**Atomic Structure**

**Atomic Structure**  
*Introduction*  
About the structure of atom a theory was put on by John Dalton in 1808. According to this theory matter was made from small indivisible particles called atoms.  
But after several experiments many particles have been discovered with in the atom which are electrons, protons, neutrons, positrons etc. For the discovery of these fundamental particles the experiments are as follows.  
1. Faraday’s experiment indicates the existence of electron.  
2. Crook’s tube experiment explains the discovery of electron and proton.  
3. Radioactivity also confirms the presence of electrons and protons.  
4. Chadwick’s experiment shows the presence of neutrons.  
The details of these experiments are given below.  
**Faraday’s Experiment**  
***Passage of Electricity Through Solution***  
In this experiment Faraday passed the electricity through an electrolytic solution. He observed that when two metal plates called electrodes are placed in an electrolytic solution and electricity is passed through his solution the ions present in the solution are moves towards their respective electrodes. In other words these ions are moves towards the oppositely charge electrodes to give up their charge and liberated as a neutral particles.  
Faraday also determined the charges of different ions and the amount of elements liberated from the electrolytic solution. Due to this experiment presence of charge particles in the structure of atoms is discovered. The basic unit of electric charge was later named as electron by Stoney in 1891.  
Diagram Coming Soon  
**Crook’s Tube Or Discharge Tube Experiment**  
***Passage of Electricity Through Gases Under Low Pressure***  
*Introduction*  
The first of the subatomic particles to be discovered was electron. The knowledge about the electron was derived as a result of the study of the electric discharge in the discharge tube by J.J. Thomson in 1896. This work was later extended by W. Crooke  
***Working of Discharge Tube***  
When a very high voltage about 10,000 volts is applied between the two electrodes, no electric discharge occurs until the part of the air has been pumped out of the tube. When the pressure of the gas inside the tube is less than 1 mm, a dark space appears near the cathode and thread like lines are observed in the rest of 0.01 mm Hg it fills the whole tube. The electric discharge passes between the electrodes and the residual gas in the tube begins to glow. These rays which proceed from the cathode and move away from it at right angle in straight lines are called cathode rays.  
***Properties of Cathode Rays***  
1. They travel in straight lines away from the cathode and produce shadow of the object placed in their path.  
2. The rays carry a negative charge.  
3. These rays can also be easily deflected by an electrostatic field.  
4. The rays can exert mechanical pressure showing that these consist of material particle which are moving with kinetic energy.  
5. The produce fluorescence when they strike the glass wall of the discharge tube.  
6. Cathode rays produce x-rays when they strike a metallic plate.  
7. These rays consists of material particle whose e/m resembles with electron.  
8. These rays emerge normally from the cathode and can be focused by using a concave cathode.  
***Positive Rays***  
In 1890 Goldstein used a discharge tube with a hole in the cathode. He observed that while cathode rays were emitting away from the cathode, there were coloured rays produced simultaneously which passed through the perforated cathode and caused a glow on the wall opposite to the anode. Thomson studied these rays and showed that they consisted of particles carrying a positive charge. He called them positive rays.  
***Properties of Positive Rays***  
1. These rays travel in a straight line in a direction opposite to the cathode.  
2. These are deflected by electric as well as magnetic field in the way indicating that they are positively charged.  
3. The charge to mass ratio (e/m) of positive particles varies with the nature of the gas placed in the discharge tube.  
4. Positive rays are produced from the ionization of gas and not from anode electrode.  
5. Positive rays are deflected in electric field. This deflection shows that these are positively charged so these are named as protons.  
***The Information Obtained From Discharge Tube Experiment***  
The negatively charge particles electrons and the positively charge particles protons are the fundamental particle of every atom.  
**Radioactivity**  
In 1895, Henry Becqueral observed that uranium and its compounds spontaneously emitted certain type of radiation which affected a photographic plate in the dark and were able to penetrate solid matter. He called these rays as radioactivity rays and a substance which possessed the property of emitting these radioactivity rays was said to be radioactivity element and the phenomenon was called radioactivity.  
