A. PHYSICAL CHEMISTRY

Chapter 1: Atomic structure :

* Fundamental Particles (electron, Proton & neutron) :-

An atom is made up of three fundamental Particles; Electrons, Protons and Neutrons.

- An electron is defined as sub-atomic Particle having a unit negative charge and a mass equal to $\frac{1}{1835}$ th the mass of the hydrogen atom. It was discovered by J.J. Thomson.
- An Proton is defined as sub-atomic Particle having a unit Positive Charge and mass equal to the mass of the hydrogen atom (1.672×10^{-24} g). It was discovered by E. Rutherford.
- An neutron is defined as sub-atomic Particle which has a neutral Charge and a mass slightly greater than that of a Proton (1.675×10^{-24} g). It was discovered by Chadwick.

An atom - electrically neutral. Since an atom is electrically neutral, the no. of electrons in an atom must be equal to the no. of Protons.

Constituent	electron	Proton	neutron
Charge	-1.602×10^{-19} Coulomb	$+1.602 \times 10^{-19}$ coulomb	neutral; 0
mass	9.11×10^{-31} kg	1.672×10^{-27} Kg	1.675×10^{-27} kg
Specific Charge (e/m ratio)	1.76×10^{8} Coulombs/gm	9.58×10^{4} Coulombs/gm	0
Mass of 1 mole	0.55 mg	1.007 gm	1.008 gm
Charge of 1 mole	96500 Coulombs = 1 F	96500 Coulombs	0

N.B :- 1 mole = Avogadro's no (N) = 6.023×10^{23}

1F = 1 Faraday = Charge of one mole of electrons ≈ 96500 Coulombs.

* Rutherford's Atomic model :-

⇒ **Postulates**

1. An atom consists of two parts :
   (i) Nucleus (ii) Extra-nuclear Part.
2. Nucleus is an extremely small Positively charged Part and is situated at the centre of an atom. It carries nearly the whole mass of an atom. The magnitude of the Positive charge on the nucleus is different for the atoms of different elements.
3. The electrons which balance the Positive charge are distributed in the extra nuclear part, i.e. space around the nucleus.
4. The extra-nuclear electrons are not stationary. These are revolving round the nucleus at high speeds in circular paths, called orbits. The centrifugal force which arises due to the rotation of electrons balances the force of attraction. This prevents the electrons to fall into nucleus; Rutherford's Picture of an atom is comparable to solar system. The nucleus representing the sun and the revolving electrons are called Planetary electrons.

⇒ **Drawbacks of Rutherford's Atomic Model (Failure) :-**

⇒ According to Rutherford's atomic model, an atom consists of a nucleus and the electrons are revolving around it. Thus, the centrifugal force which is produced by the circulation of electrons balances the force of attraction between the electrons and the nucleus.

⇒ But Clark Maxwell had shown that a charged Particle which moves under the influence of an attractive force continuously lose energy.

⇒ Since electron is also a charged Particle, it must emit radiations and thus lose energy continuously. As electron loses energy, it starts coming nearer the nucleus, i.e., its orbit would become smaller and smaller.

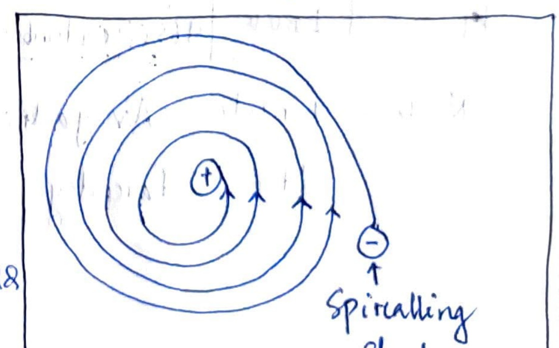


Fig: The orbit becoming smaller and smaller.

⇒ As a result of this, the electron would ultimately fall into nucleus. But we know that the revolving electrons never fall into the nucleus. Thus Rutherford's Picture of an atom is faulty.

