were given off by radioactive elements. The neutron was discovered in 1932 by James Chadwick by bombarding beryllium with α rays.

DISCOVERY OF ELECTRON:

CATHODE RAYS

During the latter half of the nineteenth century, it was found that while normally dry gases do not conduct an electric current, they do so under very low pressure and then patches of light are seen. The passage of electricity through gases as studied by a number of physicists, particularly by Faraday, Davy, Crookes and J.J. Thomson.

When a current of high voltage (10,000 volts) is passed through a gas of air kept at a very low pressure (0.01 – 0.03 mm) blue rays are seen emerging from the case. These rays are called "Cathode Rays".



CATHODE RAY EXPERIMENT (DISCHARGE TUBE)

Some of the important properties of the cathode rays studied by Sir J.J. Thomson and others are given below:

- Cathode rays come out at right angles to the surface of the cathode and move in straight lines.
- Their path is independent on the position of the anode.
- They produce phosphorescence on certain salts like ZnS and fluorescence on glass.
- They blacken photographic plates.
- The rays pass through thin sheet of metals. If the metal sheet is too thick to be penetrated the rays cast a shadow.
- They produce X-ray when they strike a metal.
- The rays ionize a gas through which they pass.
- They heat a substance on which they fall.
- They rotate a light wheel placed in their paths. This shows that cathode rays contain material particles having both mass and velocity.
- The mass of a particle present in cathode rays is found to be 1/1837 of H-atom. This shows that the particle is of sub-atomic nature.
- Cathode rays are deflected by a magnetic or an electric field showing the particle to be electrically charged, the direction of deflection shows that they are negatively charged.
- Cathode rays contain the smallest unit of negative charge.
- No cathode ray was produced when the tube was completely evacuated.
- Different gases produce same cathode rays as they have the same e/m (charge/mass) ratio. This indicates that the particles present in cathode rays are fundamental constituent of all matter.

Sir J.J. Thomson named these negatively charged sub-atomic particles as electron.
"A sub-atomic particle which is a fundamental constituent of all matter having a mass 1/1837th of a H-atom and which carries the smallest unit of negative charge is called an electron".

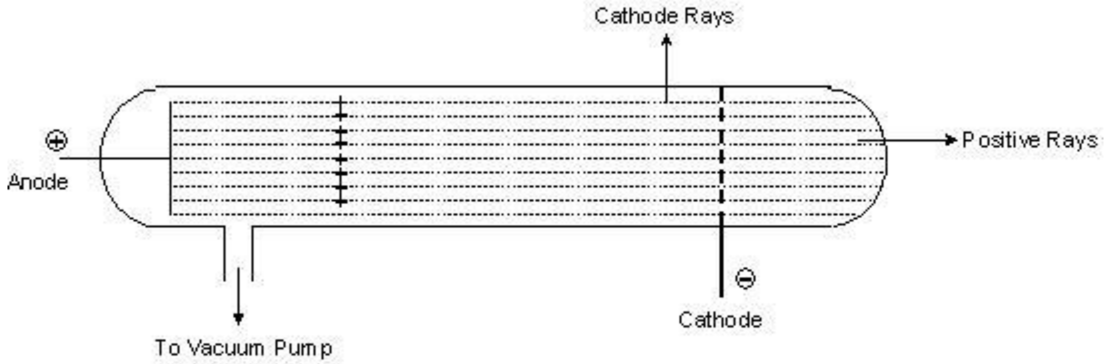
Determination of Velocity and Charge/mass (e/m) ratio of Electrons:
Sir J.J. Thomson (1897) extended the cathode ray experiment for the determination of velocity of electrons and their charge/mass ratio, The value of e/m for an electron = 1.76 x 10^8 C/g. For the H^+ ion (proton), e/m = 96500/1.008 C/g.

Millikan's Oil Drop Method: Determination of Charge on an Electron:
In 1909, Millikan measured the charge on an electron by his oil drop method. In this method a spray of oil droplets is produced by an atomizer, some of which pass through an opening into a viewing chamber, where we can observe them with a microscope. Often these droplets have an electric charge, which is picked up from the friction forming the oil droplets. A droplet may have one or more additional electrons in it, giving it a negative charge.
As the droplet falls to the bottom of the chamber, it passes between two electrically charged plates. The droplet can be suspended between them; we adjust the voltage in the plates so that the electrical attraction upward just balances the force of gravity downward. We then use the voltage needed to establish this balance to calculate the mass - to charge ratio for the droplet. Because we already know the mass of the droplet we can find the charge on it.
Millikan's found that the charge on all droplets could be expressed as whole number multiples of e, where the value of e is 1.602 x10^{-19} C. By combining e/m. ratio and 'e' we calculate mass of the electron

M_e = e / (e/m) = 1.6022 x 10^{-19} / 1.76 x 10^8
= 9.104´10^{-31} kg
This very small value shows that the electron is a subatomic particle. Thus charge on an electron = 1.602 x 10^{-19}C.