On further investigation by Maric Curic, it was found that the radiation emitted from the element uranium as well as its salts is independent of temperature and the source of the mineral but depend upon the mineral but depend upon the quantity of uranium present e.g. Pitchblende U3O8 was found to be about four times more radioactive than uranium.  
***Radioactive Rays***  
Soon after the discovery of radium it was suspected that the rays given out by radium and other radioactive substance were not of one kind. Rutherford in 1902 devised an ingenious method for separating these rays from each other by passing them between two oppositely charged plate. It was observed that the radioactive rays were of three kinds, the one bending towards the negative plate obviously carrying positive charge were called α-rays and those deflected to the positive plate and carrying -ve charge were named as β-rays. The third type gamma rays, pass unaffected and carry no charge.  
***Properties of α – RAYS***  
1. These rays consists of positively charged particles.  
2. These particles are fast moving helium nuclei.  
3. The velocity of α-particles is approximately equal to 1/10th of the velocity of light.  
4. Being relatively large in size, the penetrating power of α-rays is very low.  
5. They ionize air and their ionization power is high.  
***Properties of β – RAYS***  
1. These rays consists of negatively charged particles.  
2. These particles are fast moving electron.  
3. The velocity of β-particles is approximately equal to the velocity of light.  
4. The penetrating power of β-rays is much greater than α-rays.  
5. These rays ionizes gases to lesser extent.  
***Properties of γ – RAYS***  
1. Gamma rays do not consist of particles. These are electromagnetic radiations.  
2. They carry no charge so they are not deflected by electric or magnetic field.  
3. Their speed is equal to that of light.  
4. These are weak ionizer of gases.  
5. Due to high speed and non-material nature they have great power of penetration.  
**Chadwick Experiment (Discovery of Neutron)**  
When a light element is bombarded by α-particles, these α-particles leaves the nucleus in an unstable disturbed state which on settling down to stable condition sends out radioactivity rays. The phenomenon is known as “Artificial Radioactivity”.  
In 1933, Chadwick identified a new particle obtained from the bombardment of beryllium by α-particles. It had a unit mass and carried no charge. It was named “Neutron”.  
**Spectroscopic Experiment**  
After the discovery of fundamental particles which are electrons, protons & neutron, the next question concerned with electronic structure of atom.  
The electronic structure of the atom was explained by the spectroscopic studies. In this connection Plank’s Quantum theory has great impact on the development of the theory of structure of atom.  
**Planck’s Quantum Theory**  
In 1900, Max Planck studied the spectral lines obtained from hot body radiations at different temperatures. According to him,  
When atoms or molecules absorb or emit radiant energy, they do so in separate units of waves called Quanta or Photons.  
Thus light radiations obtained from excited atoms consists of a stream of photons and not continuous waves.  
The energy E of a quantum or photon is given by the relation  
E = h v  
Where v is the frequency of the emitted radiation and h the Planck’s constant. The value of h = 6.62 x 10(-27) erg. sec.  
The main point of this theory is that the amount of energy gained or lost is quantized which means that energy change occurs in small packets or multiple of those packets, hv, 2 hv, 3 hv and so on.  
**Spectra**  
A spectrum is an energy of waves or particles spread out according to the increasing or decreasing of some property. E.g. when a beam of light is allowed to pass through a prism it splits into seven colours. This phenomenon is called dispersion and the band of colours is called spectrum. This spectrum is also known as emission spectrum. Emission spectra are of two types.  
1. Continuous Spectrum  
2. Line Spectrum  
*1. Continuous Spectrum*  
When a beam of white light is passed through a prism, different wave lengths are refracted through different angles. When received on a screen these form a continuous series of colours bands: violet, indigo, blue, green, yellow and red (VIBGYOR). The colours of this spectrum are so mixed up that there is no line of demarcation between different colours. This series of bands that form a continuous rainbow of colours is called continuous spectrum.  
Diagram Coming Soon  
*2. Line Spectrum*  
When light emitted from a gas source passes through a prism a different kind of spectrum may be obtained.  
If the emitted from the discharge tube is allowed to pass through a prism some discrete sharp lines on a completely dark back ground are obtained. Such spectrum is known as line spectrum. In this spectrum each line corresponds to a definite wave length.  