⇒ It also failed to explain the existence of certain definite lines in the hydrogen spectrum. If the electrons were to lose energy continuously, then atomic spectrum of hydrogen should have been continuous. Infact, the spectrum of hydrogen is found to be discontinuous.

⇒ The model does not explain the structure of atoms i.e. distribution of electron & their energies.

* **Atomic number :- (Z)**

Atomic number of an element is defined as the no. of unit Positive charges or the protons present in the nucleus of an atom.

Atomic number = No. of nuclear Protons = No. of extra-nuclear electrons

It is denoted by the letter Z. It governs the properties of an element.

* **Mass number (A) :-**

The sum of the protons (p) and the neutrons (n) in an atom is called its Mass number. It is denoted by the letter (A).

i.e. Mass number = No. of Protons + No. of neutrons = P + n.

Atomic number = No. of Protons = No. of electrons = p = e.

→ The Protons and neutrons are collectively called Nucleons.

An element with mass no. A and Atomic no. Z, can be represented as:

$$^{A}_{Z}X \quad , \quad \text{No. of neutrons} = A - Z.$$

Ex:- How many Protons, electrons and neutrons are there in (i) $^{17}_{8}O$ (ii) $^{56}_{26}Fe$

Solution:- (i) $p = e = 8$, $n = 9$ (ii) $p = e = 26$, $n = 30$.

* **Isotopes, Isobars and Isotones :-**

→ **Isotopes :-** Isotopes are defined as the atoms of the same element which have same atomic no. but different mass numbers.

Isotopes are different kinds of atoms of the same element which have:

(i) same Physical and Chemical Properties.

(ii) same atomic number, i.e., no. of Protons.

(iii) same position in the Periodic table, but

(iv) different no. of neutrons and hence, different mass nos, density, atomic volume, melting Point and boiling Point.

Ex:- (i) $^{1}_{1}H$, $^{2}_{1}H$ & $^{3}_{1}H$. (ii) $^{35}_{17}Cl$ & $^{37}_{17}Cl$

→ **Isobars :-** Isobars are the atoms of different elements having the same mass no. but differ in their atomic numbers. Isobars have:

(i) different Physical and Chemical Properties.

(ii) different atomic no. i.e. the no. of Protons.

(iii) different Position in the Periodic table, and

(iv) different atomic volume, density, melting Point and Boiling Point.

Ex:- $^{40}_{18}Ar$ and $^{40}_{20}Ca$

→ **Isotones :-** Atoms of the different elements which possess the same no. of neutrons are called Isotones.

Ex:- $^{76}_{32}Ge$ and $^{77}_{33}As$ Contain the same no. of neutrons, i.e. 44 each and are thus, called Isotones.

* Bohr's Atomic Model :-

The main Postulates of Bohr's theory are :

1. An atom consists of a massive positively charged nucleus. The electrons are moving around the nucleus in certain fixed circular orbits without radiating energy. These non-radiating orbits are known as stationary states.
2. Each of the fixed circular orbits or stationary states is associated with a definite amount of energy. Hence, stationary states are also called energy levels. The energy associated with different energy levels increases with increase in distance from the nucleus. The letters K, L, M, N etc. or the numbers 1, 2, 3, 4 etc. are used to designate the different energy levels as shown in figure.

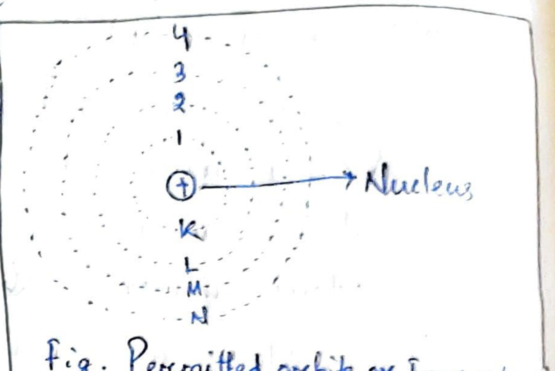


Fig. Permitted orbits or Energy levels

Energy associated with an energy level is given by the relation ;

$$E_n = \frac{-1312}{n^2} \text{ KJ mole}^{-1}$$ for a hydrogen atom.