DISCOVERY OF PROTON:

POSITIVE RAYS OR CANAL RAYS
Atoms are electrically neutral. Hence after the discovery of the negatively charged constituent (electron) of an atom, attempts were made to discover the positively charged counterpart of electrons. By using a discharge tube containing a perforated cathode. Goldstein (1886) found that some rays passed through these holes in a direction opposite to that of the cathode rays.



POSITIVE RAYS

Alt text: **POSITIVE RAYS OR CANAL RAYS**

These are called the positive rays or canal rays. J.J. Thomson (1910) measured their charge by mass ratio from which he was able to deduce that these contain positive ions. Their properties are:

- They are positively charged.
- The positive charge is either equal to or whole number multiple of the charge on an electron.
- When hydrogen gas was filled in the discharge tube the positive charge on the positive rays was equal to the negative charge on an electron, and the mass was less than the hydrogen atom.
- Unlike cathode rays the properties of positive rays are characteristics of the gas in the tube.
- The deflection of positive rays under the influence of an electric or magnetic field is smaller than that of the cathode rays for the same strength of field. This shows that the positive rays have a greater mass than that of electrons.
- The mass of the positive rays depends on the atomic weights or molecular weights of the gases in the discharge tube. The charge/mass ratio also varies because the change in positive charge on the rays. It may be either equal to or integral multiple of the charge on an electron.
- The lightest of all particles identified in positive rays from different elements was one with a mass very slightly less than that of hydrogen atom (or nearly equal to H-atom). The lightest positively charged particle is called a proton (P or P^+). Positive rays are atomic or molecular resides from which some electrons have been removed. The removed electrons constitute the cathode rays and the positive residues form the positive or canal rays.

	Positive Rays	**Cathode Rays**
H	H^+	e^-
$O \rightarrow$	O^+	e^-
$O_2 \rightarrow$	O_2^+	e^-
$O_2 \rightarrow$	O_2^{2+}	$2e^-$

The mass of a proton is very slightly less than that of a H-atom. This shows that protons are sub-atomic particles. Protons are fundamental constituent of matter because positive rays are produced by all substances.

“A sub-atomic particle, which is a fundamental constituent of all matter having a mass slightly less than that of H-atom and which carries a positive charge equal in magnitude to the charge on an electron, is called a proton”. A proton is denoted by p or p^+ of $_{+1}p$.

Comparison of Positive (Canal) Rays and Cathode Rays:

Properties	**Cathode Rays**	**Canal Rays**
Sign of Charge	Negative	Positive
Mag. of Charge	Always –1	Mostly +1, but also +2, +3…
Mass	Definite value	Variable, depends on ions
e/m	Definite value	Variable, depends on ions

DISCOVERY OF NEUTRON

After the discovery of electron and proton Rutherford (1920) had predicted the existence of a neutral fundamental particle. In 1932, Chadwick bombarded the element Beryllium with a-particles and noticed the emission of a radiation having the following characteristics.

- The radiation was highly penetrating.
- The radiation was unaffected by magnetic and electric fields which show that it is electrically neutral.
- It was found to have approximately the same mass as the protons.

The name 'neutron' was given to this sub-atomic particle. It is denoted by n or $^1{}_0n$. Bombardment of beryllium by α-particles results in the formation of carbon and neutrons are emitted.

α

Be — — → C + 1 n

0

At present there are a number of evidences which confirm that like electron, proton and neutron is also a fundamental constituent of atoms (a single exception is $^1{}_1H$ atom which does not contain any neutron)

Mass of a neutron is 1.008930 amu (1.6753×10^{-24}g or 1.6753×10^{-27} kg)

Neutron "A sub-atomic particle, which is a fundamental constituent of matter having mass approximately equal to the hydrogen atom and which is electrically neutral, is called a neutron".