Diagram Coming Soon  
*Identification of Element By Spectrum*  
Each element produces a characteristics set of lines, so line spectra came to serve as “finger prints” for the identification of element. It is possible because same element always emit the same wave length of radiation. Under normal condition only certain wave lengths are emitted by an element.  
**Rutherford’s Atomic Model**  
***Evidence for Nucleus and Arrangement of Particles***  
Having known that atom contain electrons and a positive ion, Rutherford and Marsden performed their historic “Alpha particle scattering experiment” in 1909 to know how and where these fundamental particles were located in the structure of atom.  
Rutherford took a thin of gold with thickness 0.0004 cm and bombarded in with α-particles. He observed that most of the α-particles passed straight through the gold foil and thus produced a flash on the screen behind it. This indicated that old atoms had a structure with plenty of empty space but some flashes were also seen on portion of the screen. This showed that gold atoms deflected or scattered α-particles through large angles so much so that some of these bounced back to the source.  
Based on these observations Rutherford proposed a model of the atom which is known as Rutherford’s atomic model.  
Diagram Coming Soon  
***Assumption Drawn From the Model***  
1. Atom has a tiny dense central core or the nucleus which contains practically the entire mass of the atom leaving the rest of the atom almost empty.  
2. The entire positive charge of the atom is located on the nucleus. While electrons were distributed in vacant space around it.  
3. The electrons were moving in orbits or closed circular paths around the nucleus like planets around the sun.  
4. The greater part of the atomic volume comprises of empty space in which electrons revolve and spin.  
***Weakness of Rutherford Atomic Model***  
According to the classical electromagnetic theory if a charged particle accelerate around an oppositely charge particle it will radiate energy. If an electron radiates energy, its speed will decrease and it will go into spiral motion finally falling into the nucleus. Similarly if an electron moving through orbitals of ever decreasing radii would give rise to radiations of all possible frequencies. In other words it would given rise to a continuous spectrum. In actual practise, atom gives discontinuous spectrum.  
**X-Rays and Atomic Number**  
In 1895, W.Roentgen discovered that when high energy electrons from cathode collide with the anode in the Crook’s tube, very penetrating rays are produced. These rays were named as X-rays.  
*Explanation*  
When an electron coming from the cathode strike with the anode in the crook’s tube, it can remove an electron from the inner shell of the atom. Due to removal of t his electron the electronic configuration of this ion is unstable and an electron from an orbital of higher energy drops into the inner orbital by emitting energy in form of a photon. This photon corresponds to electromagnetic radiations in the x-rays region.  
**Relationship Between Wave Length and Nuclear Charge**  
In 1911, Mosley stablished a relationship between the wave length and nuclear charge. He found that when cathode rays struck elements used as anode targets in the discharge tube, characteristic x-rays were emitted. The wave length of the x-rays emitted decreases regularly with the increase of atomic mass. On careful examination of his data Mosely found that the number of positive charges on the nucleus increases from atom to atom by single electronic unit. He called the number of positive charges as the atomic number.  
Diagram Coming Soon  
**Bohr’s Theory**  
Rutherford’s model of atom fails to explain the stability of atom and appearance of the line spectra. Bohr in 1913 was the first to present a simple model of the atom which explained the appearance of line spectra.  
Some of the postulates of Bohr’s theory are given below.  
1. An atom has a number of stable orbits or stationary states in which an electron can reside without emission or absorption of energy.  
2. An electron may pass from one of these non-radiating states to another of lower energy with the emission of radiations whose energy equals the energy difference between the initial and final states.  
3. In any of these states the electrons move in a circular path about the nucleus.  
4. The motion of the electron in these states is governed by the ordinary laws of mechanics and electrostatic provided its angular momentum is an integral multiple of h/2π  
It can be written as  
mvr = nh / 2π  
Here mvr becomes the angular momentum of the electron. Thus Bohr’s first condition defining the stationary states could be stated as  
“Only those orbits were possible in which the angular momentum of the electrons would be an integral multiple of h/2π”. These stationary states correspond to energy levels in the atom.  
