Physical Chemistry ①

1.1 :- General concept of Atomic Structure :-

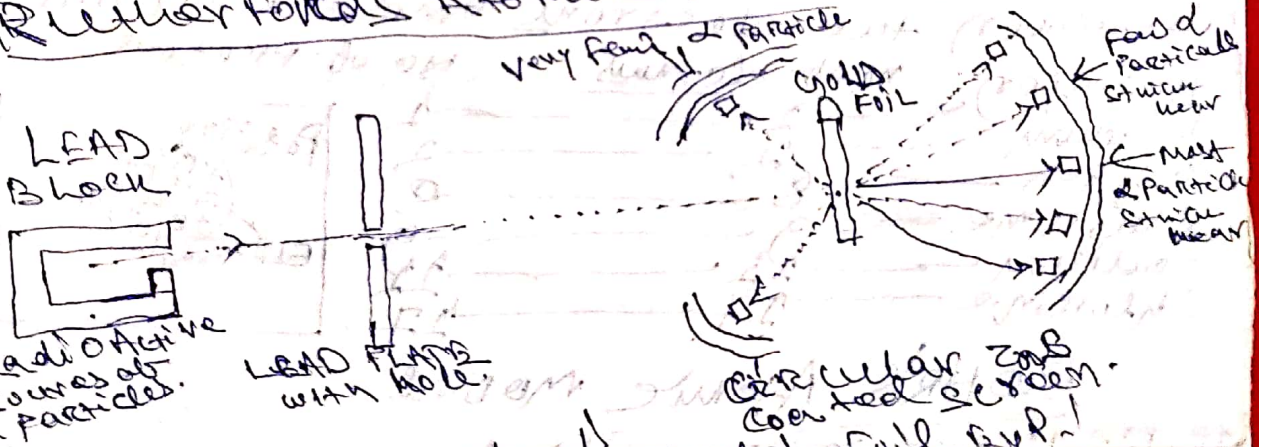
In 1808 when John Dalton put forward his atomic theory & said that "matter is made up of very small indivisible particles, called atoms". Until the close of the nineteenth century it was held that atoms cannot be sub-divided. As a result of large no of experiments conducted by Rutherford Bohr & Moseley & others revealed that atom has a complex structure. It was found that atom is made up of three fundamental particals viz - Electrons, protons & neutrons.

The cathode rays consist of tiny particles called electrons. It has been found that electrons can be emitted from some appⁿ ① By heating filaments to high temperature ② By exposing the metal surfaces to high frequency radiations as x-rays.

The electrons produced from any substance by any method has the same e/m ratio. electrons are the universal constituent of all matter.

An electron is defined as sub-atomic particles having a unit negative charge and a mass equal to $\frac{1}{1835}$ th the mass of the hydrogen atom.

Rutherford's Atomic model :-



Rutherford's gold foil exp :-

① The discharge tube experiments gave clear hint the atom consists of two sub-atomic particles.
② negatively charged particles (electrons)
③ positively charged particles (protons)

Discovery of Nucleus :-

Rutherford bombarded a thin sheet of gold (thickness 0.0000 4 cm) with α particles. α Particles (He^{++}) are obtained from a radioactive element like radium. A thick lead plate with a hole cut in it, serves to form a

Beam of α particles. A circular coated with zinc sulphide was placed on the other side of the foil.

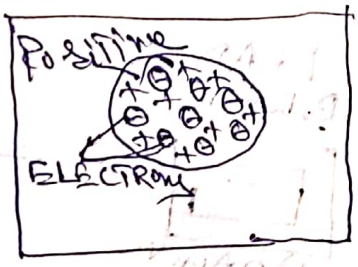
Observation:- (i) Most α particles passed straight through the gold foil & caused illumination on the zinc sulphide screen. (ii) very few beam Particles were deflected at some angles after passing through the gold foil. (iii) while a very few particles (one in 20,000) even retraced their path.