Illustration:-

The neutron is attracted towards

(A) Positive charged particles
(B) Negative charged particles
(C) Not attracted by any charge
(D) None of these

Solution:

Neutron is an uncharged particle. Hence (C) is correct.

ATOMIC TERM

Nuclide:

Various species of atoms in general.

Nucleons:

Sub-atomic particles in the nucleus of an atom, i.e., protons and neutrons.

Isotopes:

Atoms of an element with the same atomic number but different mass number.

Mass number (A):

Sum of the number of protons and neutrons, i.e., the total number of nucleons

Atomic number (Z):

The number of protons in the nucleus of an atom. This, when subtracted from A, gives the number of neutrons.

Isobars:

Atoms, having the same mass numbers but different atomic numbers, e.g., ${}_{15}P^{32}$and ${}_{16}S^{32}$.

Isotones:

Atoms having the same number of neutrons but different number of protons or mass number, e.g., ${}^{14}{}_{6}C$, ${}^{15}{}_{7}N$.

Isoelectronic species:

Atoms molecules or ions having the same number of electrons, e.g., N_2, CO, CN^-.

Nuclear isomers:

Atoms with the same atomic and mass numbers but different radioactive properties, e.g., uranium X (half life 1.4 min) and uranium Z (half life 6.7 hours).

Atomic mass unit:

Exactly equal to 1/12th of the mass of ${}_{6}C^{12}$ atom.

(a.m.u.): 1 a.m.u. = 1.66×10^{-24} g ≈ 931.5 MeV

Illustration:

The ion that is isoelectronic with CO is

(A) CN^- (B) O_2^+

(C) O_2^- (D) N_2^+

Solution:

Both CO and CN^- have 14 electrons. Hence (A) is correct

Illustration:-

Find the number of neutrons in a neutral atom having atomic mass 23 and number of electrons 11.

Solution:

Number of protons = number of electrons = 11

Number of neutrons = atomic mass – number of protons =23–11 = 12

Illustration

How many protons, electrons and neutrons are present in 0.18 g_{15}^{30}?

Solution:

No. of neutrons in one atom = (30 – 15) = 15

0.18 g $^{30}_{15}P$ = 0.18 / 30 = 0.006 mole

Now, number of $^{30}_{15}P$ atoms in 0.006 mole = 0.006 x 6.02 x 10^{23}

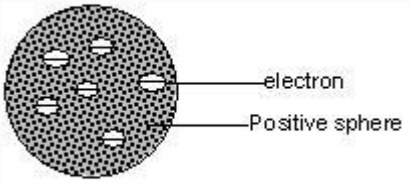
Number of electrons in 0.006 mole of $^{30}_{15}P$ = Number of protons in 0.006 mole$^{30}_{15}P$ = 15 x 0.006 x 6.02 x 10^{23} = 5.418 x 10^{22} and number of neutrons = 5.418 x 10^{22}

ATOMIC MODELS

We know the fundamental particles of the atom. Now let us see, how these particles are arranged in an atom to suggest a model of the atom.

Thomson's Model:

J.J. Thomson, in 1904, proposed that there was an equal and opposite positive charge enveloping the electrons in a matrix. This model is called the plum – pudding model after a type of Victorian dessert in which bits of plums were surrounded by matrix of pudding.

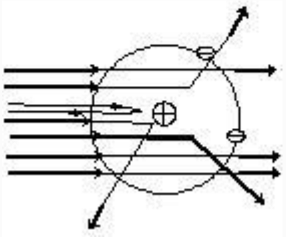


This model could not satisfactorily explain the results of scattering experiment carried out by Rutherford who worked with Thomson.

Rutherford's Model:

α– particles emitted by radioactive substance were shown to be dipositive Helium ions (He^{++}) having a mass of 4 units and 2 units of positive charge.

Rutherford allowed a narrow beam of α–particles to fall on a very thin gold foil of thickness of the order of 0.0004 cm and determined the subsequent path of these particles with the help of a zinc sulphide fluorescent screen. The zinc sulphide screen gives off a visible flash of light when struck by an a particle, as ZnS has the remarkable property of converting kinetic energy of α particle into visible light. [For this experiment, Rutherford specifically used α particles because they are relatively heavy resulting in high momentum].



