B.Sc-II (Hons.), Paper-III B (Inorganic chem)

Group-A Atomic structure (By Dr. Birendra Kumar, Maharaja College, Ara)

⇒ Determination of electronic charge by Mullikan's method or Oil drop method

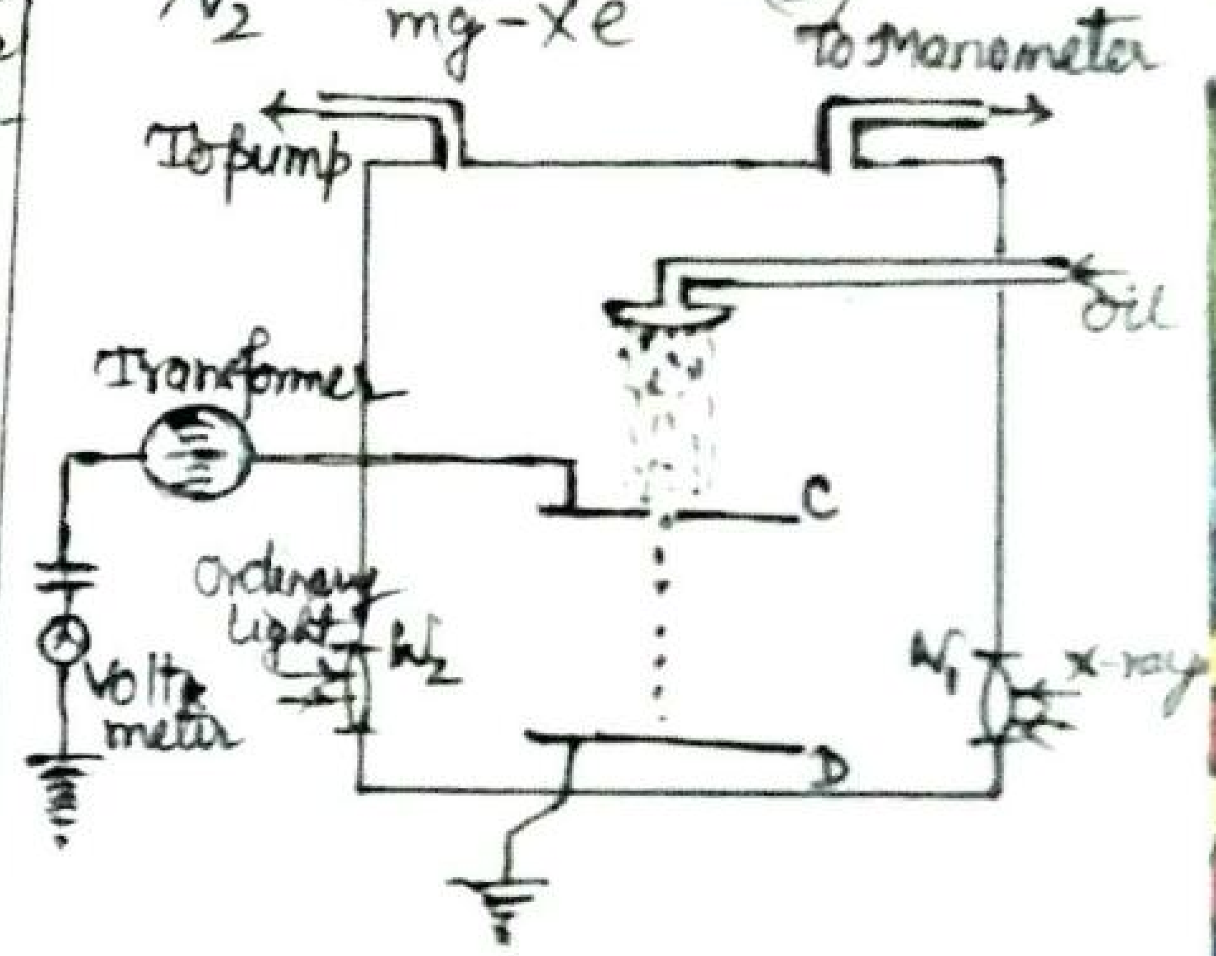
Charge on electron, i.e; electronic charge first determined by Townstand in 1897 later in 1903 Thomson invented a method to determine electronic charge, based on the principle:

If ionised gas is passed through moist atmosphere then on ion small droplets of water form cloud which can be seen by microscope. (i) These droplets move with different velocities in the presence & absence of electric field (ii) If downward velocity of the electric charged water drops is V_1 and in the presence of electro static force 'X', their velocity of downward fall is V_2, then $\frac{V_1}{V_2} = \frac{mg}{mg + Xe}$ —① [Where m = mass of a drop, e = electronic charge, X = potential diff., g = acceleration due to gravity]

Thus, determining V_1 & V_2, electronic charge can be calculated.