*Calculation of Radius of Orbits*  
Consider an electrons of charge e revolving.  
Atomic number and e the charge on a proton.  
Let m be the mass of the electro, r the radius of the orbit and v the tangential velocity of the revolving electron.  
The electrostatic force of attraction between the nucleus and the electron according to Coulomb’s law  
= Z e x e / r2  
Diagram Coming Soon  
The centrifugal force acting on the electron.  
= mv2 / r  
Bohr assumed that these two opposing forces must be balanced each other exactly to keep the electron in an orbit.  
Therefore  
Ze2 / r2 = m v2 / r  
Multiply both sides by r  
r x Ze2 / r2 = r x m v2 / r  
Ze2 / r = m v2  
OR  
r = Ze2 / m v2 ……………… (1)  
The Bohr’s postulate states that only those orbits are possible in which  
mvr = nh / 2π  
Therefore,  
V = nh / 2πmr  
Substituting the value of V in eq (1)  
r = Ze2 / m(nh/2πmr)2  
or  
r = Ze2 x 4π2 mr2/n2h2  
or  
1/r = 4π2mZe2/n2h2  
cr  
r = n2h2 / 4π2mZe2 …………… (2)  
This equation gives the radii of all the possible stationary states. The values of constants present in this equation are as follows.  
H = 6.625 x 10(-27) ergs sec OR 6.625 x 10(-37) J.s  
Me = 9.11 x 10(-28) gm OR 9.11 x 10(-31) kg  
E = 4.802 x 10(-10) e.s.u OR 1.601 x 10(-19) C  
By substituting these values we get for first shell of H atom  
r = 0.529 x 10(-8) m OR 0.529  
The above equation may also be written as  
r = n2 (h2 / 4π2mZe2) x n2 a0 ……………….. (3)  
For the first orbit n = 1 and r = 0.529. This is the value of the terms in the brackets sometimes written as a0 called Bohr’s Radius. For the second shell n = 2 and for 3rd orbit n = 3 and so on.  
**Hydrogen Atom Spectrum**  
***Balmer Series***  
The simplest element is hydrogen which contain only one electron in its valence shell.  
Balmer in 1885 studied the spectrum of hydrogen. For this purpose he used hydrogen gas in the discharge tube. Balmer observed that hydrogen atom spectrum consisted of a series of lines called Balmer Series. Balmer determined the wave number of each of the lines in the series and found that the series could be derived by a simple formula.  
***Lyman Series***  
Lyman series is obtained when the electron returns to the ground state i.e. n = 1 from higher energy level n(2) = 2, 3, 4, 5, etc. This series of lines belongs to the ultraviolet region of spectrum.  
***Paschen Series***  
Paschen series is obtained when the electron returns to the 3rd shell i.e. n = 3 from the higher energy levels n2 = 4, 5, 6 etc. This series belongs to infrared region.  
***Bracket Series***  
This series is obtained when an electron jumps from higher energy levels to 4th energy level.  
**Heisenberg Uncertainty Principle**  
According to Bohr’s theory an electron was considered to be a particle but electron also behaves as a wave according to be Broglie.  
Due to this dual nature of electron in 1925 Heisenberg gave a principle known as Heisenberg Uncertainty Principle which is stated as,  
It is impossible to calculate the position and momentum of a moving electron simultaneously.  
It means that if one was known exactly it would be impossible to known the other exactly. Therefore if the uncertainty in the determination of momentum is Δpx and the uncertainty in position is Δx then according to this principle the product of these two uncertainties may written as  
Δpx . Δx ≈ h  
So if one of these uncertainties is known exactly then the uncertainty in its determination is zero and the other uncertainty will become infinite which is according to the principle.  
**Energy Levels and Sub-Levels**  
According to Bohr’s atomic theory, electrons are revolving around the nucleus in circular orbits which are present at definite distance from the nucleus. These orbits are associated with definite energy of the electron increasing outwards from the nucleus, so these orbits are referred as Energy Levels or Shells.  
These shells or energy levels are designated as 1, 2, 3, 4 etc K, L, M, N etc.  
