ATOMIC STRUCTURE

1. John Dalton 1801, believed that matter is made up of extremely minute indivisible particles, called atoms.
2. J.J. Thomson 1897, produced cathode rays by passing electric discharge through gas at low pressure. Cathode rays consists of electrons. Production of cathode rays show that atom contains electrons. The properties of cathode rays are :
   (a) They travel in a straight line with high velocity and cast shadow.
   (b) They cause rotary motion.
   (c) They produce fluorescence when strike the glass walls of dischage tube, coated with ZnS
   (d) They are deflected from straight path by electric and magnetic field which shows hat they consits of minute particles electron carrying – ve charge.
3. From the analysis of anode rays or positive rays; also produced during the production of cathode rays; it is possible to show that the lightest positive particle in the atom is proton. Since atom is electrically netural hence number of protons is equal to number of electrons.
4. Rutherford's Experiment : In 1911, Rutherford observed that when α-particles emitted from Radium struck thin metallic sheets, many of them passed through the sheet with no change in their path but a few of them got deflected hrough 90° or through larger angles. He concluded that :
   (a) As most of the α-particles passed underflected, the atom must predominantly consists of empty spcae.
   (b) As a few α-particles carrying +ve charge are strongly deflected there mus be a heavy +ve charged body present in each atom and the volume occupied by this is only a minute fraction of the total volume of an atom. He called this +vely charged body as nucleus. It is surounded by small negatively charged particles called electrons, at relatively large distances from the nucleus.

   In order to explain why the electrons do not fall into the nucleus due o elecrostatic attraction. Rutherford proposed that elecrons are revolving round the nucleus at high velocities. The cenrifugal force arising from this motion just balances the force of electrosatic atraction.
5. Objections to Rutherford's Model : Whenever an electric charge is subjected to acceleration, it emits radiation and loses energy. As a result of this, the orbit will become smaller and the electrons will drop on the nucleus. This, however, does not happen.
6. Neil's Bohr Atomic Theory (1913): It is based on the following assumptions :
   (a) The electrons moves around the +vely charged nucleus in a circula orbit, he centripetal force for this motion is balanced by the electrostatic atraction.
   (b) The electrons can rotate only in certain orbits which are known as stationary or quantized orbits. When the electron moves in these orbits it cannot emit any radiation.
   (c) The electrons radiates a quantum of energy of frequency v only when it jumps from an orbit of higher energy to an orbit of low energy. If E_1 and E_2 are the eneries of the electron in two successive orbits, then

$$E_2 - E_1 = h\nu \text{ (h-Planck's constant)}$$
$$h = 6.62 \times 10^{-27} \text{ erg}$$
$$\nu = \frac{c}{\lambda}$$
$$c = 3 \times 10^{10} \text{ cm/s}, \ \lambda = \text{wavelength}$$

   The energy of the electrons in an orbit is cahracterised by quantunm number 'n'.

$$E_n = \frac{2\pi^2 Z^2 e^4 m}{h^2 n^2} \text{erg / electron} \quad = -2.178 \times 10^{-18} \text{J} \left(\frac{Z^2}{n^2}\right)$$

Wheren, Z-atomic number; m and e are mass and charge of the electron respectively.

The radius of the paths in which can electron can revolve is given by

$$r = \frac{n^2h^2}{4\pi^2me^2Z} = 0.53n^2 Å$$

(1 Å = 10^{-8} cm)

When an electron jumps from an outer orbit in which its quantum number is 'n_2' to an inner orbit in which it is 'n_1'; the energy emitted as radiation is given by :

$$E_{n_2} - E_{n_1} = \frac{2\pi^2Z^2e^4m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

and the frequency expressed in wave number will be

$$\bar{\nu} = \frac{2\pi^2Z^2e^4m}{h^3c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where R is the Rydberg constant. For hydrogen, R is 109677.8 cm^{-1}.

<u>We can concluded two important points from Bohr model :</u>

(a) The model correctly fits the quantized energy level of the hydroen atom as infered from, its emission spectrum. These energy level correspond o certain allowed circular orbitas for the electrons.