Here, n is the number of the energy level.

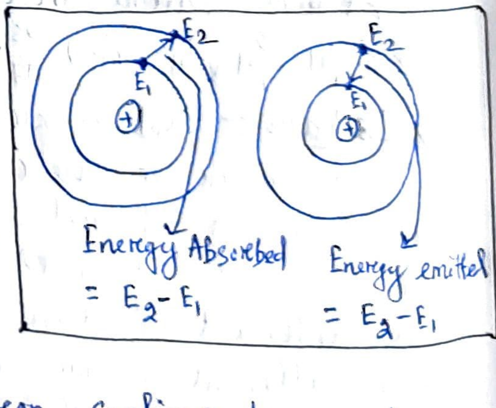
Different energy levels are not equally spaced, i.e., the energy difference between two successive energy levels is not the same. It goes on decreasing with the increase in the value of "n".

3. Only those orbits are permitted in which the angular momentum (mvr) of an electron is a whole number multiple of $h/2\pi$ and is given by the relation.

$$mvr = n\frac{h}{2\pi}$$

where $n = 1, 2, 3 \ldots$, h is Planck's constant, m and v represent the mass and tangential velocity respectively and r is the radius of the orbits.

4. So long as an electron revolves in a particular orbit, it can neither emit nor absorb energy.
5. The energy is emitted or absorbed discontinuously in the form of quanta or small packets only. The electronic transitions occurs from (a) higher to lower orbit by emission of energy and (b) lower to higher by absorption of energy. The amount of energy emitted or absorbed ; $\Delta E = E_2 - E_1 = h\nu$



6. Since energy cannot be lost continuously, an electron continues to move in a particular energy level without losing energy. Such a state of the atom is known as normal or ground state.
7. On gaining energy from an external source, electron jumps from a lower energy level to a higher energy level. Such a state of the atom is known as excited state. However, the excited state being unstable, excited electron jumps down almost immediately to lower level (either directly or in steps) by losing energy in the form of light radiation of suitable wavelength. This accounts for

the spectral lines in the hydrogen spectrum and atomic spectra of other atoms.

8. All the laws of Classical Physics are applicable to electron, i.e. the Position, velocity, momentum Can be Calculated accurately.

* Bohr-Bury Scheme (Arrangement of Planetary Electrons):

Bohr and Bury (1921) gave the following rules for the distribution of electrons in different orbits.

1. The maximum no. of electrons that can be present in an orbit is equal to $2n^2$ where n is the no. of the orbit. Note the maximum no. of electrons in various shells.

No. of the shell (n)		No. of electron ($2n^2$)
K-shell	1	$2\times1^2 = 2$
L-Shell	2	$2\times2^2 = 8$
M-shell	3	$2\times3^2 = 18$
N-Shell	4	$2\times4^2 = 32$

2. The outermost orbit of an element Cannot Contain more than 8 electrons and the orbit immediately before it, i.e., Penultimate orbit Cannot contain more than 18 electrons.

3. It is not always necessary to Complete an orbit before the next orbit starts filling. In fact a new orbit starts filling when the Previous orbit gets electrons.

Ex:- (i) In Hydrogen, Z=1, i.e. P = e = 1 & n = 0.
So it Contains one Proton in the nucleus and one electron is revolving around it.

(ii) In Oxygen, Z=8, i.e. P = e = 8, and n = 8
So its nucleus Contains 8 Protons and 8 neutrons. 8 electrons are revolving (i.e. 2 in K-shell and 6 in L-shell) around the nucleus.

* Aufbau's Principle (Building up):

According to this Principle, the electrons are filled in various orbitals in order of their increasing energies.

Thus, an orbital with lowest energy will be filled first. The energy content of the two subshells can be Compared by means of (n+l) rule as explained below:

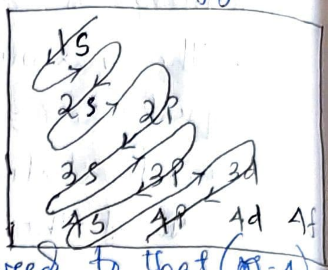
(i) The subshell with lower (n+l) value will Possess lower energy and will be filled first, e.g., 4s-subshell is filled first than 3d-subshell.