From this experiment it was concluded that (i) most of the space in an atom is empty. (ii) The scattering of α particles in all direction further reveals that there is a heavy positive charge at the centre of the atom which causes repulsion.

Drawbacks of Rutherford's Atomic model

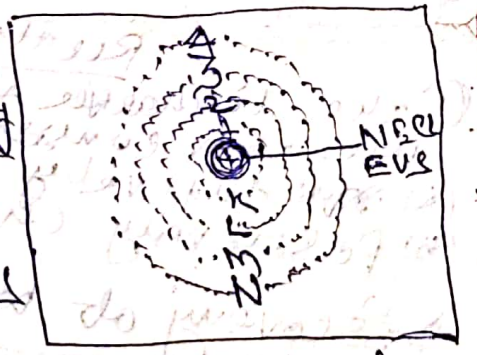
According to rutherford's atomic model, an atom consists of a nucleus and the electrons are revolving around it. The centrifugal force which is produced by the circulation of electron balances the force of attraction between the electrons and the nucleus.

	no of electrons	no of protons
Hydrogen	1	1
Helium	2	2
oxygen	8	8
Fluorine	9	9
Sodium	11	11
Chlorine	17	17



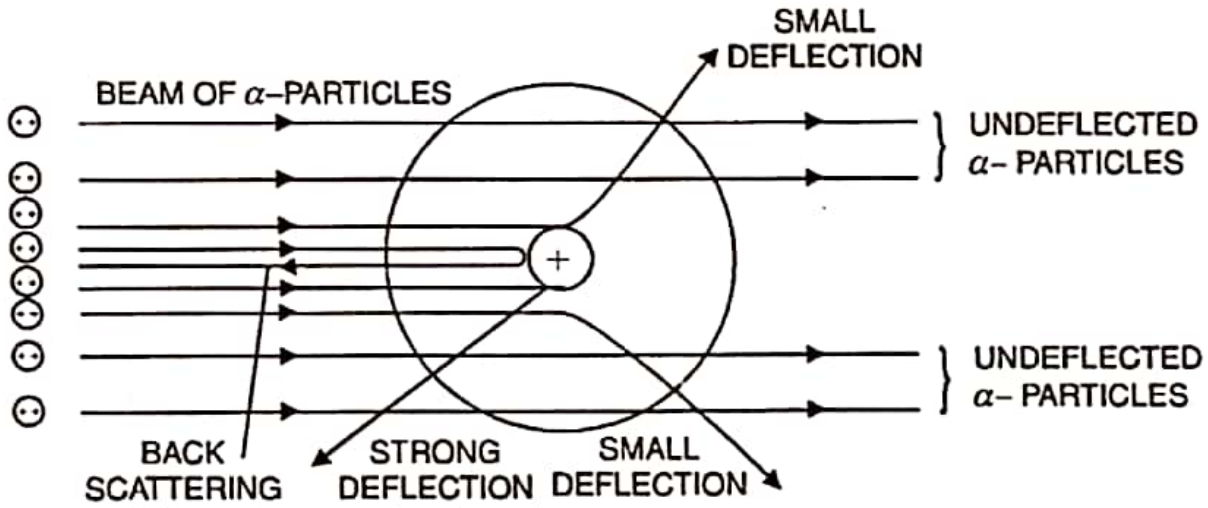
BOHR's Atomic model

Dr. Niels Bohr (1913) modified Ruther bord's model of atom with help of Quantum theory of radiation Proposed by Max Plank.



The main Postulates of Bohr's theory are :-

(i) An atom consists of a massive positively charged nucleus. The electrons are moving around the nucleus in certain fixed



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SUBJECT

① 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. 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. 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

n is the number of the energy level.

Different energy levels are not equally spaced i.e the energy different 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 ~~either~~ neither emits nor absorbs energy.