(b) As the electron becomes more tightly bound, its energy becomes more negative relative to the zero energy reference state (corresponding to the electron being an infinite distance fom the nucleus) ie as the electron is brought closer to the nucleus, enegy is released from the system.

(c) A general equation for the electron moving from one level ($n_{initial}$) to another level (n_{final}):

ΔE = energy of level n_{final} – energy of level $n_{initial}$ = $E_{final} - E_{initial}$

$$(-2.178\times10^{-18}\,J)\left(\frac{1^2}{n_{final}^2}\right) - (2.178\times10^{-18}\,J)\left(\frac{1^2}{n_{initial}^2}\right)$$

$$= -2.178\times10^{-18}\,J\left(\frac{1^2}{n_{final}^2} - \frac{1^2}{n_{initial}^2}\right)$$

8. Modern structure of Atom : Atom consists of two parts (A) Nucleus (B) Extra nuclear particles called electrons.

(A) Nucleus : The nucleus of an atom has a radius of about 10^{-13} cm whereas the atomic radius is about 1×1^{-8} cm. The nucleus contains different kinds of particles known as nuclear particles or nucleon. The various nuclear particles are as follows :

(a) Proton (H^+ or p) : The characteristics of a proton are as follows :

(i) Absolute mass = 1.66×10^{-24} g

(ii) Relative mass = 1 amu

(iii) Relative charge = + 1 unit

(iv) Absolute charge = $+ 1.6 \times 10^{-19}$ coulomb = $+ 4.8 \times 10^{-10}$ e.s.u.

(v) Atomic number = + 1

(vi) Inventor : Goldstein in 1886 in "anode Rays Experiments".

(b) Positron (e^+) :

(i) It is an antiparticle of electron because it has same negligible mass and same amount of charge as of the electron but he charge is +ve.

(ii) Absolute mass = 9.1×10^{-28} g

(iii) Relative mass = $\frac{1}{1836}$ amu

(iv) Relative cahrge = + 1 unit

(v) Atomic number = + 1

(vi) Inventor : Wilson in 1927 in his "Cloud Chamber Experiment".

(c) Positive meson (π^+)

(i) Relative mass = (200 to 300) × $\frac{1}{1836}$ amu

(ii) Relative charge = + 1

(iii) Atomic number = + 1

(iv) Inventor : C. Anderson in 1939 in "Cosmic Rays Experiment".

(d) Negative meson (π^-) :

(i) Relative mass = $(200 \text{ to } 300) \times \frac{1}{1836}$ amu

(ii) Relative chage = – 1 unit

(iii) Atomic number = – 1 unit

(iv) Invenor : C. Anderson in 1947 in "Cosmic Rays Experiments".

(e) Neutron (n) :

(i) Relative mass = 1.0083 amu

(ii) Relative charge = zero

(iii) Atomic number = zero

(iv) Inventor : J. Chadwick in 1932 by bombading Lithum and Beryllium metals with α-particles.

(f) Neutrino

(i) Relative mass : Variable mass less than that of an electron.

(ii) Relative charge = Zero

(iii) Inventor : Allen and Rodebeck in 1952.

(g) Antiproton (p^-) :

(i) Relative mass = To that of a proton.

(ii) Relative chage = Negative.

(iii) Inventor : Segree in 1956.

(B) Extra Nuclear Particles; "Electrons" : The electrons can be discussed under following points:

(a) Characteristics of electron (e^-) : These are as follows :

(i) Absolute mass = 9.11×10^{-28} g

(ii) Relative mass = $\frac{1}{1836}$ amu

(iii) Absolute charge = -1.6×10^{-19} coulomb = -4.8×10^{-10} e.s.u.

(iv) Atomic number = – 1

(v) Inventor : J.J. Thomson in 1897 in "Cathode-Rays Experimnent".

(vi) $\frac{\text{Charge}}{\text{Mass}}$ or $\frac{e}{m}$ ratio of electron was first measured by Mulliken in 1909 by means of "Oil-drop Experiment".