Observation:

Majority of the a–particles pass straight through the gold strip with little or no deflection.
Some α–particles are deflected from their path and diverge.
Very few α–particles are deflected backwards through angles greater than 90°.
Some were even scattered in the opposite direction at an angle of 180°[Rutherford was very much surprised by it and remarked that "It was as incredible as if you fired a 15–inch shell at a piece of tissue paper and it came back and hit you"]. There is far less difference between air and bullet than there is between gold atoms and α-particle assuming of course that density of a gold atom is evenly distributed. The distance of nucleus from where the α - particle returns back through 180° is called distance of closet approach and is given by

$r_o = q_1 q_2 / 4\pi\varepsilon_o \, (1/2mv^2)$

Conclusions:

The fact that most of the α - particles passed straight through the metal foil indicates the most part of the atom is empty.
The fact that few α - particles are deflected at large angles indicates the presence of a heavy positively charge body i.e., for such large deflections to occur α - particles must have come closer to or collided with a massive positively charged body.
The fact that one in 20,000 have deflected at 180° backwards indicates that volume occupied by this heavy positively charged body is very small in comparison to total volume of the atom.

Conclusions of a-Scattering Experiment:

On the basis of the above observation, and having realized that the rebounding α-particles had met something even more massive than themselves inside the gold atom, Rutherford proposed an atomic model as follows.

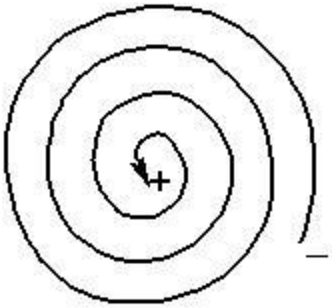
- All the +ve charge and nearly the total mass of an atom is present in a very small region at the centre of the atom. The atom's central core is called nucleus.
- The size of the nucleus is very small in comparison to the size of the atom. Diameter of the nucleus is about 10^{-13}cm while the atom has a diameter of the order of 10^{-8} cm. So, the size of atom is 10^5 times more than that of nucleus.
- Most of the space outside the nucleus is empty.
- The electrons, equal in number to the net nuclear positive charge, revolve around the nucleus with fast speed just like planets around the sun.

- The centrifugal force arising due to the fast speed of an electron balances the coulombic force of attraction of the nucleus and the electron remains stable in its path. Thus according to him atom consists of two parts (a) nucleus and (b) extra nuclear part.

Defects in Rutherford's Atomic Model:

- **Position of electrons:** The exact positions of the electrons from the nucleus are not mentioned.

Stability of the atom: Bohr pointed out that Rutherford's atom should be highly unstable. According to the law of electro–dynamics, when a charged body moves under the influence of an attractive force, it loses energy continuously in the form of electromagnetic radiation. The electron should therefore, continuously emit radiation and lose energy. As a result of this a moving electron will come closer and closer to the nucleus and after passing through a spiral path, it should ultimately fall into the nucleus.

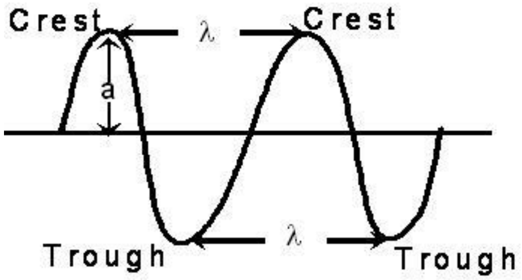


It was calculated that the electron should fall into the nucleus in less than 10^{-8}sec. But it is known that electrons keep moving outside the nucleus.

To solve this problem Neils Bohr proposed an improved form of Rutherford's atomic model.

SOME IMPORTANT CHARACTERISTICS OF A WAVE

A wave is a sort of disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. Every wave has five important characteristics, namely, wavelength (λ), frequency (v), velocity (c), wave number(v ¯) and amplitude (a).



Electronic Magnetic Radiation:

Ordinary light rays, X–rays,λ–rays, etc. are called electromagnetic radiations because similar waves can be produced by moving a charged body in a magnetic field or a magnet in an electric field. These radiations have wave characteristics and do not require any medium for their propagation.

- **Wavelength (λ):** The distance between two neighbouring troughs or crests is known as wavelength. It is denoted by l and is expressed in cm, m, nanometers (1 nm $=10^{-9}$ m) or Angstrom (1 Å$=10^{-10}$ m).

- **Frequency (v):** The frequency of a wave is the number of times a wave passes through a given point in a medium in one second. It is denoted by n(nu) and is expressed in cycles per second (cps) or hertz (Hz) 1Hz = 1cps.