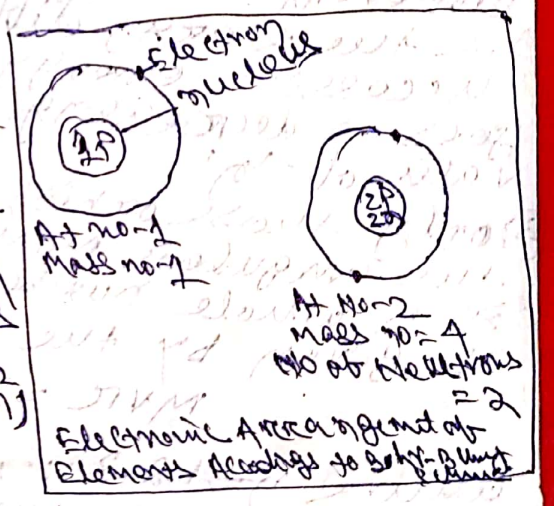
⑤ Higher to lower orbit by emission of energy and lower to higher by absorption of energy. absorbed $\Delta E = E_2 - E_1$ or $h\nu = E_2 - E_1$

(6) All the laws of classical physics are applicable to electron, i.e. the position velocity, momentum can be calculated accurately.

Diff - Difference between Bohr's model and Rutherford's model of the atom is that Bohr's model is based on the concept of quantization of energy and angular momentum of the electron. Quantization means that a quantity can vary only discontinuously to get a specific value. According to Bohr's theory, electron can move only in certain permitted orbits with definite amount of energy and angular momentum. Thus, quantization is the key point of Bohr's theory. Rutherford's model does not give any idea about the permitted orbits.

BOHR-BURY SCHEME
(Arrangements of Planetary electrons)

Bohr & Bury (1921) gave the 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. The maximum no of electrons in various shells.

no of 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 outer most 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) (1) Hydrogen - It is the first element. Its atomic no is one. It contains one proton in the nucleus & one electron is revolving around it.

(2) Helium :- It is the second element. Its atomic no is two & mass no is 4. Therefore its nucleus contains 2 protons & 2 neutrons. Two electrons are revolving around it.

Elements	At No (Z)	Mass No (A)	No of electrons & protons
Hydrogen	1	1	1
Helium	2	4	2
Lithium	3	7	3
Beryllium	4	9	4
Boron	5	11	5
Carbon	6	12	6
Nitrogen	7	14	7
Oxygen	8	16	8
Fluorine	9	19	9
Neon	10	20	10
Sodium	11	23	11
Magnesium	12	24	12
Aluminium	13	27	13
Silicon	14	28	14
Phosphorus	15	31	15
Sulphur	16	32	16
Chlorine	17	35	17
Argon	18	40	18

ELECTRONIC CONFIGURATION AND AUFBAU PRINCIPLE

AUFBAU PRINCIPLE - GERMAN : Aufbau (means building up)

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

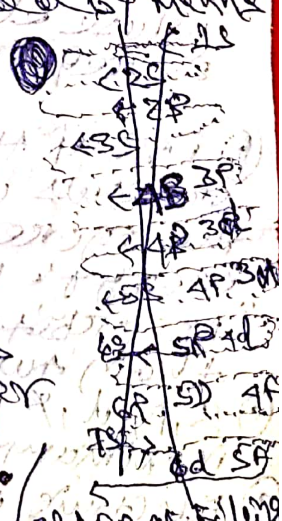
(1) The sub shell with lower (n+l) value will possess lower energy and will be filled first. eg: 4s sub shell is filled first than 3d subshell.

(a) For 4s sub shell :- n+l = 4+0 = 4

(b) 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 & is filled first.

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



ORDER OF FILLING UP orbit

According to the 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 sub-shell 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.