On this theory, Mullikan developed a method, called Oil drop or Mullikan's method. In this method, the following modifications have been made:

(i) In place of water drops, oil drops are used (ii) Velocity of oil drops is calculated in upward direction (in the presence of electric field) and the velocity is called V_2, Thus, by using following formula, electronic charge (e) is calculated: $V_1/V_2 = \frac{mg}{mg - Xe}$ —(2)



Working principle: A cubical container/chamber, in which air is pumped out to create low pressure, used. Oil drops are dropped through shower and oil drops are charged by X-rays through window (W_1). Oil drops are seen through microscope by passing ordinary light through window (W_2). In this apparatus, two metal plates are attached to high voltage electric source. Oil drops come down through a pore present in the upper plate. Thus, falling time of oil drops from C to D is noted through microscope. Now, electric potential developed between C & D and the time of upward movement, i.e; D to C of the drops is noted. After these observations, it is seen that the time of downward flow of oil drops is 13.6 sec, and the time of upward movement is 12.5 sec. Knowing the distance between the two plates, V_1 and V_2 are calculated. Then charge on electron/electronic charge is found by formula (2). The determined charge (by Mullikan) on electron is found to be 4.8×10^{-10} esu or 1.6×10^{-19} coulomb.

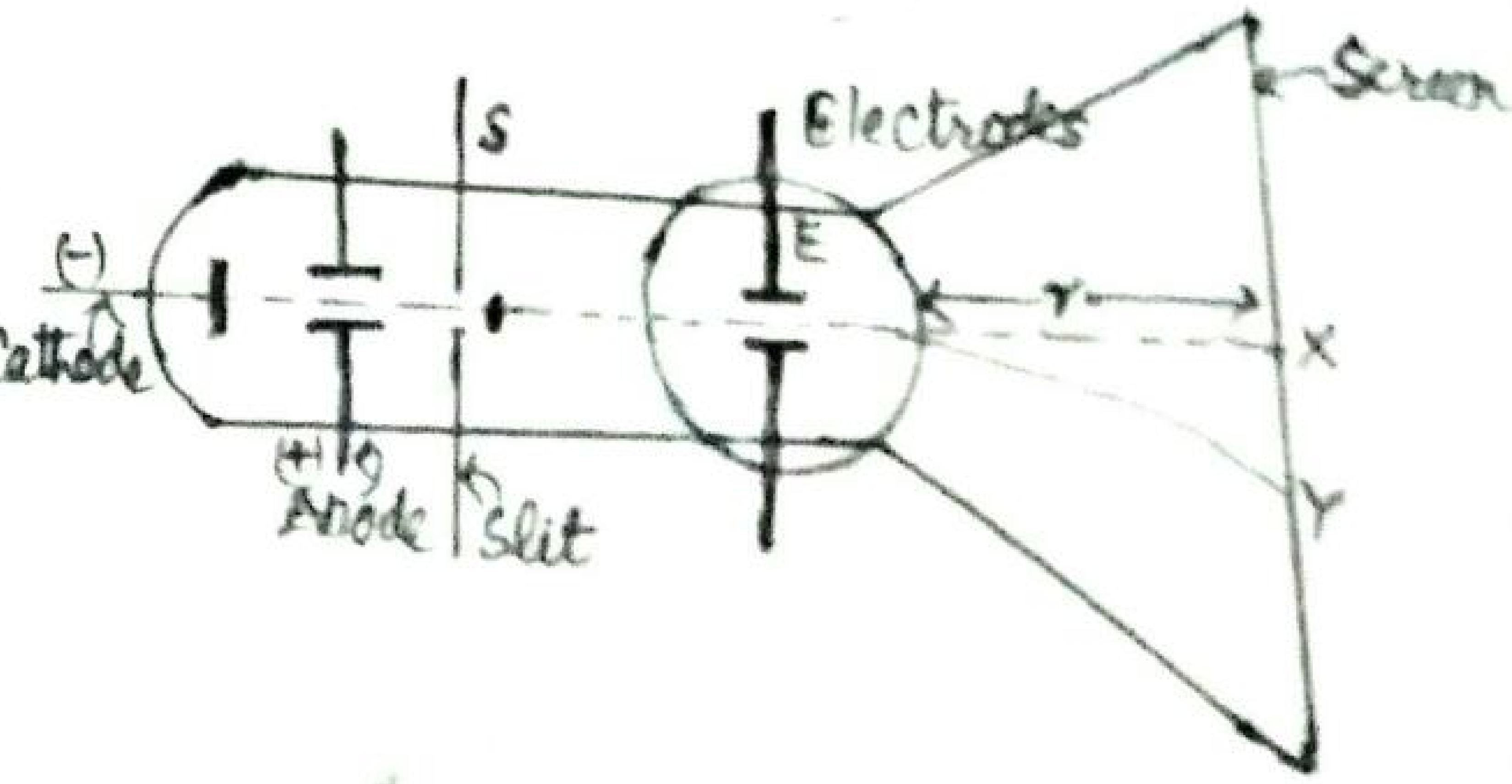
Charge on electron is also calculated by following formula: $e = F/N$ (Where F = one faraday of electricity = 96500 coulombs = 9650 emu = $9650 \times 3 \times 10^{10}$ esu, N = Avogadro No = 6.023×10^{23})

$$e = 9650 \times 3 \times 10^{10} / 6.023 \times 10^{23} = 4.802 \times 10^{-10} \text{ esu.}$$

⇒ Determination of electronic charge & mass ratio (e/m) by Thomson's method

Thomson determined electronic charge (e) & mass (m) ratio, i.e. e/m by using a discharge tube expt. of cathode ray, i.e; fast moving electron. When high voltage electric field is applied in a highly evacuated bulb, a cathode ray (flow of fast moving electron) emitted from cathode. Cathode rays are deflected by magnetic and electric field. This principle was used in the determination.