(a) Principal quantum no. 'n' : It represents the distance between electron and nucleus, ie he main energy shell in which particular electron is present. It mainly decides the energy of the electron in the orbit. It also gives the no. of electrons that may be accomodated in each shell. The capacity of each shell being given as $2n^2$. It decides the size of the shell.

$$mvr = \frac{nh}{2\pi}$$

$$E = -\frac{2\pi^2 mZ^2 e^4 \mu}{h^2}$$

E = Energy of electron in a particular level,

e = Electron charge, m = Mass of electron,

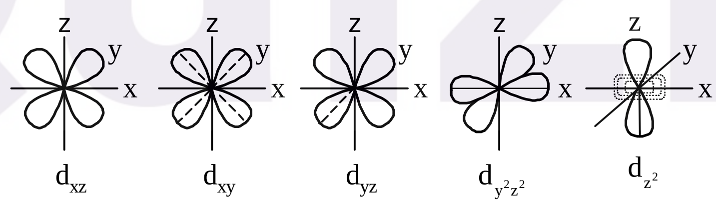
Z = Atomic number, h = Planck's constant.

(b) Azimuthal or secondary or subsidiary quantum number 'l' : It represents the no. of subshells can have the values 0 to (n – 1). It gives the shape of he subshell.

The volume of space where probability of finding an electron is maximum, is called orbital or subshell.

Properties :	s	p	d	f	g
shape	Spin	Dumb-bell	Double dumb-bell	Complicated	–
No. of sub-subshells	1	3	5	7	9
l	0	1	2	3	4
Max. no. of electrons	2	6	10	14	18

$$mvr = \frac{h}{2\pi}\sqrt{l(l+1)}$$



(c) Magnetic quantum no. 'm' : This gives he no. of orbitals in a subshell (under the influence of magnetic field). It takes only integral values rom – l to + l through zero m = 2l +1 for any value of l,

$m = n^2$

e $\quad$ l = 0 m = 1

In s-subshell there is only one sub-subshell.

In p-subshell there are p_x p_y p_z where x, y, z refer to the axis perpendicular to each other.

In d-subshell there are d_{xy}, d_{yz}, $d_{zx,}$ $d_{x^2-y^2}$ and d_{z^2}

In f-subshell there are 7 orbitals.

(d) Spin quantum no. 's' : When an electron rotates around a nucleus, it spins around its axis. It spin os cockwise it is written as as $+\frac{1}{2}$ or $\uparrow$. If anticlockwise then it is $-\frac{1}{2}$ or $\downarrow$ (even no. e).

$$mvr = \frac{h\sqrt{s(s+1)}}{2\pi}$$

We can write allowed combinations of quantum numbers for the first four shells as below :

n	l	m	Orbital rotation	Number of orbitals in subshell	Number of orbitals in shell
1.	0	0	1s	1	1
2.	0 1	0 -1, +1	2s 2p	1 3	4
3.	0 1 2	0 -1,0, +1 -2, -1,0,+1,+2	3s 3p 3d	1 3 5	9
4	0 1 2 3	0 -1,0, +1 -2, -1, 0, +1, +2 -3, -2, -1, 0, +1, +2, +3	4s 4p 4d 4f	1 3 5 7	16

(D) The Quantum Mechanical Description of the Atom :

(i) de-Brogle's theory : Bohr reated electron as a paticle. However, de Broglie suggested that electron has a dual nature, i.e. it behaves both as a particle as well as wave. The wavelength λ of a moving particle is

$$\lambda = \frac{h}{mv} \qquad ...(1)$$

v and m are the velocity and mass of moving particle respectively. If r is radius of the wave, $2\pi r$ it circumference, then

$$\lambda n = 2\pi r \qquad ...(2)$$

Thus, according to wave theory an electron is a stationary wave moving around the nucleus in a circular path. The wave character was later on conformed by Davison Germer (1927) and Thomson (1928).