Element	At. No.	Electronic configuration	Correct
Nitrogen	7	$1s^2 2s^2 2p_x^2 2p_y^1$ (wrong)	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
Oxygen	8	______	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
Fluorine	9	______	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
Neon	10	______	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

Nitrogen N = 7

Oxygen O = 8

Fluorine = 9

Neon = 10

Application of Hund's Rule

Method of write electronic configuration

(a) The atomic no of the element whose electronic configuration is required. eg:- P - no. of e's = 15 (Phosphorus)

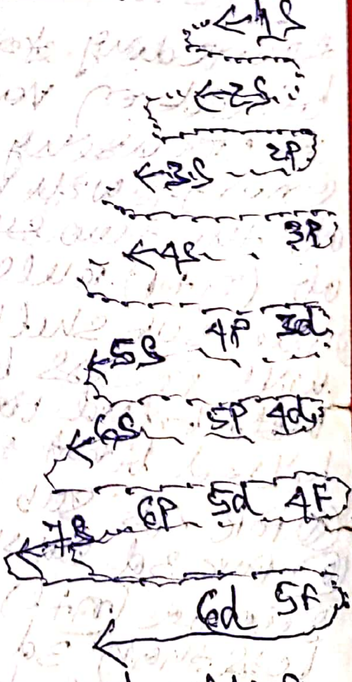
(b) Fill up the electrons in atomic orbitals which are written in the increasing order of their energy. Keep in mind that "An orbital cannot have more than two electrons".

(c) s, p, d, & f sub-shells can have maximum of 2, 6, 10, & 14 electrons

(c) Electrons in orbitals belonging to each of the p, d, & f sub shells & each orbitals contains one electron first & then pairing take place.

eg. Electronic configuration of Phosphorus (Z = 15 & no of e's = 15) $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$.

Hydrogen to Tin = 50 Remember.



ORDER of Filling of Orbitals

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PHYSICAL CHEMISTRY

Sign: Invigilator

ATOMIC WEIGHT OR ATOMIC MASS

The atomic mass of an element is defined as the relative average mass of the atom as compared to the mass of carbon atom [C^{12}] taken as 12. Atomic mass of an element means as to how many times it is heavier than 1/12th the mass of an atom of carbon (C^{12}).

The atomic mass of an element = mass of one atom of an element / 1/12th the mass of one atom of C^{12}

MOLECULAR WEIGHT OR MOLECULAR MASS

The molecular mass of a substance is defined as the average relative mass of one molecule of it as compared to the mass of an atom of carbon.

GRAM MOLECULAR MASS OR GRAM MOLE

The amount of the substance in grams which is numerically equal to its molecular mass is called its gram molecular mass (GMM). Gram molecular mass of the substance is defined as the mass of Avogadro number of its molecules in grams. All substances contain the same number of molecules i.e. 6.023×10^{23}

EQUIVALENT MASS OR WEIGHT

Equivalent mass of a substance is the number of parts by mass of it that combine with or displaces directly or indirectly

1.008 Parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine.

Second Def^n :- Equivalent mass of a salt is defined as that mass which combines with one gram equivalent of another salt.

The equivalent mass of an ion is the ratio of its ionic mass to the total number of positive or negative charges on it.

$$\text{Equivalent mass of an ion} = \frac{\text{Ionic mass}}{\text{Total no of Positive or negative charge on the ion.}}$$

CONCEPT OF CHEMICAL BOND

A chemical bond is defined as a force of attraction which holds together the constituent atoms in a molecule.

CHEMICAL BONDS

Such compounds which are formed by the transference of one or more electrons from one atom to the other are called electrovalent or ionic compounds and the type of linkage is called electrovalent or ionic linkage.

Ionic bond formation, the electron affinity of an element should be high.

Characteristics of Ionic compounds.

Characteristics of Covalent Compound

1. Low melting & boiling points.
2. Bad conductors.
3. Solubility
4. Slow rate of reactions.
5. Isomerism.

(6) Co-ordinate or Dative Bond

A co-ordinate bond is formed when one atom with complete octet donates its pair of electrons to the other atom. The donated pair is counted for the stability of both the atoms.