  The frequency of a wave is inversely proportional to its wave length (λ)

  $$v \propto 1 / \lambda \quad \text{or } v = c / \lambda$$

- **Velocity:** The distance travelled by the wave in one second is called its velocity. It is denoted by c and is expressed in cm sec^{-1}.

  $$c = v\lambda \text{ or } \lambda = c / v$$

- **Wave number** (v^{-})**:** It is defined as number of wavelengths per cm. It is denoted by v^{-} and is expressed in cm^{-1}.

  $$v^{-} = 1 / \lambda \text{ or } v^{-} = v / c$$

- **Amplitude:** It is the height of the crest or depth of the trough of a wave and is denoted by a. It determines the intensity or brightness of the beam of light.

- **Electromagnetic Spectrum:** The arrangement of the various types of electromagnetic radiation in order of increasing or decreasing wavelengths or frequencies is known as electromagnetic spectrum.

ATOMIC SPECTRUM

If the atom gains energy the electron passes from a lower energy level to a higher energy level, energy is absorbed that means a specific wave length is absorbed. Consequently, a dark line will appear in the spectrum. This dark line constitutes the ***absorption spectrum.***

If the atom loses energy, the electron passes from higher to a lower energy level, energy is released and a spectral line of specific wavelength is emitted. This line constitutes the ***emission spectrum.***

Types of Emission Spectra:

- **Continuous spectra:** When white light from any source such as sun or bulb is analysed by passing through a prism, it splits up into seven different wide bands of colour from violet to red (like rainbow). These colour are so continuous that each of them merges into the next. Hence the spectrum is called as continuous spectrum.

- **Line spectra:** When an electric discharge is passed through a gas at low pressure light is emitted. If this light is resolved by a spectroscope, It is found that some isolated colored lines are obtained on a photographic plate separated from each other by dark spaces. This spectrum is called line spectrum. Each line in the spectrum corresponds to a particular wavelength. Each element gives its own characteristic spectrum.

PLANCK’S QUANTUM THEORY

When a black body is heated, it emits thermal radiations of different wavelengths or frequency. To explain these radiations, Max Planck put forward a theory known as Planck’s quantum theory. The main points of quantum theory are

Substances radiate or absorb energy discontinuously in the form of small packets or bundles of energy.

The smallest packet of energy is called ***quantum***. In case of light the quantum is known as photon***.***

The energy of a quantum is directly proportional to the frequency of the radiation. E µ n (or) E = hn where n is the frequency of radiation and h is Planck’s constant having the value 6.626 X $10^{–27}$ erg –sec or 6.626 X $10^{–34}$ J–sec.

A body can radiate or absorb energy in whole number multiples of a quantum hn, 2hn,3hn………..nhn. Where ‘n' is the positive integer.

Neils Bohr used this theory to explain the structure of atom.

Illustration:

The wave number of a radiation is 400 cm^{-1}. Find out its

(a) Wavelength (b) Frequency
(c) J per photon (d) kcal per mol of photons
(e) KJ per mol of photons

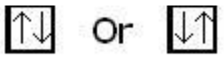
Solution:

(a) $v^{-} = 1 / \lambda$ or $\lambda = 1 / v^{-} = 1 / 400cm^{-1} = 2.5 \times 10^{-3}$ cm
(b) $v = c / \lambda = c \times v^{-} = 3 \times 10^{-10}$ cm/s x 400 $cm^{-1} = 1.2 \times 10^{-7}$ s^{-1}
(c) $E_{photon} = hn = hc / \lambda = h \times c \times v^{-}$
$= 6.626 \times 10^{-34}$ Js x 3 x 10^{8} cm/s x 400 cm^{-1}
$= 7.95 \times 10^{-21}$J
(d) $E_{photon} = 7.95 \times 10^{-21}$J
For 1 mol of photon energy = 7.95×10^{-21}J x 6.022×10^{23} mol^{-1}
= (4.7875×10^{3} J mol^{-1}) (1 kcal/4184 J)
= 1.14 kcal mol^{-1}
(e) E = (4.7875×10^{3} J mol^{-1}) (1 kJ/1000J)
= 4.7875 kJ mol^{-1}

Pauli’s Exclusion Principle:

According to this principle, an orbital can contain a maximum number of two electrons and these two electrons must be of opposite spin.