From eq. (1) and (2), we have

$$2\pi r = \frac{nh}{mv} \text{ or } mvr = \frac{nh}{2\pi}$$

(ii) According to Schrodinger, the electron does not move round the nucleus in fixed orbits, but may, infact, be anywhere with different probabilities. The probability of its presence near the nucleus is greatest and as the distance from nucleus increases the probability decreases. Schrodinger from mathematical treatment of wave motion gave a general wave equation describing the behaviour of a small particle. Consider a system such as a stretched string. For its vibration.

$$\psi = A \sin \frac{2\pi x}{\lambda}$$

Where, x = displacement, Ψ = wave function, A = amplitude of the wave, λ = wavelength

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - P.E.)\,\psi = 0$$

ψ^2 for an electron at a given point indicates the probability of occurrence of the electron at that point.

If above equation is solved by Ψ several solutions are found. Among those solutions, the solutions which are single valued and containuous function are permitted solution. They are called as eigen functions.

(a) radialnode or spherical node : number of radialnode = n – l – 1.

(b) Angular node or nodal plane : no. of Angular node = l.

$\therefore$ Total node = n – 1 – 1 + l = n – 1

(ii) Heisenber'g uncertainty principle : It states "It is impossible to determine simultaneously both the psoition and the velocity of a moving electron". Let Δx be the uncertainty in determining its position and Δp the uncetaintly in determining its momentum at the same time then according to Heisenber'g principle in case of electron, the product of uncertainty of velocity and position is propportional to Planck's constant and can never be less than $\frac{h}{2\pi}$

RULES FOR FILLING OF ELECTRONS IN THE ORBITAL(S)

There are three rules :

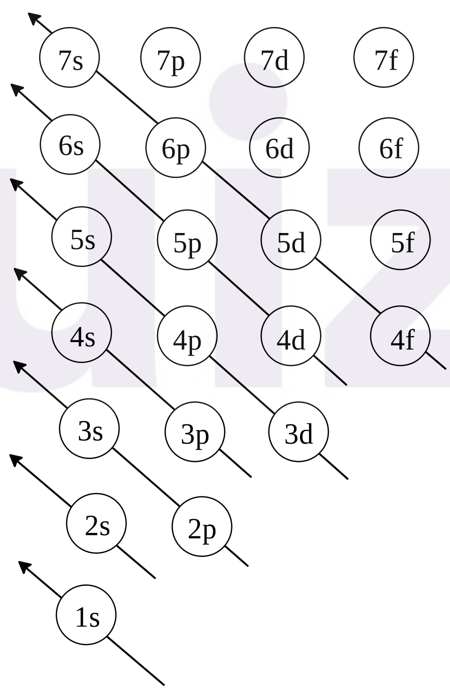
1. The Aufbau Principle

According to it an electron enters the orbital that has the minumum energy.

or

As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these atomic orbitals.

The energy of different atomic orbitals is as follows :



Thus the increasing order of energy is :

$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 5f \rightarrow 6d \rightarrow 7p$

2. Hund's Rule

It states that electron pairing in any s, p, d or f-orbital is not possible unitl all the available orbitals of the same orbital contain one electron each. It means an electron occupies a vacant orbit in the same orbital and pairing can start when all the orbitals are filled up. Pairing occurs only after filling 3, 5 and 7 electrons in p, d and f-orbitals respectively.

For example, the configuration of carbon atom may be written as :

C : $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

1s 2s 2p

Similarly for nitrogen may be written as :

N : $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

1s 2s 2p

Likewise for oxygen :

O : $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

1s 2s 2p

3. Pauli Exclusion Principle

It states that no two electrons in an atom can have all the four quantum number identical. In other words, maximum number of electrons in an orbital can be two with opposite spin.

For example, the value (s) of the quantum number (s) 11th and 12th electron of magnesium is as follows :

11th electron ; $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

12th electron ; $n = 3, l = 0, m = 0, s = -\frac{1}{2}$

ATOMIC SPECTRA

When the sunlight is passed through prism, it is dispersed into 7 colour which is called as spectra. If the atom is excited and then examined through spectroscope. We see no. of lines. This is called line spectra or atomic spectra.

1. Atomic spectra of hydrogen

Bohr (1913) proposed that an electron moves only in the orbit in which angular momentum of the electron is equal to $\left(\frac{2h}{2\pi}\right)$. Such orbits are called 'Stationary States' by Bohr.