The spectral lines which correspond to the transition of an electron from one energy level to another consists of several separate close lying lines as doublets, triplets and so on. It indicates that some of the electrons of the given energy level have different energies or the electrons belonging to same energy level may differ in their energy. So the energy levels are accordingly divided into sub energy levels which are denoted by letters s, p, f (sharp, principle, diffuse & fundamental).  
The number of sub levels in a given energy level or shell is equal to its value of n.  
e.g. in third shell where n = 3 three sub levels s, p, d are possible.  
**Quantum Numbers**  
There are four quantum numbers which describe the electron in an atom.  
***1. Principle Quantum Number***  
It is represented by “n” which describe the size of orbital or energy level.  
The energy level K, L, M, N, O etc correspond to n = 1, 2, 3, 4, 5 etc.  
If  
n = 1 the electron is in K shell  
n = 2 the electron is in L shell  
n = 3 the electron is in M shell  
***2. Azimuthal Quantum Number***  
This quantum number is represented by “l” which describes the shape of the orbit. The value of Azimuthal Quantum number may be calculated by a relation.  
l = 0 —-> n – 1  
So for different shell the value of l are as  
n = 1 K Shell l = 0  
n = 2 L Shell l = 0, 1  
n = 3 M Shell l = 0, 1, 2  
n = 4 N Shell l = 0, 1, 2, 3  
when l = 0 the orbit is s  
when l = 1 the orbit is p  
when l = 2 the orbit is d  
when l = 3 the orbit is f  
***3. Magnetic Quantum Number***  
It is represented by “m” and explains the magnetic properties of an electron. The value of m depends upon the value of l. It is given by  
m = + l —-> 0 —-> l  
when l = 1, m has three values (+1, 0, -1) which corresponds to p orbital. Similarly when l = 2, m has five values which corresponds to d orbital.  
***4. Spin Quantum Number***  
It is represented by “s” which represents spin of a moving electron. This spin may be either clockwise or anticlockwise so the values for s may be +1/2 or -1/2.  
**Pauli’s Exclusion Principle**  
According to this principle  
No two electrons in the same atom can have the same four quantum number.  
Consider an electron is present in 1s orbital. For this electron n = 1, l = 0, m = 0. Suppose the spin of this electron is s = +1/2 which will be indicated by an upward arrow ↑. Now if another electron is put in the same orbital (1s) for that electron n = 1, l = 0, m = 0. It can occupy this orbital only if the direction of its spin is opposite to that of the first electron so s = -1/2 which is symbolized by downward arrow ↓. From this example, we can observe the application of Pauli’s exclusion principle on the electronic structure of atom.  
**Electronic Configuration**  
The distribution of electrons in the available orbitals is proceeded according to these rules.  
1. Pauli Exclusion Principle  
2. Aufbau Principle  
3. (n + l) Rule  
4. Hund’s Rule  
The detail of these rules and principles is given below.  
***1. Aufbau Principle***  
It is states as  
The orbitals are filled up with electrons in the increasing order of their energy.  
It means that the orbitals are fulled with the electrons according to their energy level. The orbitals of minimum energy are filled up first and after it the orbitals of higher energy are filled.  
***2. Hund’s Rule***  
If orbitals of equal energy are provided to electron then electron will go to different orbitals and having their parallel spin.  
In other words we can say that electrons are distributed among the orbitals of a sub shell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.  
***3. (n + l) Rule***  
According to this rule  
The orbital with the lowest value of (n + l) fills first but when the two orbitals have the same value of (n + l) the orbital with the lower value of n fills first.  
For the electronic configuration the order of the orbital is as follows.  
1s, 2s, 2p, 3s, 4s, 3d, 4p, 5s, 4d, 5p, 6s etc.  
**Atomic Radius**  
For homonuclear diatomic molecules the atomic radius may be defined as  
The half of the distance between the two nuclei present in a homonuclear diatomic molecules is called atomic radius.  
It may be shown as  
In case of hetronuclear molecular like AB, the bond length is calculated which is (rA + rB) and if radii of any one is known the other can be calculated.  
For the elements present in periodic table the atomic radius decreases from left to right due to the more attraction on the valence shell but it increases down the group with the increase of number of shells.  