ⓐ For 4s-subshell : $n + l = 4 + 0 = 4$

ⓑ For 3d-subshell : $n + l = 3 + 2 = 5$

Since $(n+l)$ value for 4s-subshell is less than 3d, the 4s-subshell has lower energy and is filled first.

(ii) The sub-shell with lower value of n possesses lower energy if $(n+l)$ values for both the subshells are equal.



e.g., 3p-subshell is filled first than 4s.

ⓐ For 3p-subshell : $n + l = 3 + 1 = 4$

ⓑ For 4s-subshell : $n + l = 4 + 0 = 4$.

The value $(n = 3)$ is less for 3p-subshell as compared to that $(n = 4)$ for 4s-subshell. Hence, 3p-subshell has lower energy than 4s-subshell and is filled first.

The above two rules are applied to calculate the energy of various subshells. So the increasing order of various subshells is as follows :

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f$.

★ **Hund's Rule of Maximum Multiplicity** :- According to this rule "No electron pairing takes place in p, d, and f-subshells until each degenerate orbital in the given subshell contains one electron."

OR

Orbitals of same sub-shell first get single filled, then pairing occurs.

OR

Degenerate orbitals first get single filled and then pairing occurs.

Ex:

Element	At. No.	Electronic Configuration: Wrong	Electronic Configuration: Correct
Nitrogen	7	$1s^2 2s^2 2p_x^2 2p_y^1$	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
Oxygen	8	$1s^2 2s^2 2p_x^2 2p_y^2$	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
Fluorine	9	$1s^2 2s^1 2p_x^2 2p_y^2 2p_z^2$	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

★ **Electronic Configuration** :- It is governed by following rules :

1. Aufbau Principle 2. Hund's rule of maximum multiplicity

Following procedure is used to write the electronic configuration of elements :

(i) Note the atomic no. of the element whose electronic configuration is required e.g. Phosphorous $(P = 15)$ i.e. no. of electrons = 15.

(ii) Fill up the electrons in atomic orbitals, which are written in the increasing order of their energy. Keep in mind that:

ⓐ An orbital cannot have more than two electrons.

ⓑ s, p, d and f - sub-shells can have maximum of 2, 6, 10 and 14 e^-s respectively.

(iii) While filling electrons in orbitals belonging to each of the p, d and f - subshells, see that each orbital contains one electron first and then pairing takes place, e.g., the electronic configuration of Phosphorus (Z = 15 and no. of e^-s = 15) is $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$ and not $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^0$.

Element	Symbol	At. No.	Electronic Configuration
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p_x^1$
Carbon	C	6	$1s^2 2s^2 2p_x^1 2p_y^1$
Nitrogen	N	7	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
Oxygen	O	8	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
Fluorine	F	9	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
Neon	Ne	10	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminium	Al	13	$1s^2 2s^2 2p^6 3s^2 3p_x^1$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
Sulphur	S	16	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

Chromium	Cr*	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$
Manganese	Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$
Iron	Fe	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
Cobalt	Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
Nickel	Ni	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$
Copper	Cu*	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
Zinc	Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

* Exceptional Configuration of Cr and Cu :-

From the above configuration, it is important to note that there are two irregularities in the general trend. The electronic configurations of Cr and Cu show deviation from the expected configuration. The electronic configurations for these atoms are expected to be : Cr : [Ar] $4s^2\ 3d^4$ and Cu : [Ar] $4s^2\ 3d^9$.

However, the actual configurations are :

Cr : [Ar] $4s^1\ 3d^5$ and Cu : [Ar] $4s^1\ 3d^{10}$

This is because the half filled and fully filled configurations, i.e. d^5, d^{10}, f^{14} have lower energy or more stability. Thus, in order to become more stable, one of the 4s electrons goes into 3d orbitals so that 3d orbitals get half or fully filled configurations in Cr and Cu respectively.