For this purpose, cathode ray was passed through an electric field (X) and deflection (X to Y) was noted on the screen. Now, magnetic field of intensity (H) is also applied on it is so adjusted that the deflection is neutralised (return back from Y to X).



If m, e and v are the mass of electron, charge of electron/electronic charge and velocity of moving electron/cathode ray respectively, Centrifugal force ($\frac{mv^2}{r}$) gives the deflection produced by electric field of intensity (X) and it is neutralised by magnetic field of intensity (H).

$$\therefore Hev = \frac{mv^2}{r} \quad \ldots (1)$$

$$\text{and, } Hev = Xe \quad \ldots (2)$$

From equation (1) & (2), $v = \frac{X}{H}$

Putting this (v) value in equation (1), we get $e/m = \frac{X}{H^2 r}$ ——— (3)

Thus, knowing the value of X & H, the value of e/m has been determined. r is the distance of the screen from the magnet.

The value of e/m was found to be 1.7×10^8 coulombs/gm.

→ **Russel-Saunders Symbol/Term**

It is an abbreviated description of the total angular momentum quantum numbers in a multi-electronic system. However, even a single electron can be described by a term symbol. The Russel-Saunders symbol or Term of a given system is represented as $^{2S+1}L_J$; where S = Total or resultant spin angular momentum quantum no. ($= \Sigma m_s$, m_s = Spin Q. No.); 2S+1 = Spin multiplicity; L = Total or resultant orbital angular momentum quantum no. ($= \Sigma m_l$, m_l = magnetic Q. No.); J = Total or resultant angular momentum = |L+S| to |L−S|.

* Ground state term symbol for less than half filled orbital = $^{2S+1}L_{J_{min}}$ (i.e., J = |L−S|)
* Ground state term symbol for half/more than half filled orbital = $^{2S+1}L_{J_{max}}$ (i.e., J = |L+S|)

Determination of Russel-Saunders ground/excited state term symbol: The determination of Russel-Saunders term symbol for a given system (e.g. d^2) involves following steps:

1. First of all electronic configuration (outer) of given system is shown in box-representation according to Hund's rule. e.g., d^2 system as [↑|↑| | |]
2. The total spin angular momentum quantum no. (S) is known by Σm_s (where m_s = spin Q. No; generally unpaired electrons are taken consideration). $m_s = +\frac{1}{2}$ for clockwise spin (↑) and $m_s = -\frac{1}{2}$ for anticlockwise spin (↓). e.g., for d^2 system, $S = +\frac{1}{2} + \frac{1}{2} = 1$.
3. Then, spin multiplicity is known by (2S+1). e.g., for d^2 system, spin multiplicity = 2×1+1 = 3.
4. The total orbital angular momentum quantum no. (L) is known by Σm_l (where m_l = magnetic quantum no.) The value of L ranges from (l_1+l_2) to (l_1-l_2). L value will decide spectroscopic symbol. The values of m_l for s, p, d & f orbitals are as follows:

$m_l = 0$ [ ] s-orbital ($l=0$)

m_l: +1 0 −1 [| |] p-orbital ($l=1$)

m_l: +2 +1 0 −1 −2 [| | | |] d-orbital ($l=2$)

m_l = +3 +2 +1 0 −1 −2 −3 [| | | | | |] f-orbital ($l=3$)

L-value :	0	1	2	3	4	5
spectroscopic symbol :	S	P	D	F	G	H

e.g., for d^2 system, +2 +1 0 −1 −2 [↑|↑| | |] d-orbital; L = +2+1 = 3, So Spectroscopic symbol is F

5. Now, total angular momentum quantum no. (J) is known. J arises due to L-S coupling in multi-electronic system. J can have the values ranging from |L+S| to |L−S|. For half filled or more than half filled, high J-value, i.e., |L+S| and for less than half filled, low J-value, i.e., |L−S| is used. e.g., for d^2 system J = |L−S| = 3−1 = 2 (Since it is less than half filled system.)
6. Finally, spin multiplicity (2S+1) is written as superscript on LHS and total angular momentum (J) as subscript on RHS of spectroscopic symbol corresponding to L-value as follows: $^{(2S+1)}L_J$.

Thus, for d^2 system, Russel-Saunders ground state term/symbol = $^3F_2$, while excited state term symbol = $^3F_4$ (Since R-S term symbols = $^3F_4$, $^3F_3$, $^3F_2$)

$^3F \rightarrow {}^3F_4, {}^3F_3$ ↑ (J = |L+S| to |L−S| = 4 to 2, ...