When an electron jumps from one orbit to anoher it either loses or gains energy in he form of radiation. The energy of radiation is given by :

$$E_2 - E_1 = hv$$

or $$\nu = \frac{E_2 - E_1}{h}$$

or $$\frac{c}{\lambda} = \frac{E_2 - E_1}{h}$$

or $$\frac{1}{\lambda} = \frac{E_2 - E_1}{ch}$$

Therefoe line in the spectrum of 'H' results from the dropping of electron excited to hiher stationary states back to lower, or less energetic states. Each line was ascribed to a transfer to the electron from an orbit of some n value to an orbit of some lower n value. Using this, Bohr was able to account for the observed wavelength of the lines in Lyman, Balmer and Paschen series.

Balmer (series is found in)	visble.
Paschen	near infra-red.
Brackett	far infra-red.

Pfund	Lyman	Balmer	far infra-red	Paschen
2000Å	4000Å	6000Å	800Å	1800Å

Wavelengths of these series were determined from he following expression.

$$\frac{l}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where R_H = Rydberg's constanat

n_1 = 1 for Lyman

= 2 for Blamer

= 3 for Paschen

= 4 for Brackett

= 5 for Pfund

It failed to systems conaining more than on electron.

2. The hydrogen atom

It can be discussed as below :

(a) In quantum mechanical model the electron is described as a wave. Thsi representation leads to a series of wave functions (orbitals) that describe the possible energies and special distributions available to the electorn.

(b) In agreement with the Heisenberg's uncertainty principle, the model cannot specify the detailed electron motons. nstead, the square of the wave function represents the probability distribution of the electron in that orbital. This approach allows us to picture orbitals in terms of probability distributions, or electron density maps.

(c) The size of an orbital is arbitarily defnied as the surface that contains 90% of the total electron probability.

(d) The hydrogen atom has many types of orbitals. n the ground state the single electron resides in the 1st orbital. The electron can be excited to higher energy orbitals if the atom absorbs energy.

3. Few Terms

(a) Mass Defect : Actual mass of atom is not equal to the sum of mass of e, p and n present in it, eg for chlornie

$_{17}Cl^{35}$ = 17 (1.007276) amu + 18(1.008665) amu + 17.(0.0005486) amu = 35.289005 amu

However, the mass of chlorine has been accurately determined as 34.96885 amu. This difference between the two values (35.28901 amu – 34.96885 amu) = 0.32016 amu is known as mass defect.

This difference, expressed in its energy equivalent, is called the binding energy of the nucleons (neutrons + protons) in the nucleus of the atom in questions.

(b) Isotopes : Atoms of an element havnig the same atomic no., but different at. wt. are called isotopes.

e.g. $^{35}_{17}Cl$ and $^{37}_{17}Cl$; $^{1}_{1}H$, $^{2}_{1}D$ and $^{3}_{1}T$; $^{16}_{8}O$, $^{17}_{8}O$ and $^{18}_{8}O$

Isotopes have the same no. of protons and electrons but different no. of neutrons. They have the same chemical properties. The fractional at. wt. of an element is due to the different proportion in which vaious isotopes are present in it, eg chlorine has two isotopes $_{17}Cl^{35}$ and $_{17}Cl^{37}$ present in the ratio 3 : 1.

$$\text{Average at. wt.} \frac{3\times35+1\times37}{4}=35.5\text{ amu}$$

(c) Iobars : Atoms having the same no. of neutrons but different no. of protons are called isotones, eg.

$^{30}_{14}Si$, $^{31}_{15}P$

(e) Isoelectronic ions or Molecules : Species having same no. of electron but different charge of nucleus are known as Isoelectronic ions, e.g.

(i) O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}, Al^{3+}

(ii) NO_3^{-}, CO_3^{2-}, $COCl_2$

(iii) NH_3, H_3O^{+}

(iv) N_2, CO, CN^{-}

(v) NCs^{-} and Cs_2

(vi) H^{-}, He, Li^{+}

(f) Isodiaphers : Atoms having same isotopic numbers. i.e. same value of (n–p) but different atomic as well as mass number.