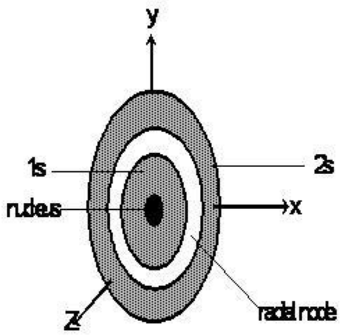
Two electrons in an orbital can be represented by



SHAPES AND SIZE OF ORBITALS

An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (90–95%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the azimuthal quantum number l, while the orientation of orbital depends on the magnetic quantum number (m). Let us now see the shapes of orbitals in the various subshells.

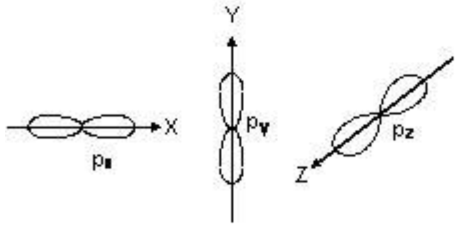
s–orbital:These orbitals are spherical and symmetrical about the nucleus. The probability of finding the electron is maximum near the nucleus and keeps on decreasing as the distance from the nucleus increases. There is vacant space between two successive s–orbitals known as radial node. But there is no radial node for 1s orbital since it is starting from the nucleus.



The size of the orbital depends upon the value of principal quantum number (n). Greater the value of n, larger is the size of the orbital. Therefore,
2s–orbital is larger than 1s orbital but both of them are non-directional and spherically symmetrical in shape.

p–orbital (l=1):

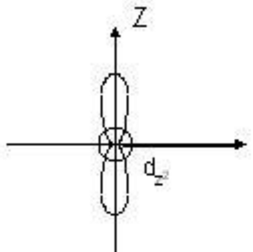
The probability of finding the p–electron is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb–bell shape for the p–orbital. For p–orbital l = 1. Hence, m = –1, 0, +1. Thus, p–orbital have three different orientations. These are designated as p_x, p_y & p_z depending upon whether the density of electron is maximum along the *x* y and z axis respectively. As they are not spherically symmetrical, they have directional character. The two lobes of p–orbitals are separated by a nodal plane, where the probability of finding electron is zero.



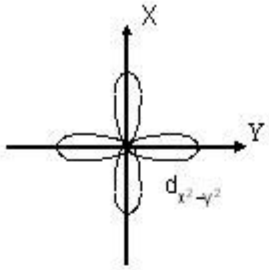
The three p-orbitals belonging to a particular energy shell have equal energies and are called degenerate orbitals.

d–orbital (= 2):

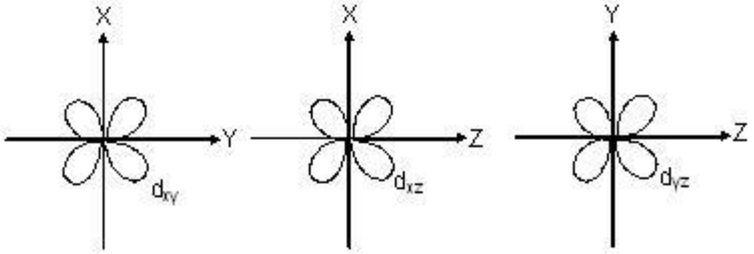
For d–orbitals, *l* = 2. Hence m = –2,–1, 0, +1, +2. Thus there are 5d orbitals. They have relatively complex geometry. Out of the five orbitals, the three (d_{xy}, d_{yz}, d_{zx}) project in between the axis and the other two d_{z}^{2} and $d_{z^{2}-y^{2}}$ lie along the axis.



Dough–nut shape or Baby soother shape



Clover leaf shape



Chemical Bonding:

Chemical bonding is the major part of chemistry which is an interaction between two or more atoms that holds them together by reducing the potential energy of their electrons. In other words Bonds are the like chemists "glue" - which hold atoms together in molecules or ions. Valence electrons are the outer shell electrons of an atom which take part in chemical bonding.

Atoms gain or lose electrons to attain a more stable noble gas - like electron configuration (octet rule). There are two ways in which atoms can share electrons to satisfy the octet rule:

Ionic Bonding - occurs when two or more ions combine to form an electrically-neutral compound

The positive cation "loses" an electron (or 2 or 3)

The negative anion "gains" the electron (or 2 or 3)

The anion steals the electrons from the cation.