(i) The type of bond is formed between two dissimilar atoms A & B.
(ii) Atom A has one or more lone pairs of electrons. Atom B is short of a pair of electrons than the nearest inert gas configuration.
(iii) Atom A donates the lone pair of electrons to the atom B. As a result, both atoms get inert gas configuration. Atom A is called donor while atom B is called acceptor atom. The bond formed is called co-ordinate or dative bond.
(iv) The dative bond is a directional bond.

CONCEPT OF ARRHENIUS

ARRHENIUS CONCEPT OF Acid & Base

(i) Acids are those substance which yield H^+ ions in aqueous solution.

Eg. HCl, CH_3COOH, H_2SO_4 are acids because they dissociate as below.

$$HCl(g) + aq \rightleftharpoons H^+(aq) + Cl^-(aq)$$

$$HNO_3(l) + aq \rightleftharpoons H^+(aq) + NO_3^-(aq)$$

$CH_3COOH_{(l)} + OH^-_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$

BRONSTED-LOWRY CONCEPT of Acid & Base

J.N. Bronsted & T.M Lowry Independently and Simultaneously (1923) put forward a more general concept for acid & bases. According to this concept

(1) Acid is a substance (molecule or ion) which has a tendency to donate a proton to any other substance, and.

A base is a substance (molecule or ion) which has a tendency to accept a proton from any other substance.

While an acid is a proton donor, a base is a proton acceptor. An acid or a base may be a neutral molecule, cation or an anion.

Acids :- $HCl \rightleftharpoons H^+ + Cl^-$

$H_3O^+ \rightleftharpoons H^+ + H_2O$

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

Similarly, $HNO_3, H_2SO_4, CH_3COOH, H_2O, H_2S$, NH_4^+, HCO_3^- etc. are acids.

Bases :- $NH_3 + H^+ \rightleftharpoons NH_4^+$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$

$H_2O + H^+ \rightleftharpoons H_3O^+$

Similarly :- $RNH_2, CN^-, HS^-, NO_2^-$ etc. are bases and they have a tendency to take up proton.

SALT :- A salt is defined as a crystalline compound which is formed by the complete neutralisation of aqueous strong acid with strong or aqueous solution of a strong base.

When an acid completely reacts with a base, we get a salt & water.

Types of salt :- Normal salts :- These are the salts which are formed from strong acids HCl, H_2SO_4, HNO_3 & strong bases (NaOH, KOH)

Eg = NaCl, K_2SO_4, Na_2SO_4.

Acid salts :- Basic salts, Double salts, Complex salts & mixed salts.

pH of a solution is defined as the negative logarithm of the hydrogen ion concentration in moles per litre.

Mathematically $pH = \log_{10} \frac{1}{[H^+]} = -\log [H^+]$

In pure water $[H^+] = 1.0 \times 10^{-7}$

∴ pH of pure (neutral) water $= -\log [10^{-7}] = 7$

Thus the pH value of pure water is equal to 7.

If pH of the solution is given, then $[H^+] = 10^{-pH}$. $pK_a = -\log K_a$.

Substance	pH
Blood	7.3 - 7.5
Milk	6.8
Lemon Juice	2.25 - 2.40
Tomato Juice	4.0 - 4.45
Saliva	6.5 - 7.5
Gastric Juice	1.2 - 3.0
Coffee	5.0
Lime water	10.5

IMPORTANCE of pH in Industries?

Many chemical & biochemical reactions are known to take place at a certain pH value or within a narrow pH range. Consequently the concept of pH is of great importance in industry. where for the control of operations containing regulation of true pH value has to be carried out. Some exp which depicts the imp of pH value & pH control.

(1) water for domestic use.
(2) water treatment.
(3) sewage treatment.
(4) corrosion.
(5) boiler corrosion.
(6) scale formation in boilers.
(7) in chemical industry.
(8) in sugar industry.
(9) in electroplating.
(10) effluents from chemical industries either acidic ($pH < 7$) or alkaline.