**Ionic Radius**  
Ionic radius is defined as  
The distance between nucleus of an ion and the point up to which nucleus has influence of its electron cloud.  
When an electron is removed from a neutral atom the atom is left with an excess of positive charge called a cation e.g  
Na —-> Na+ + c-  
But when an electron is added in a neutral atom a negative ion or anion is formed.  
Cl + e- —-> Cl-  
As the atomic radius, the ionic radii are known from x-ray analysis. The value of ionic radius depends upon the ions that surround it.  
Ionic radii of cations have smaller radii than the neutral atom because when an electron is removed. The effective charge on the nucleus increases and pulls the remaining electrons with a greater force.  
Ionic radii of anions have a large radii than the neutral atom because an excess of negative charge results in greater electron repulsion.  
Radius of Na atom = 1.57  
Radius of Na+ atom = 0.95 (smaller than neutral atom)  
Radius of Cl atom = 0.99  
Radius of Cl- atom = 1.81 (larger than neutral atom)  
**Ionization Potential**  
*Definition*  
*The amount of energy required to remove most loosely bounded electron from the outermost shell of an atom in its gaseous state is called is called ionization potential energy.*  
It is represented as  
M(gas) —-> M+(gas) + e- ………………. ΔE = I.P  
The energy required to remove first electron is called first I.P. The energy required to remove 2nd or 3rd electron is called 2nd I.P or 3rd I.P  
M(gas) —-> M+(gas) + e- ………………. ΔE = 1st I.P  
M+(gas) —-> M++(gas) + e- …………….ΔE = 2nd I.P  
M++(gas) —-> M+++(gas) + e- ………… ΔE = 3rd I.P  
The units of I.P is kilo-Joule per mole.  
***Factors on which I.P Depends***  
*1. Size of the Atom*  
If the size of an atom is bigger the I.P of the atom is low, but if the size of the atom is small then the I.P will be high, due to fact if we move down the group in the periodic table. The I.P value decreases down the group.  
*2. Magnitude of Nuclear Charge*  
If the nuclear charge of atom is greater than the force of attraction on the valence electron is also greater so the I.P value for the atom is high therefore as we move from left to right in the periodic table the I.P is increased.  
*3. Screening Effect*  
The shell present between the nucleus and valence electrons also decreases the force of attraction due to which I.P will be low for such elements.  
**Electron Affinity**  
*Definition*  
The amount of energy liberated by an atom when an electron is added in it is called electron affinity.  
It shows that this process is an exothermic change which is represented as  
Cl + e- —-> Cl- ………… ΔH = -348 kJ / mole  
***Factors on which Electron Affinity Depends***  
*1. Size of the Atom*  
If the size of atom is small, the force of attraction from the nucleus on the valence electron will be high and hence the E.A for the element will also be high but if the size of the atoms is larger the E.A for these atoms will be low.  
*2. Magnitude of the Nuclear Charge*  
Due to greater nuclear charge the force of attraction on the added electron is greater so the E.A of the atom is also high.  
*3. Electronic Configuration*  
The atoms with the stable configuration has no tendency to gain an electron so the E.A of such elements is zero. The stable configuration may exist in the following cases.  
1. Inert gas configuration  
2. Fully filled orbital  
3. Half filled orbital  
**Electronegativity**  
*Definition*  
  
*The force of attraction by which an atom attract a shared pair of electrons is called electronegativity.*  
***Application of Electronegativity***  
*1. Nature of Chemical Bond*  
If the difference of electronegativity between the two combining atoms is more than 1.7 eV, the nature of the bond between these atoms is ionic but if the difference of electronegativity is less than 1.7 eV then the bond will be covalent.  
*2. Metallic Character*  
If an element possesses high electronegativity value then this element is a non-metal but if an element exist with less electronegativity, it will be a metal.  
***Factors for Electronegativity***  
*1. Size of the Atom*  
If the size of the atom is greater the electronegativity of the atom is low due to the large distance between the nucleus and valence electron.  
*2. Number of Valence Electrons*  
If the electrons present in the valence shell are greater in number, the electronegativity of the element is hig