Covalent Bonding - occurs when two or more atoms combine to form an electrically-neutral compound.

The electrons are shared between the two atoms.

Both atoms don't have charge in the beginning and the compound remains with zero charge.

The chemical activity of an atom is determined by the number of electrons in its valence shell. With the help of concept of chemical bonding one can define the structure of a compound and is used in many industries for manufacturing products.

INTRODUCTION

A molecule is formed if it is more stable and has lower energy than the individual atoms. Normally only electrons in the outermost shell of an atom are involved in bond formation and in this process each atom attains a stable electronic configuration of inert gas. Atoms may attain stable electronic configuration in three different ways by loosing or gaining electrons by sharing electrons. The attractive forces which hold various constituents (atoms, ions etc) together in different chemical species are called chemical bonds. Elements may be divided into three classes.

- Electropositive elements, whose atoms give up one or more electrons easily, they have low ionization potentials.
- Electronegative elements, which can gain electrons. They have higher value of electronegativity.
- Elements which have little tendency to loose or gain electrons.

Three different types of bond may be formed depending on electropositive or electronegative character of atoms involved.

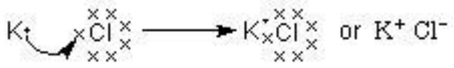
Electropositive element + Electronegative element = Ionic bond (electrovalent bond)

Electronegative element + Electronegative element = Covalent bond or less electro positive + Electronegative element = Covalent bond

Electropositive + Electropositive element = Metallic bond.

ELECTROVALENCY

This type of valency involves transfer of electrons from one atom to another, whereby each atom may attain octet in their outermost shell. The resulting ions that are formed by gain or loss of electrons are held together by electrostatic force of attraction due to opposite nature of their charges. The reaction between potassium and chlorine to form potassium chloride is an example of this type of valency.



Here potassium has one electron excess of it’s octet and chlorine has one deficit of octet. So potassium donates it’s electron to chlorine forming an ionic bond.

$Ca^{++} O^{2-}$ (Ionic bond)

Here the oxygen accepts two electrons from calcium atom. It may be noted that ionic bond is not a true bond as there is no proper overlap of orbitals.

Criteria for Ionic Bond:

One of the species must have electrons in excess of octet while the other should be deficit of octet. Does this mean that all substance having surplus electron and species having deficient electron would form ionic bond? The answer is obviously no. Now you should ask why? The reasoning is that in an ionic bond one of the species is cation and the other is anion. To form a cation from a neutral atom energy must be supplied to remove the electron and that energy is called ionization energy. Now it is obvious that lower the ionization energy of the element the easier it is to remove the electron. To form the anion, an electron adds up to a neutral atom and in this process energy is released. This process is called electron affinity.

So for an ionic bond one of the species must have low ionization energy and the other should have high electron affinity. Low ionization energy is mainly exhibited by the alkali and alkaline earth metals and high electron affinity by the halogen and chalcogens. Therefore this group of elements are predominant in the field of ionic bonding.

Energy Change During the Formation of Ionic Bond

The formation of ionic bond can be consider to proceed in three steps

(a) Formation of gaseous cations

$A(g) + I.E. \rightarrow A^+ (g) + e^-$

The energy required for this step is called ionization energy (I.E)

(b) Formation of gaseous anions

$X(g) + e^- \rightarrow X^-(g) + E.A$

The energy released from this step is called electron affinity (E.A.)

(c) Packing of ions of opposite charges to form ionic solid

$A+(g) + X–(g) \rightarrow AX(s) + energy$

The energy released in this step is called lattice energy.

Now for stable ionic bonding the total energy released should be more than the energy required.

From the above discussion we can develop the factors which favour formation of ionic bond and also determine its strength. These factors have been discussed below:

(a) Ionization energy: In the formation of ionic bond a metal atom loses electron to form cation. This process required energy equal to the ionization energy. Lesser the value of ionization energy, greater is the tendency of the atom to form cation. For example, alkali metals form cations quite easily because of the low values of ionization energies. **(b) Electron affinity:** Electron affinity is the energy released when gaseous atom accepts electron to form a negative ion. Thus, the value of electron affinity gives the tendency of an atom to form anion. Now greater the value of electron affinity more is the tendency of an atom to form anion. For example, halogens having highest electron affinities within their respective periods to form ionic compounds with metals very easily.

(c) Lattice energy: Once the gaseous ions are formed, the ions of opposite charges come close together and pack up three dimensionally in a definite geometric pattern to form ionic crystal.

Since the packing of ions of opposite charges takes place as a result of attractive force between them, the process is accompanied with the release of energy referred to as lattice energy. Lattice energy may be defined as the amount of energy released when one mole of ionic solid is formed by the close packing of gaseous ion.

In short, the conditions for the stable ionic bonding are:

(a) I.E. of cation forming atom should be low:

(b) E.A. of anion – forming atom should be high;

(c) Lattice energy should be high.

Determination of lattice energy

The direct calculation of lattice enthalpy is quite difficult because the required data is often not available. Therefore lattice enthalpy is determined indirectly by the use of the Born – Haber cycle. The cycle uses ionization enthalpies, electron gain enthalpies and other data for the calculation of lattice enthalpies. The procedure is based on the Hess's law, which states that the enthalpy of a reaction is the same, whether it takes place in a single step or in more than one step. In order to understand it let us consider the energy changes during the formation of sodium chloride from metallic sodium and chlorine gas. The net energy change during the process is represented by ΔH_f.

Example 1:

Calculate the lattice enthalpy of $MgBr_2$. Given that

Enthalpy of formation of $MgBr_2$ = -524 kJ mol^{-1}

Some of first & second ionization enthalpy ($IE_1 + IE_2$) = 148 kJ mol^{-1}

Sublimation energy of Mg = +2187 kJ mol^{-1}

Vaporization energy of $Br_2(I)$ = +31kJ mol^{-1}

Dissociation energy of $Br_2(g)$ = +193kJ mol^{-1}

Electron gain enthalpy of Br(g) = -331 kJ mol^{-1}

Solution:

$$\Delta H^o_f = S + I.E. + \Delta H_{vap} + D + 2 \times E.A. + U$$

Or $U = \Delta H^o_f - (S + I.E. + \Delta H_{vap} + D + 2 \times E.A.)$

Or $U = -524 - [2187 - 148 + 31 + 193 + 2 \times (-331)]$

$$= -524 - 1897 = -2421 \text{ kJ mol}^{-1}$$

Characteristics of ionic compounds :

The following are some of the general properties shown by these compounds

(i) Crystalline nature : These compounds are usually crystalline in nature with constituent units as ions. Force of attraction between the ions is non-directional and extends in all directions. Each ion is surrounded by a number of oppositely charged ions and this number is called co-ordination number. Hence they form three dimensional solid aggregates. Since electrostatic forces of attraction act in all directions, therefore, the ionic compounds do not posses directional characteristic and hence do not show stereoisomerism.

(ii) Due to strong electrostatic attraction between these ions, the ionic compounds have high melting and boiling points.

(iii) In solid state the ions are strongly attracted and hence are not free to move. Therefore, in solid state, ionic compounds do not conduct electricity. However, in fused state or in aqueous solution, the ions are free to move and hence conduct electricity.

(iv) Solubility : Ionic compounds are fairly soluble in polar solvents and insoluble in non-polar solvents. This is because the polar solvents have high values of dielectric constant which defined as the capacity of the solvent to weaken the force of attraction between the electrical charges immersed in that solvent. This is why water, having high value of dielectric constant, is one of the best solvents.

The solubility in polar solvents like water can also be explained by the dipole nature of water where the oxygen of water is the negative and hydrogen being positive, water molecules pull the ions of the ionic compound from the crystal lattice. These ions are then surrounded by water dipoles with the oppositely charged ends directed towards them. These solvated ions lead an independent existence and are thus dissolved in water. The electrovalent compound dissolves in the solvent if the value of the salvation energy is higher than the lattice energy of that compounds.

$$AB + \text{Lattice energy} \rightarrow A^+ + B^-$$

These ions are surrounded by solvent molecules. This process is exothermic and is called salvation.

$A^+ + x(solv.) \rightarrow [A(solv.)_x]^+ + energy$

$B^- + y(solv.) \rightarrow [B(solv.)_y]^- + energy$

The value of solvation energy depend on the relative size of the ions. Smaller the ions more is the solvation. The non-polar solvents do not solvate ions and thus do not release energy due to which they do not dissolve ionic compounds.

(v) Ionic reactions: Ionic compound furnish ions in solutions. Chemical reactions are due to the presence of these ions. For example

$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$

$BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$